OXYGEN AND SULPHUR HETEROCYCLES DERIVED FROM CHLOROALDEHYDES

by

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A thesis submitted to
THE UNIVERSITY OF CAPE TOWN
in fulfilment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY

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August 1984

My thanks to ....

.... my supervisor, Professor Harry M.N.H. Irving, from watching whom I learned, among other things, much about careful experimental chemistry, and who remembers being banished, with his sulphur compounds, to work in the "outdoor laboratory", with only an umbrella to keep off the Oxford winter snow

.... Dr. Klaus Koch and Professor Luigi Nassimbeni who befriended me and taught me many things.

.... my wife Janine who helped

.... my mother who made it possible.

ABSTRACT

Chloral (2,2,2-trichloroethanal) may be trimerised, tetramerised and polymerised, to form parachloral (2,4,6-tris(trichloromethyl)-1,3,5-trioxane), metachloral (2,4,6,8-tetrakis(trichloromethyl)-1,3,5,7-tetroxacane) and polychloral, respectively. Parachloral has two isomers; the *cis*-isomer, anchored in the expected chair conformation, and the *trans*-isomer which chooses a classical boat conformation in the solid state. This unusual behaviour is attributed to a trans-annular intramolecular hydrogen bond. An analysis of the conformational equilibria occuring in solution, was carried out for *trans*-parachloral, using the techniques of dipole moment measurement and infrared and nmr spectroscopy. It is proposed that at ordinary temperatures in solution, only twist and boat conformers, in rapid equilibrium, are present. The structures and energies of these conformers are discussed.

X-ray crystallography revealed an unusual kind of isomerism in the related trioxane, parabutylchloral (2,4,6-tris(1',1',2'-trichloropropyl)-1,3,5-trioxane). Both isomers exist in *cis*-chair conformations, but differ in the chirality of the β-carbon atoms in the side chains. A comparison of the mass spectral fragmentations of parachloral and parabutylchloral is included. The structure of a related five-membered heterocycle, *trans*-chloralide (*trans*-2,5-bis(trichloromethyl)-1,3-dioxolan-4-one), was also investigated by *x*-ray crystallography. The *cis*-isomer of chloralide is reported for the first time. The unusual mechanism, in which carbon monoxide acts as a nucleophile, by which chloralide is formed from chloral and fuming sulphuric acid, has been elucidated using ^{13}C-labelling. The dehydrochlorination of chloralide under unexpected conditions, is also discussed.

The isomerism in a series sulphur-containing analogues of parachloral was investigated. 2-*Trans*-dithioparachloral (2-*trans*-2,4,6-tris(trichloromethyl)-1-oxa-3,5-dithiane) and its dehydrochlorination product, *trans*-2,6-bis(trichloromethyl)-4-dichloromethylene-1-oxa-3,5-dithiane, were shown by *x*-ray crystallography to prefer twist conformations in the solid state, thereby avoiding axial trichloromethyl groups. The same is thought to be true of *trans*-trithioparachloral (*trans*-2,4,6-tris(trichloromethyl)-1,3,5-trithiane). A comparative study of the effects on the ^{1}H and ^{13}Cnmr spectra, of structural changes in these six-membered heterocycles, is discussed at length. Some introductory preparative work was done, regarding the potential use of 1,3,5-trithiane 1,3,5-trioxides with three axial sulphoxide groups, as terdentate ligands.

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1 INTRODUCTION

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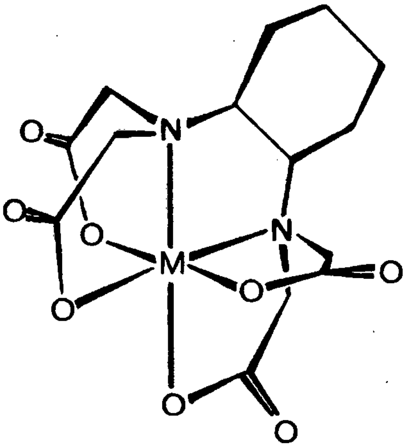
1.1 STEREOCHEMISTRY AND CHELATION

The *trans*-isomer of 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid forms metal complexes (1.1) of much greater stability than does the *cis*-isomer (Sillén and Martell, 1964). Although no structural details of complexes of the *cis*-isomer are available, molecular models reveal serious and unavoidable steric compression of glycinate methylene hydrogen atoms against cyclohexane hydrogen atoms. Complexes of the *trans*-isomer are not troubled by such steric crowding.



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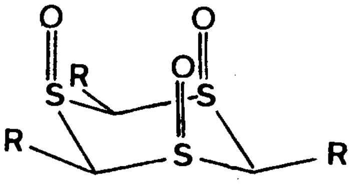
Similarly, of the possible isomers of a 1,3,5-trithiane 1,3,5-trioxide, only that isomer with three axial sulphoxide groups (1.2) is expected to be a useful terdentate ligand. The configurations of the other isomers would, at best, permit bidenticity. The original aim of this project was to prepare the trisulphoxide (1.2) and examine its behaviour as a ligand. The molecule seems ideally suited to form metal complexes with bisadamantane structures (1.3). The rigidity of the chair in (1.2) is not expected to allow much variation in the inter-oxygen distances and a fair degree of size-selectivity is therefore anticipated.



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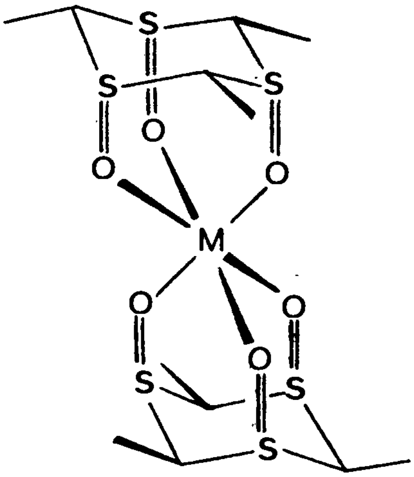

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1.2 HETEROCYCLES DERIVED FROM CHLOROALDEHYDES

A structural examination of a related series of heterocycles, the 1,3,5-trioxanes and 1-oxa-3,5-dithianes was considered a suitable preamble to the main work. The study proved so absorbing however, and opened so many avenues, that it now constitutes the major part of this dissertation.

A comprehensive investigation of these six-membered heterocycles was carried out by Chattaway and Kellett during the period from 1928 to 1930. Almost invariably, they used as their starting material chloral hydrate, 2,2,2-trichloroethan-1,1-diol, which is dehydrated by sulphuric acid to form chloral (1.4), a very reactive aldehyde like its relatives bromal and iodal. Under the influence of sulphuric acid, chloral trimerises to form parachloral (1.5) and in the presence of hydrogen sulphide, to form dithio- and trithioparachlorals (1.6) and (1.7) (Figure 1.1). Each of

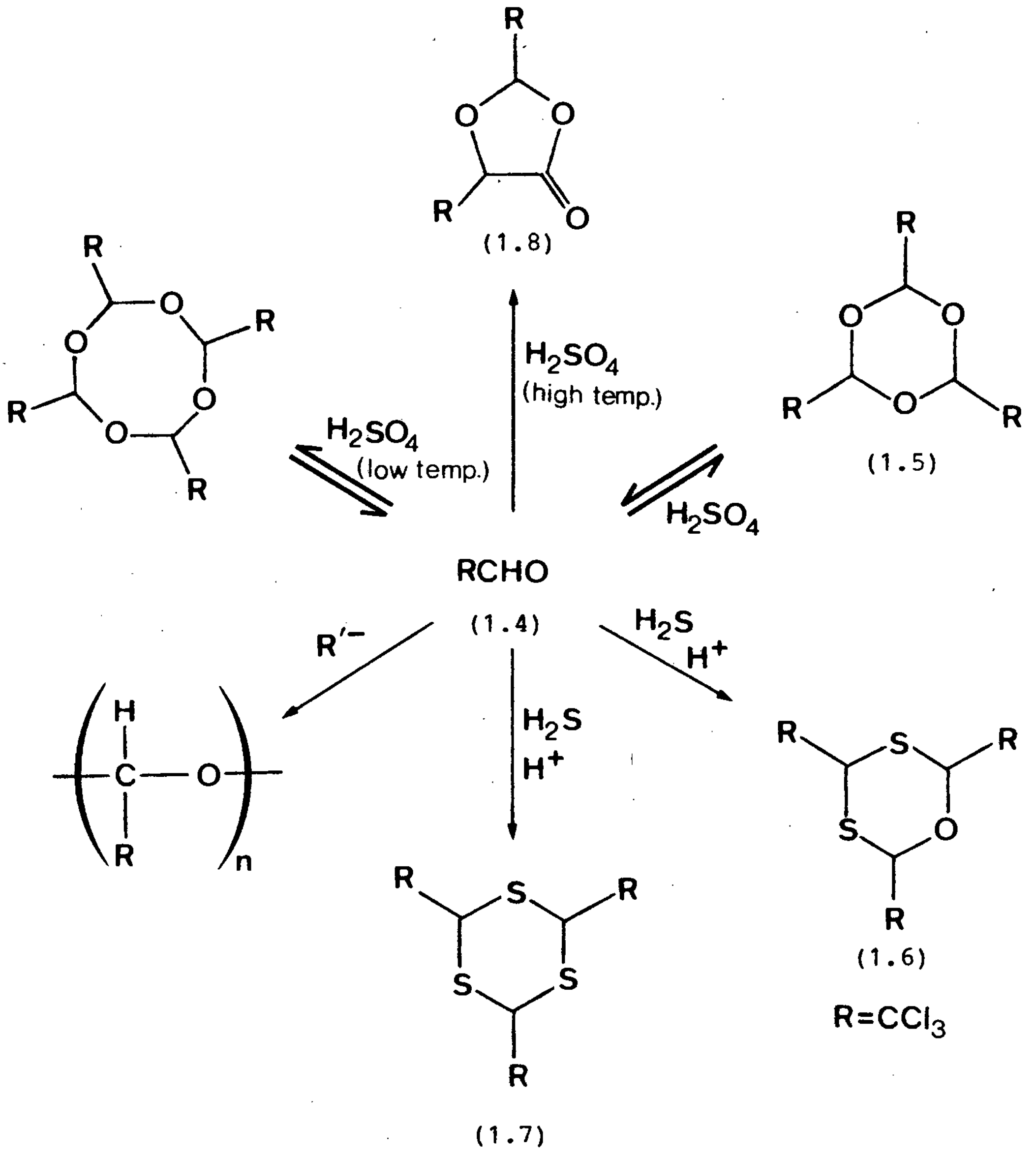


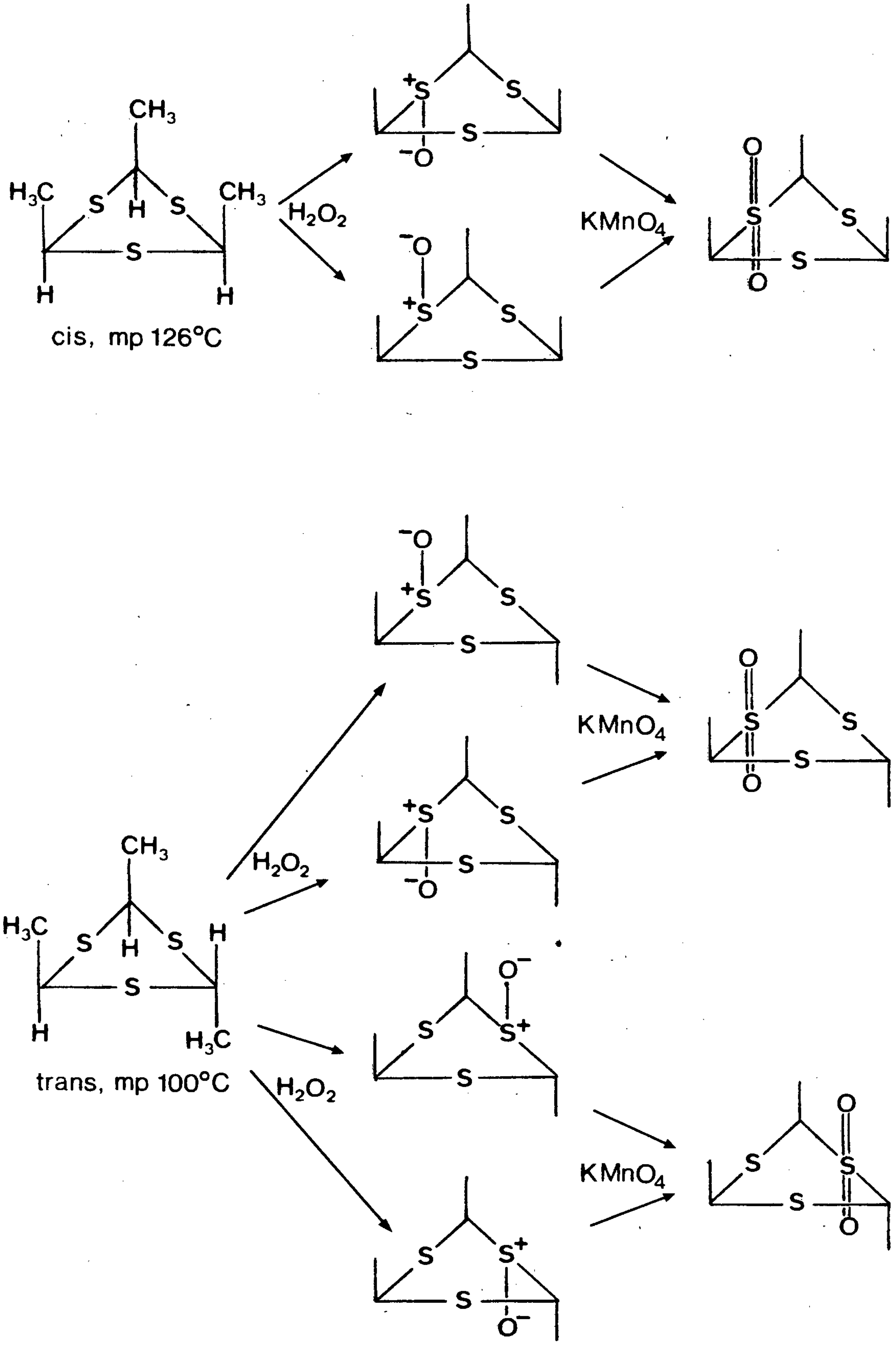
Figure 1.1. Polymerisation and other reactions of chloral (1.4). In concentrated sulphuric acid, low temperatures favour tetramer formation, while high temperatures favour formation of chloralide (1.8).

these compounds display geometric isomerism and various physical techniques have been used to establish the configurations and conformations of the isomers.

Trans-parachloral has been shown to prefer a boat conformation in the solid state. This unusual behaviour is attributed to a trans-annular intramolecular hydrogen bond. A detailed analysis of the conformational equilibria of this compound in solution has been carried out, using mainly nmr spectroscopy (Chapter 2). The *trans*-isomers of 2,4,6-tris-(trichloromethyl)-1-oxa-3,5-dithiane (1.6) and its dehydrochlorination product 2,6-bis(trichloromethyl)-4-dichloromethylene-1-oxa-3,5-dithiane, have been shown by *x*-ray crystallography, to adopt twist conformations in the solid state (Chapter 5). Collectively, these results indicate that a chair conformation is unable to bear the strain imposed upon it by an axial trichloromethyl group.

The isomerism in a related trioxane, parabutylchloral, was found by *x*-ray crystallography, to be of an unusual kind: due to the asymmetry of the substituent carbon atoms in a β-position to the trioxane ring (Chapter 3). The structure of another related compound, chloralide (1.8) (Figure 1.1), has also been examined, and the mechanism of its formation, in which carbon monoxide acts as a nucleophile, has been established using ^{13}C-labelling (Chapter 4). Some introductory work regarding the preparation of the ligand (1.2) and its predicted structural features, is also discussed (Chapter 6).

Considering the dearth of physical techniques available to them, the achievements of the early chemists are highly admirable. In illustration of the practical expertise of the time, the wet-chemical technique used by Chattaway and Kellett (1930) to determine the configurations of the



Scheme 1.1. Process used by Chattaway and Kellett (1930) to determine the configurations of the geometric isomers of 2,4,6-trimethyl-1,3,5-trithiane. For each isomer, only half the predicted number of monosulphoxides was isolated.

two isomers of 2,4,6-trimethyl-1,3,5-trithiane is outlined in Scheme 1.1. The isomer which yields two monosulphones must have the *trans*-configuration. The work involved many trial oxidations to establish the exact conditions under which the trithiane is oxidised to a monosulphoxide and the monosulphoxide to a monosulphone. Oxidation products were isolated by series of precise fractional crystallisations, monitored by melting-point measurements and laborious elemental analyses. In all, two years of painstaking work was involved. Today, the isomers of 2,4,6-trimethyl-1,3,5-trithiane can be distinguished by just a glance at their nmr spectra.

The dissertation closes with a discussion of future projects which could grow from this work.

1.3 REFERENCES

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L.G. Sillén and A.E. Martell (1964) "Stability Constants of Metal Ion Complexes", Chem. Soc. Special Publ. No. 17, p.690.

2

CONFORMATIONAL ANALYSIS OF PARACHLORAL, 2,4,6-TRIS(TRICHLOROMETHYL)-1,3,5-TRIOXANE

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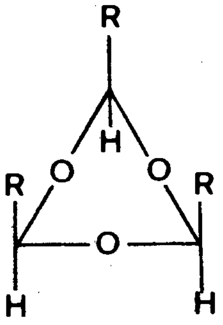
2.1 *INTRODUCTION*

The first volume of Justus Liebig's Annalen der Chemie carried a report by Liebig himself, of a new compound, which he named chloral (Liebig, 1832). Almost a century later, chloral was found to trimerise in the same way as acetaldehyde (Chattaway and Kellett, 1928). Paraldehyde had already been shown to be a trimer of acetaldehyde (Burstyn, 1902) and a six-membered ring of alternate carbon and oxygen atoms was suggested for its structure. More recently, an electron diffraction study showed the ring to be puckered, and the ring bonds to be staggered (Carpenter and Brockway, 1936).

Chattaway and Kellett (1928) separated two forms (α and β) of parachloral, the trimer of chloral, and supposed them to be *cis* and *trans* isomers, (2.1) and (2.2), by analogy with paraldehyde. Conformational analysis being unborn, in early depictions planar rings were drawn. The compounds were found to be colourless crystalline solids with sharp melting points (116° and 152°C respectively), soluble in most organic solvents but insoluble in water. They are comparatively stable, being unaffected by boiling aqueous alkali, for example. Distillation under ordinary pressure leads to dissociation, but under reduced pressure, the compounds distil unchanged.



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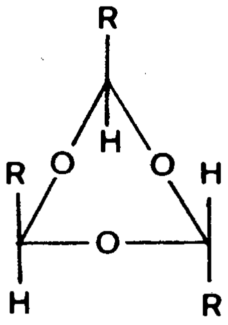

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$R = CH_3$

$R = CCl_3$

Soon after proton nmr became available to chemists, Novak and Whalley (1958) used the new technique to investigate the structures of α- and β-parachloral. The spectrum of the β-isomer consists of only one signal, showing the equivalence of the three ring protons and establishing the *cis* structure (2.3). The α-isomer gives a spectrum consisting of two signals of intensity ratio 1:2, suggesting either of the structures (2.4) or (2.5). Nmr results being inconclusive, these workers compared the calculated dipole moments of (2.4) and (2.5) with the measured dipole moment of the α-isomer, thereby assigning the *cis*,*trans*-chair conformation to α-parachloral (see Section 2.6.1). A group theoretical analysis of the vibrational spectra of the parachlorals was also carried out and gave support to the above assignments (see Section 2.6.2).

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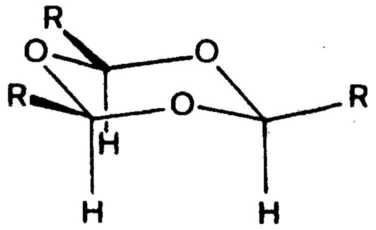

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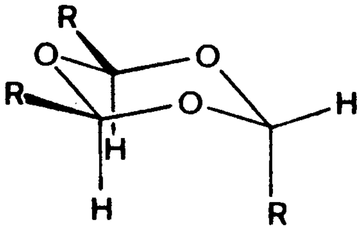

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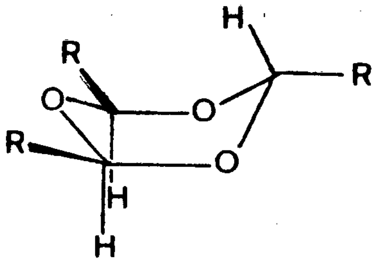

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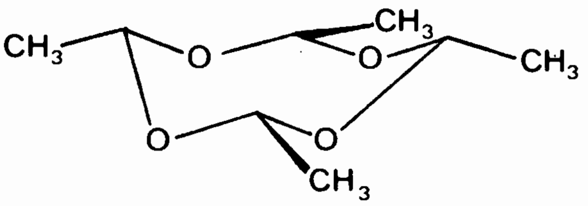
A recent *x*-ray crystallographic study showed that α-parachloral adopts a boat conformation in the solid state (Hay and Mackay, 1980). The β-isomer, in common with *cis*,*cis*-2,4,6-tricyclohexyl-1,3,5-trioxane (Diana and Ganis, 1963), both isomers of 2,4,6-tris(1',1',2'-trichloropropyl)-1,3,5-trioxane (Archer *et al.*, 1984) and both isomers of 2,4,6-trimethyl-1,3,5-trithiane (Sekido *et al.*, 1977; Hirokawa *et al.*, 1977; Valle *et al.*, 1969), has the expected chair conformation in the solid state.

Polymerisation of aldehydes may also produce tetramers, the so-called meta-aldehydes. Crystalline metaldehyde (the tetramer of acetaldehyde) has been shown to exist as a symmetric eight-membered heterocycle (Pauling and Carpenter, 1936). The crown conformation (2.6) is preferred in the solid state. Metachloral, the tetramer of chloral, is thought to exist predominantly in the crown conformation in solution (Baron *et al.*, 1962). Chloral can also be polymerised to polychloral (2.7) whose



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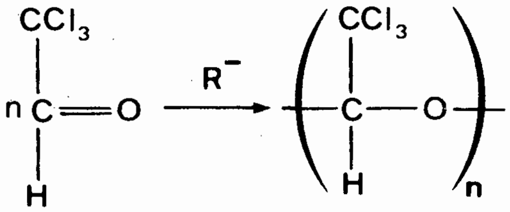


(2.7)

structure has not been completely determined due to its intractable nature. Various physical techniques, including magic angle ^{13}Cnmr spectroscopy, have been applied to the problem, tentatively suggesting a isotactic 4_1-helical structure for polychloral (Harris *et al.*, 1983).

2.2 CONFORMATION OF α-PARACHLORAL IN THE SOLID STATE

It is perhaps not surprising that α-parachloral assumes a non-chair conformation in the solid state, considering the bulk of the CCl_3 substituents, but what is surprising is that it chooses a classical boat rather than a twist conformation. This result was verified independently in this laboratory (Irving, 1980). As the torsion angles show (Figure 2.1) the boat is slightly distorted (ideal torsion angles are zero and 60°). Also, the angles θ_1 and θ_2 (Figure 2.1) between the plane defined by C2—O3—O5—C6 and the planes defined by O1—C2—C6 and O3—C4—O5 are

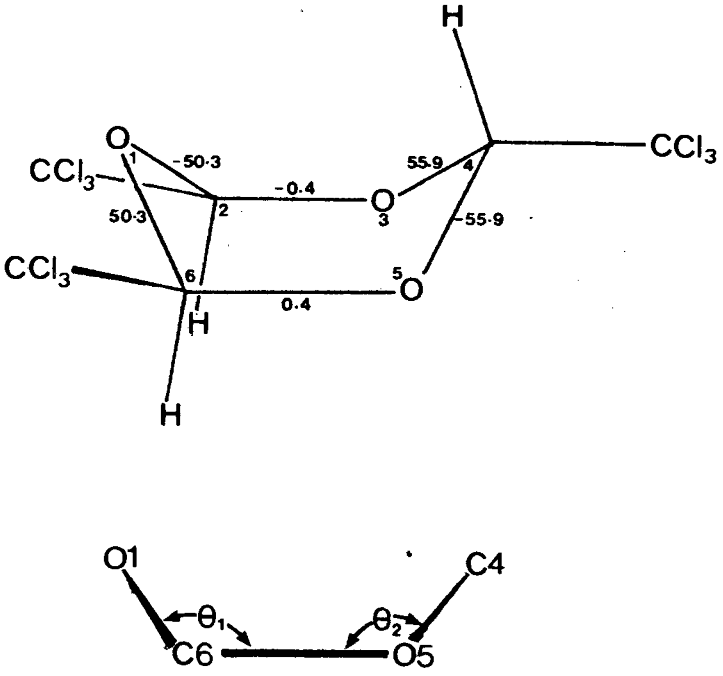
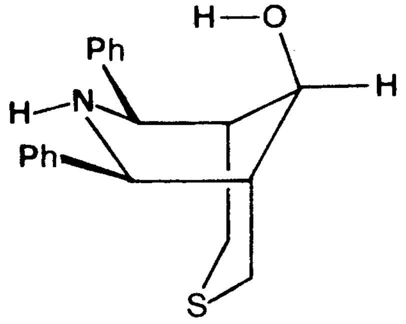


Figure 2.1. Some torsion angles showing flattening of the boat conformation of α-parachloral.

130.2° and 128.3°* respectively, showing that the boat is slightly flattened (ideally, θ = 125.3°). Nevertheless, the structure is a classical boat in the sense that a (crystallographic) mirror plane divides the molecule, passing through atoms O1 and C4, so that the "bottom" of the boat defined by C2—O3—O5—C6 is perfectly planar.

Although the search for non-chair conformations has been keen, very few classical boats have been found. Another rare specimen has recently been reported (Eliel *et al.*, 1982) in which one ring of the compound 3-thia-7-aza-6,8-diphenylbicyclo[3.3.1]nonan-9-ol exhibits a boat conformation (2.8). However, this boat is restrained in the classical conformation rather than in a twist conformation, by the rigidity of the chair to which it is fused.



(2.8)

To understand the surprising behaviour of α-parachloral, an excursion into the concepts of conformational analysis will be helpful.

2.3 *SOME IDEAS ABOUT CONFORMATIONAL ANALYSIS*

Conformational processes in cyclohexane, the model six-membered ring system, are fairly well understood and the relative energies of stable

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* Hay and Mackay incorrectly report an angle of $\theta_2 = 148.9°$.

conformers and the barriers separating them have been measured and calculated (Eliel *et al.*, 1967; Anet and Anet, 1975). According to the earliest ideas, cyclohexane can choose either a chair or a boat conformation, both being free from angle strain. While early workers viewed these as static, rigid structures, their fluxionality has now been realised. It is also now understood that the torsional strain (arising from eclipsed carbon—carbon bonds) and the steric strain (from compression of the "flagpole" hydrogen atoms) which destablise the boat conformer, are noticeably relieved in the twist conformer, making the latter the more stable state. Nevertheless, the boat-twist energy difference in cyclohexane is small, so that in solution, twist conformers are rapidly interconverting *via* the boat transition state. There are six indistinguishable twist conformers, and since the process which interconverts them brings about no apparent change in structure, it is known as pseudorotation. The chair conformer, the predominant form at room temperature by a factor of a few thousand, being free from torsional and steric strain, lies at the bottom of a deep potential well. The molecular mechanical energy hypersurface for the conformational processes occuring in cyclohexane is shown in Figure 2.2.

Chair interconversion is thought to proceed, as shown in Figure 2.3, *via* a half-chair transition state to a twist conformer, then to another twist conformer by pseudorotation, and finally *via* another half-chair transition state to the alternative chair conformation.

Although in cyclohexane itself, twist conformers are present in vanishingly small proportions at room temperature, when a large substituent, such as t-butyl, is forced to occupy an axial position on a cyclohexane ring, one or more twist conformers become at least comparable

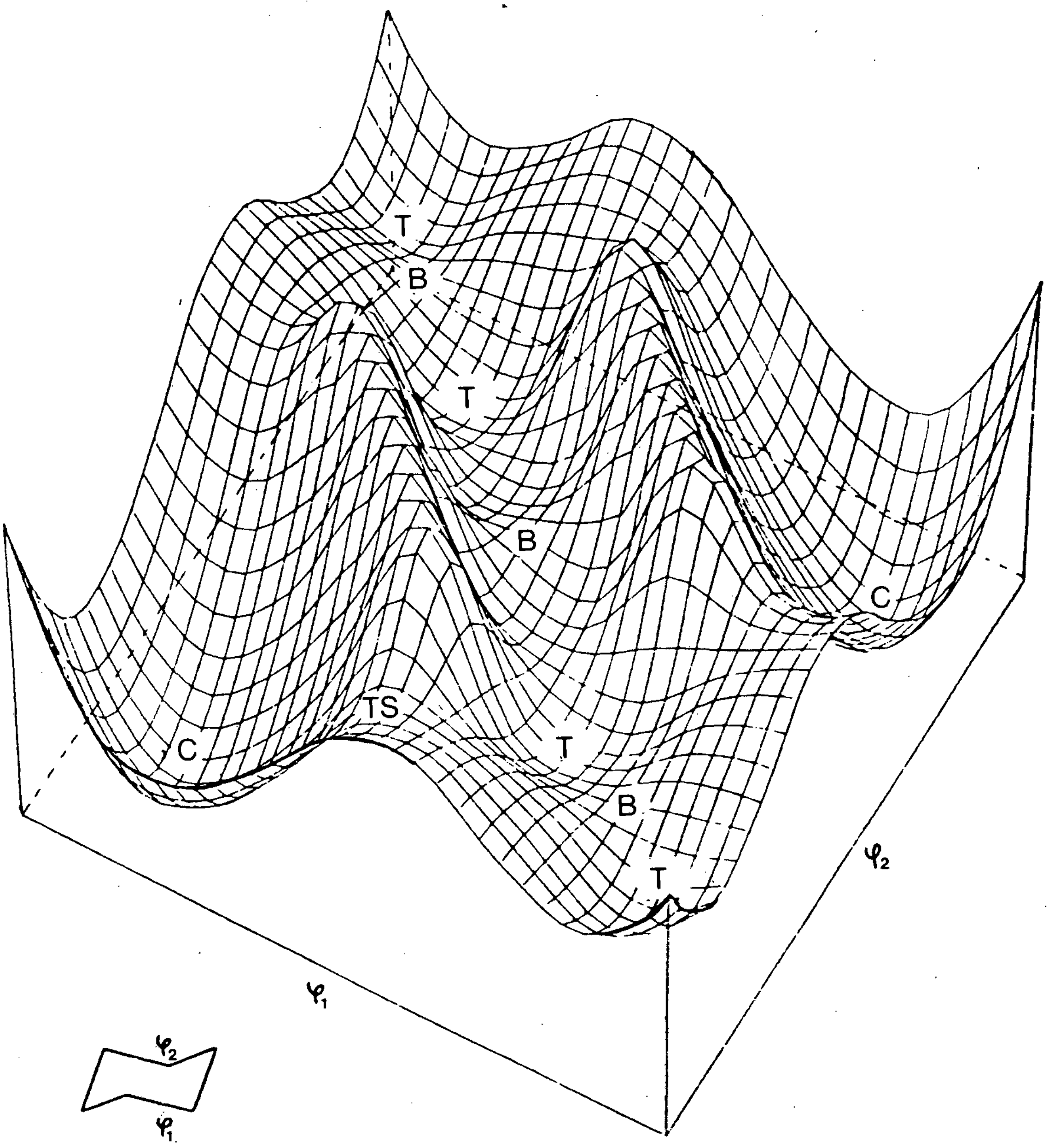


Figure 2.2. The energy surface for cyclohexane as a function of the dihedral angles ψ_1 *= C1—C2—C3—C4 and* ψ_2 *= C1—C6—C5—C4 (Sandström, 1982).*

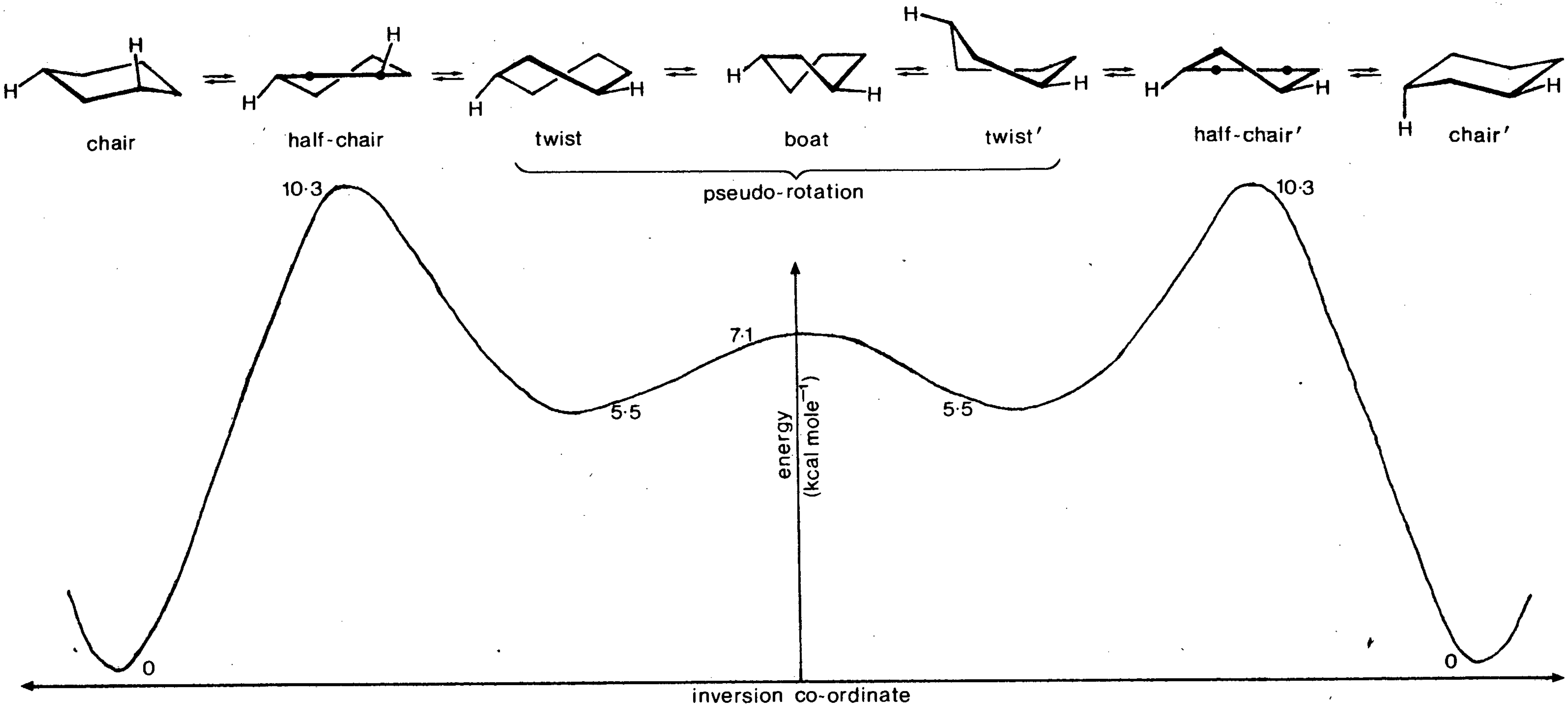
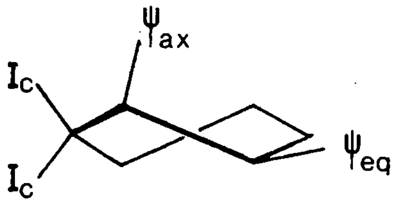


Figure 2.3. Ring inversion in cyclohexane - structures and energetics. Positions of hydrogen atoms are shown.

in energy to the strained chair, if not more stable than it. Whereas a chair conformation has two distinguishable positions (axial and equatorial) for substitution, a twist conformation (2.9) has three: pseudo-axial, ψ_{ax}, pseudo-equatorial, ψ_{eq}, and isoclinal, I_c. Only ψ_{eq}



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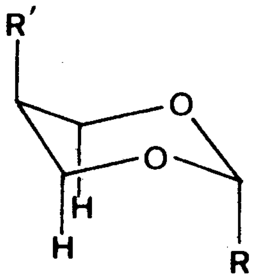


(2.10)

and I_c are unhindered positions and a twist conformer will provide relief to a sterically strained chair only if bulky groups can occupy unhindered positions. Thus, some of the possible twist conformers will not be stable. Stated clearly; "If a molecule is so encumbered as to be forced into a twist conformation, the encumbrance will raise the energy of most possible twist conformers, leaving very few possible twist conformers from the original pseudorotation circuit open to the molecule." (Kellie and Riddell, 1972).

The introduction of heteroatoms into the ring further alters the energy profile for conformational interconversion. The following factors are partly responsible:

(i) Barriers to rotation about single bonds decrease in the order C—C > C—N > C—O ~ C—S. Although the barriers are not understood, experimental data shows that freedom of rotation about a C—A bond depends upon the number of substituents on atom A. In oxane therefore, the barrier to chair inversion is lower than that in cyclohexane.

(ii) A heterocyclic ring containing oxygen or nitrogen has shorter endocyclic bonds since C—O and C—N bond lengths are shorter than C—C bond lengths. It has been observed for example, that the preference of a substituent, R, for the equatorial position is much greater in 1,3-dioxanes (2.10) than in cyclohexane since the substituent's interaction with the *syn*-axial hydrogen atoms is greater in the dioxane.

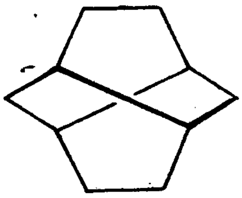
(iii) The axial substituent, R', in (2.10) is less encumbered than in the corresponding cyclohexane derivative because the *syn*-axial hydrogens are absent. Oxygen lone-pairs evidently cause little or no steric interference. As witness to this, among the very few six-membered cyclic compounds displaying evidence of axial t-butyl groups, are the 1,3-dioxane derivatives (2.10) with R = R' = t-butyl (Eliel and Knoeber, 1966, 1968).

(iv) The anomeric effect makes a polar substituent, *e.g.*, R = OMe, in (2.10) more stable in an axial position (Eliel, 1975).

2.4 *EXAMPLES OF MOLECULES PREFERRING NON-CHAIR CONFORMATIONS*

The search for non-chair conformations has not been easy, mainly as a result of their instability. Also, the difference in structure and energy between a relatively stable twist conformer and another possible stable conformer is, in general small, and considerable time and effort was required to develop and perfect physical techniques suitable for the detection of such subtle differences. Diffraction methods have been used only sparingly and so, little "concrete" evidence is available. Although it may sometimes be found that crystal structures do not give the true conformational picture, because of strong intermolecular forces, it has been noted from experience that "the geometry in a molecular lattice often corresponds closely to the geometry of one of the major conformers occuring in the liquid state or in solution" (Balasubramanian, 1962).

Despite the difficulties, however, the search has yielded some good examples. The first was found in a steroid by Barton (1957), one of the earliest pioneers of conformational analysis. Some molecules, as a result of bridging in their structures, constrain at least one six-membered ring into a non-chair conformation; for example, twistane (2.11) (Whitlock, 1962; Tichy, 1972) and bicyclo[2.2.2]octane (2.12) (Yokeziki *et al.*, 1970), the twist relative of adamantane. A classic example of a molecule apparently having an inherent preference for a non-chair conformation, is found in cyclohexan-1,4-dione (2.13), which has been shown to exist as a twist conformer in the solid state, in solution and in the gas phase (Grothard and Hassel, 1963; Mossel *et al.*, 1963; Allinger and Freiberg, 1961; Bastiansen *et al.*, 1971).



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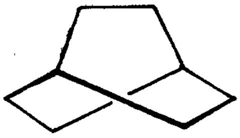

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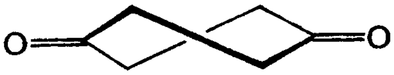

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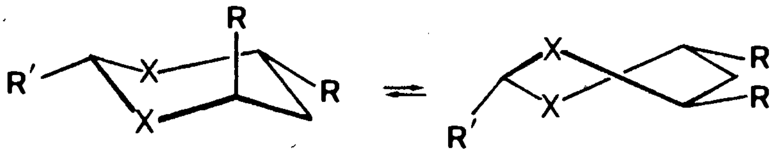
The most interesting examples are those in which a molecule is forced into a non-chair conformation because of unbearable strain in the chair form. In these cases, chair–non-chair equilibria are often observed in solution. In the compounds (2.14),(2.15) and (2.16), severe 1,3-*syn*-diaxial interactions present in the chair forms, may be substantially

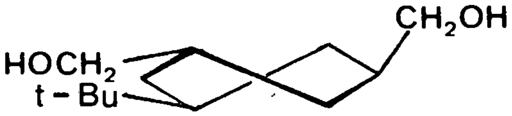


(2.14) $X = CH_2$ $R' = H$ $R = t-Bu$

(2.15) $X = CH_2$ $R = R' = t-Bu$

(2.16) $X = O$ $R' = H$ $R = t-Bu$

relieved in certain twist forms with ψ_{eq} or I_c t-butyl groups (Allinger *et al.*, 1968; van Bekkum *et al.*, 1968; Eliel, 1975). (2.17) and (2.18) provide examples of this class of compounds, whose solid state structures have been determined (van Koningsveld, 1981; Tsuboyama *et al.*, 1977).



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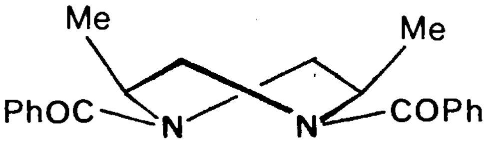
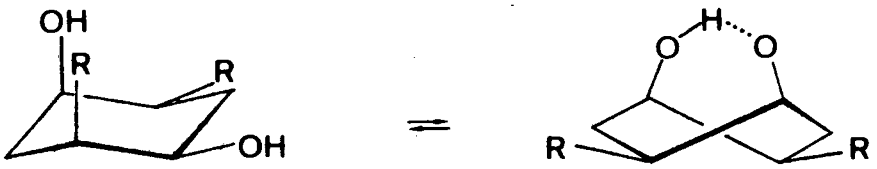


(2.18)

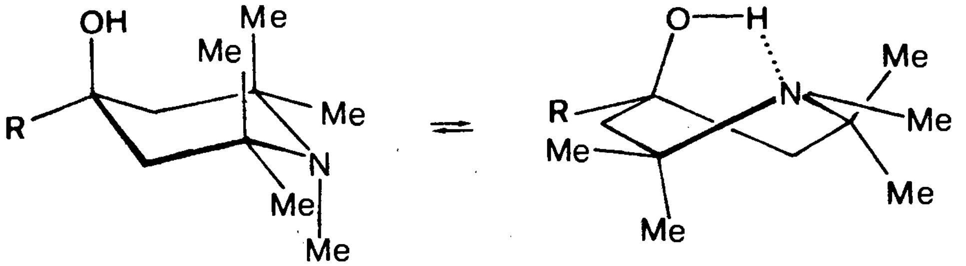
A few cases are known in which twist conformers are stabilised by intra-molecular hydrogen bonding. Infrared studies show that in (2.19) in CCl_4 solution, trans-annular hydrogen bonding is important (Stollow *et al.*, 1964). This can only take place in the twist conformer and the extent of



(2.19)

hydrogen bonding is a direct indication of the position of the chair-twist equilibrium. Thus, it was found that the percentage of twist conformer present in solution increases with increasing bulk of substituent. For R = i-propyl or R = cyclohexyl, 80% of molecules are in the twist conformation. Only for such bulky substituents as t-butyl or t-pentyl does the diol exist completely in the twist conformation. This shows that even with the added bonus of hydrogen bonding in the twist conformer, a cyclohexane chair must be very seriously crowded before the twist form is adopted completely.

One of the earliest examples of a non-chair conformation exhibited intramolecular hydrogen bonding. Substantial proportions of (2.20) were found to exist in a non-chair form, assumed to be the twist conformer (Lyle, 1957). Once again, this form was detected by hydrogen bonding evidence in infrared spectroscopy. In an attempt to study this structure, Cygler (1980) carried out an *x*-ray crystallographic study of (2.21). Unfortunately, the molecule chooses to bear the *syn*-axial interactions, and prefers the chair conformation in the solid state. With a t-butyl substituent on the nitrogen, the situation would surely have been different. The related compound (2.8) also has a trans-annular hydrogen bond, as its crystal structure shows.* The stabilising effect of these



(2.20) **R** = **Ph**
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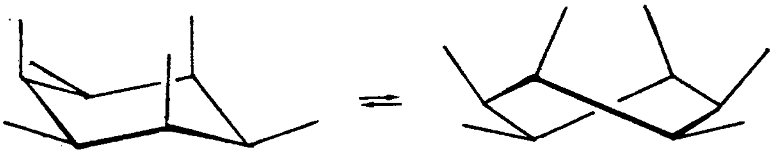
* Although the authors did not report the hydrogen bond, crystallographic evidence seems to indicate its presence. Correspondence with the authors has begun.

hydrogen bonds no doubt largely compensates for the inherent strains in these boat conformations.

A twist conformation will only be preferred by a molecule if some or all of the strains encumbering the chair form are substantially relieved. There are compounds in which a twist conformation which offers sufficient relief from strain in the chair, cannot be constructed. For example, in r-1-*cis*-2,3,4,5,6-hexamethylcyclohexane (2.22), a twist form without two ψ_{ax} substituents cannot be constructed. Thus, in spite of the great steric strain of three *syn*-axial methyl groups, the compound appears to prefer a chair conformation (Werner *et al.*, 1970).



(2.22)

2.5 α-*PARACHLORAL AGAIN*

In the present case of α-parachloral, the interaction between the axial trichloromethyl group and the *syn*-axial hydrogens in the chair conformation is formidable. This is further aggravated (relative to the cyclohexane case) by the short ring bonds, and the molecule prefers a non-chair conformation with all CCl_3 groups in unhindered positions. As Figure 2.4 shows, the trichloromethyl group and the t-butyl group are of comparable size. α-Parachloral may therefore be compared with the molecules (2.14)-(2.16), in which a t-butyl group occupies an axial

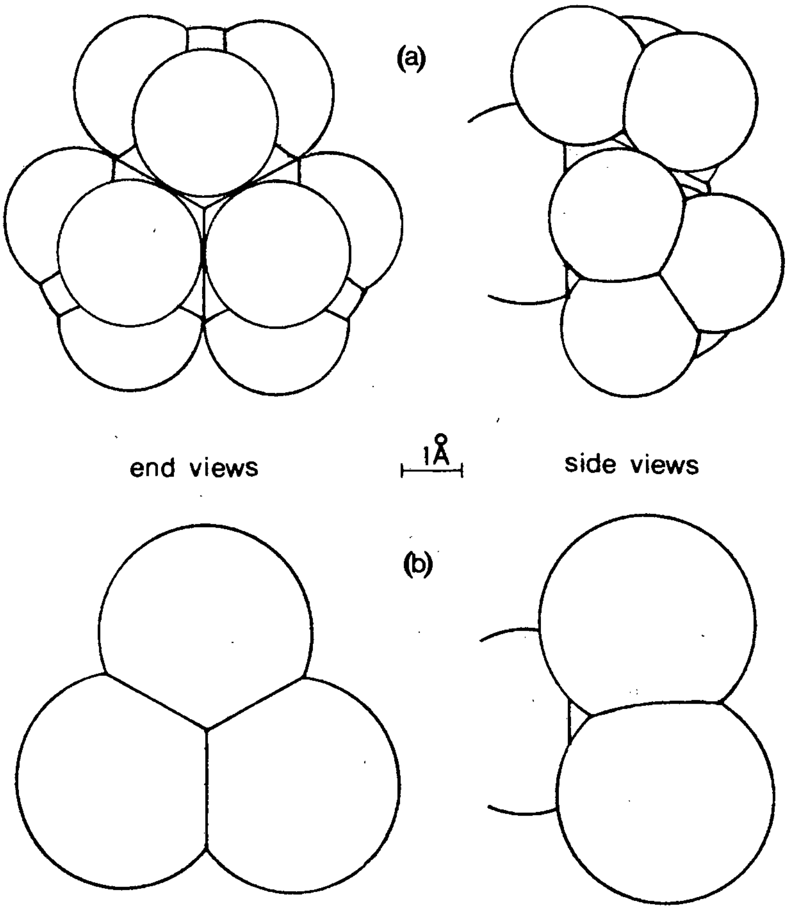


Figure 2.4. Relative sizes of (a) t-butyl and (b) CCl_3 groups.

position in the chair conformer. However, the analogy should be used with caution in view of the vastly different polarisabilities of the two groups.

Hay and Mackay (1980) report a trans-annular hydrogen bond in α-parachloral, with a non-bonded O•••H distance of 2.6 Å. The hydrogen atom positions were revealed in the difference maps of the final refinements and then further refined. Thus, not much reliance can be placed on their final positions. In the study carried out in this laboratory, hydrogen atom positions were geometrically determined. In either case, as Figure 2.5 shows, H2 is within hydrogen bonding range of O1 (O•••H van der Waals distance is 2.7 Å). It is now well accepted that C—H groups can act as acids in hydrogen bonding (Green, 1974). This occurs most commonly in compounds in which the C—H bond is "activated" by an electron-withdrawing substituent on the carbon atom, thus making it effectively more electronegative. Thus, compounds such as trichloromethane, pentachloroethane and triethoxymethane are well characterised hydrogen bonding acids.

The idea of a trans-annular hydrogen bond in α-parachloral is quite acceptable since the hydrogen atoms are likely to be considerably acidic due to the electron withdrawing influence of the CCl_3 substituents and the ring oxygen atoms. Figure 2.5 shows that the hydrogen bond must be quite bent, but this is well accepted for intramolecular hydrogen bonds (Joesten and Schaad, 1974). There must be considerable torsional strain in this molecule due to eclipsed ring bonds, and the hydrogen bond could be the factor which stabilises the boat form with respect to the twist form. If a twist conformer were adopted, the O1•••H2 distance would increase sufficiently to preclude hydrogen bonding. Of course, the

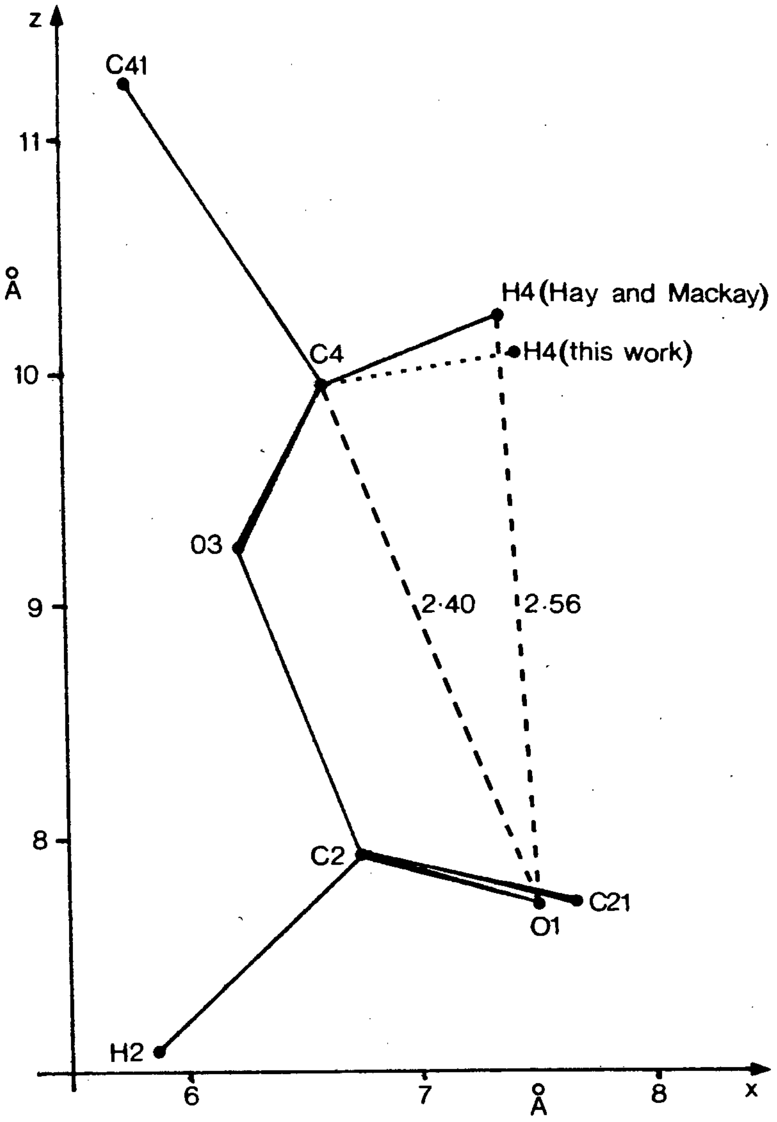


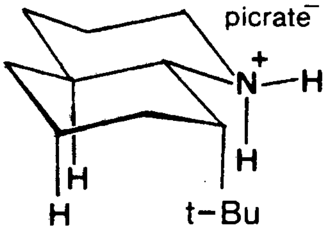
Figure 2.5. Intramolecular hydrogen bonding in α-parachloral.

torsional strain in the boat conformer of a trioxane ring is much less than that in the boat form of a cyclohexane ring; in the former, the hydrogen atoms and substituents on the ring carbon atoms are eclipsed by oxygen lone-pairs, which apparently offer little steric resistance (Section 2.3). Furthermore, the usual interaction between the flagpole hydrogens which destabilises a cyclohexane boat, is absent in α-parachloral. In fact, it could be said that this interaction is stabilising rather than destabilising. Crystal packing forces appear to have little effect on the conformation of α-parachloral, since the only intermolecular non-bonded contacts in the crystal structure are between chlorine atoms. It is interesting to note that the only two examples of molecules in non-chair conformations, stabilised by hydrogen bonding, whose crystal structures have been determined (α-parachloral and (2.8)) have been in boat conformations. The other examples, (2.19), (2.20) and (2.21) either have not had their structures determined, or exist as chairs in the solid state.

2.6 CONFORMATION OF α-PARACHLORAL IN SOLUTION

Although it is generally accepted that the solid state conformation of a molecule will be important in solution, it is possible in the present case that in solution, the chair conformation may be present to some extent. The existence of a chair form of α-parachloral may be intuitively excluded after consideration of models and van der Waals distances, because the interaction between the axial CCl_3 group and the *syn*-axial hydrogens would be so formidable. However, the recently proved existence of an unlikely decahydroquinoline derivative, lends credibility to the idea. Hargrave and Eliel (1979) determined the crystal structure of

(2.23) and found the A ring to be in a chair conformation and supporting an axial t-butyl group. The molecule bears considerable distortion to accommodate the bulky axial group. For example, the bond joining the t-butyl group to the A ring is not staggered, so as to minimise the severe *syn*-axial interactions. Valence angles in the A ring are distorted, some by as much as 9°. There are a few other proven examples of very bulky substituents occupying axial positions ((2.24) van Koningsveld, 1973), demonstrating that a cyclohexane chair can, with surprisingly little deformation, accommodate a group as bulky as t-butyl or trichloromethyl.



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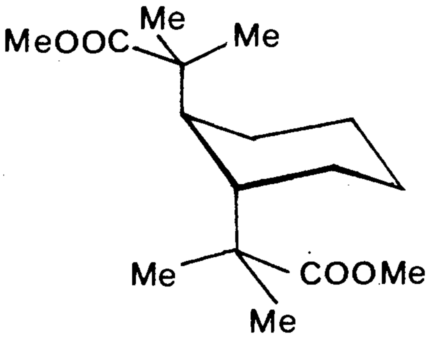


(2.24)

Thus, in α-parachloral, it is possible that in solution, chair and non-chair conformations are comparable in energy. Furthermore, it is difficult to assess the relative stabilities of boat and twist forms. Structurally, α-parachloral is far removed from the model compound cyclohexane, and the usual conformational energy scale has been severely upset. A number of attempts have been made in this work to establish the new energy order. The art of detecting non-chair forms and chair-twist equilibria has been much improved in recent years and the following methods in order of decreasing reliability, are in vogue: diffraction (electron and *x*-ray) and microwave techniques; nmr (especially ^{13}C) and other spectroscopy (especially infrared); ORD-CD, dipole moment measurements and kinetics.

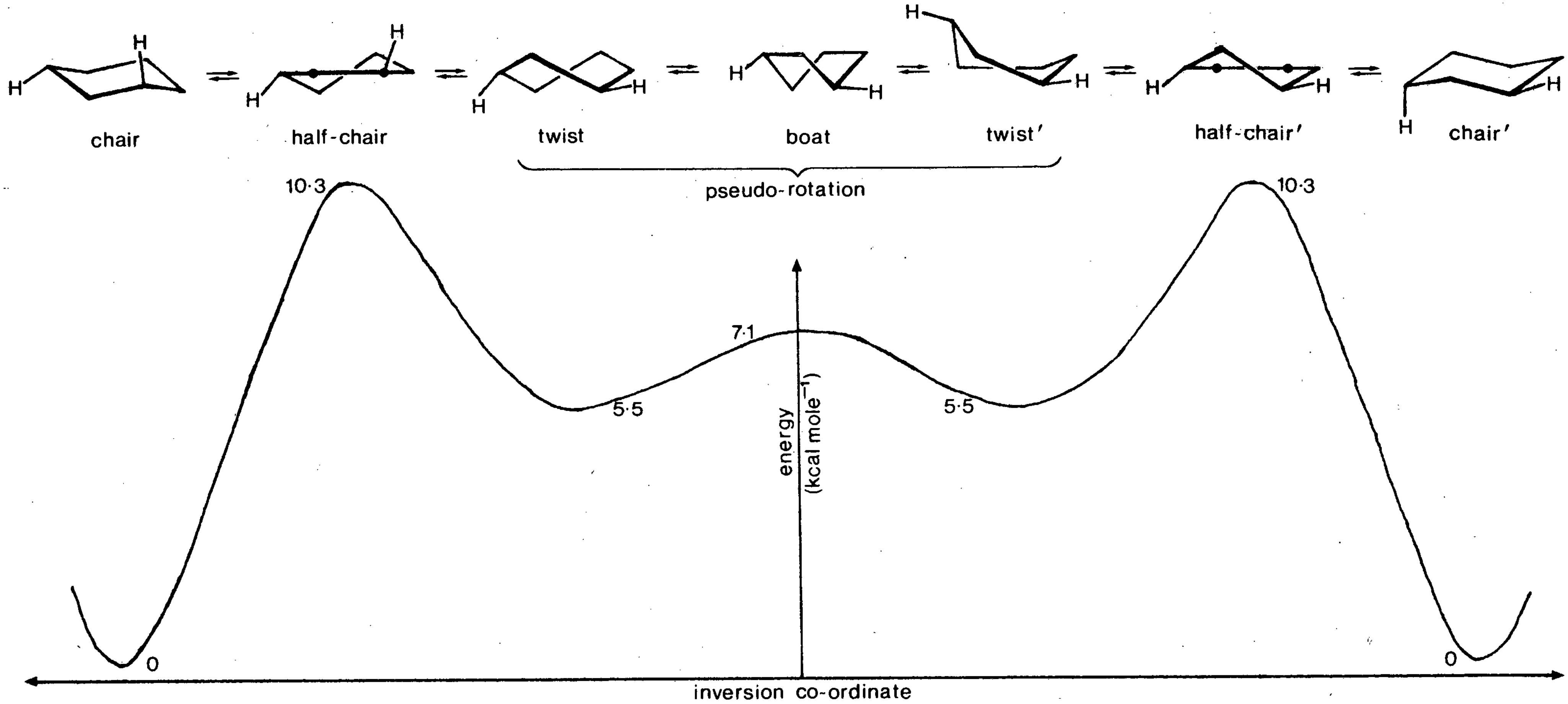
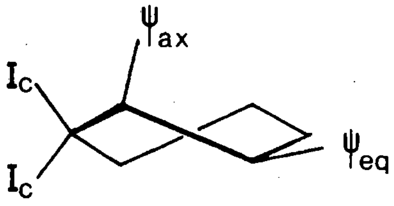


Figure 2.3. Ring inversion in cyclohexane - structures and energetics. Positions of hydrogen atoms are shown.

in energy to the strained chair, if not more stable than it. Whereas a chair conformation has two distinguishable positions (axial and equatorial) for substitution, a twist conformation (2.9) has three: pseudo-axial, ψ_{ax}, pseudo-equatorial, ψ_{eq}, and isoclinal, I_c. Only ψ_{eq} and I_c are unhindered positions and a twist conformer will provide relief to a sterically strained chair only if bulky groups can occupy unhindered positions. Thus, some of the possible twist conformers will not be stable. Stated clearly; "If a molecule is so encumbered as to be forced into a twist conformation, the encumbrance will raise the energy of most possible twist conformers, leaving very few possible twist conformers from the original pseudorotation circuit open to the molecule." (Kellie and Riddell, 1972).



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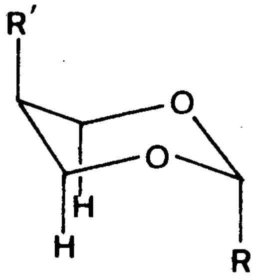


(2.10)

The introduction of heteroatoms into the ring further alters the energy profile for conformational interconversion. The following factors are partly responsible:

(i) Barriers to rotation about single bonds decrease in the order C—C > C—N > C—O ~ C—S. Although the barriers are not understood, experimental data shows that freedom of rotation about a C—A bond depends upon the number of substituents on atom A. In oxane therefore, the barrier to chair inversion is lower than that in cyclohexane.

(ii) A heterocyclic ring containing oxygen or nitrogen has shorter endocyclic bonds since C—O and C—N bond lengths are shorter than C—C bond lengths. It has been observed for example, that the preference of a substituent, R, for the equatorial position is much greater in 1,3-dioxanes (2.10) than in cyclohexane since the substituent's interaction with the *syn*-axial hydrogen atoms is greater in the dioxane.

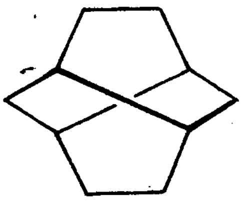
(iii) The axial substituent, R', in (2.10) is less encumbered than in the corresponding cyclohexane derivative because the *syn*-axial hydrogens are absent. Oxygen lone-pairs evidently cause little or no steric interference. As witness to this, among the very few six-membered cyclic compounds displaying evidence of axial t-butyl groups, are the 1,3-dioxane derivatives (2.10) with R = R' = t-butyl (Eliel and Knoeber, 1966, 1968).

(iv) The anomeric effect makes a polar substituent, *e.g.*, R = OMe, in (2.10) more stable in an axial position (Eliel, 1975).

2.4 *EXAMPLES OF MOLECULES PREFERRING NON-CHAIR CONFORMATIONS*

The search for non-chair conformations has not been easy, mainly as a result of their instability. Also, the difference in structure and energy between a relatively stable twist conformer and another possible stable conformer is, in general small, and considerable time and effort was required to develop and perfect physical techniques suitable for the detection of such subtle differences. Diffraction methods have been used only sparingly and so, little "concrete" evidence is available. Although it may sometimes be found that crystal structures do not give the true conformational picture, because of strong intermolecular forces, it has been noted from experience that "the geometry in a molecular lattice often corresponds closely to the geometry of one of the major conformers occuring in the liquid state or in solution" (Balasubramanian, 1962).

Despite the difficulties, however, the search has yielded some good examples. The first was found in a steroid by Barton (1957), one of the earliest pioneers of conformational analysis. Some molecules, as a result of bridging in their structures, constrain at least one six-membered ring into a non-chair conformation; for example, twistane (2.11) (Whitlock, 1962; Tichy, 1972) and bicyclo[2.2.2]octane (2.12) (Yokeziki *et al.*, 1970), the twist relative of adamantane. A classic example of a molecule apparently having an inherent preference for a non-chair conformation, is found in cyclohexan-1,4-dione (2.13), which has been shown to exist as a twist conformer in the solid state, in solution and in the gas phase (Grothard and Hassel, 1963; Mossel *et al.*, 1963; Allinger and Freiberg, 1961; Bastiansen *et al.*, 1971).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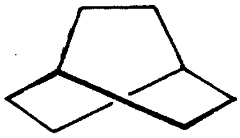
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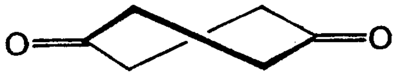

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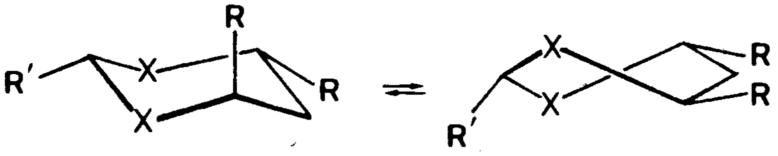

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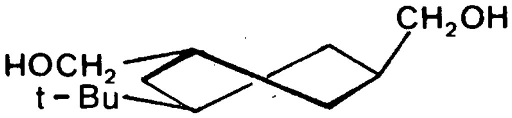

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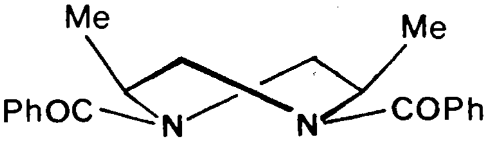

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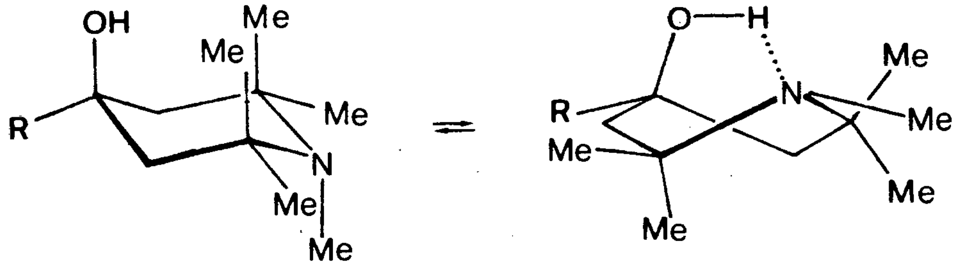

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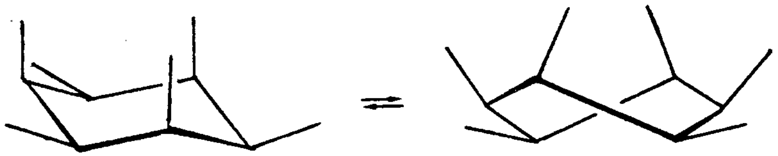

(2.22)

2.5 α-*PARACHLORAL AGAIN*

In the present case of α-parachloral, the interaction between the axial trichloromethyl group and the *syn*-axial hydrogens in the chair conformation is formidable. This is further aggravated (relative to the cyclohexane case) by the short ring bonds, and the molecule prefers a non-chair conformation with all CCl_3 groups in unhindered positions. As Figure 2.4 shows, the trichloromethyl group and the t-butyl group are of comparable size. α-Parachloral may therefore be compared with the molecules (2.14)-(2.16), in which a t-butyl group occupies an axial

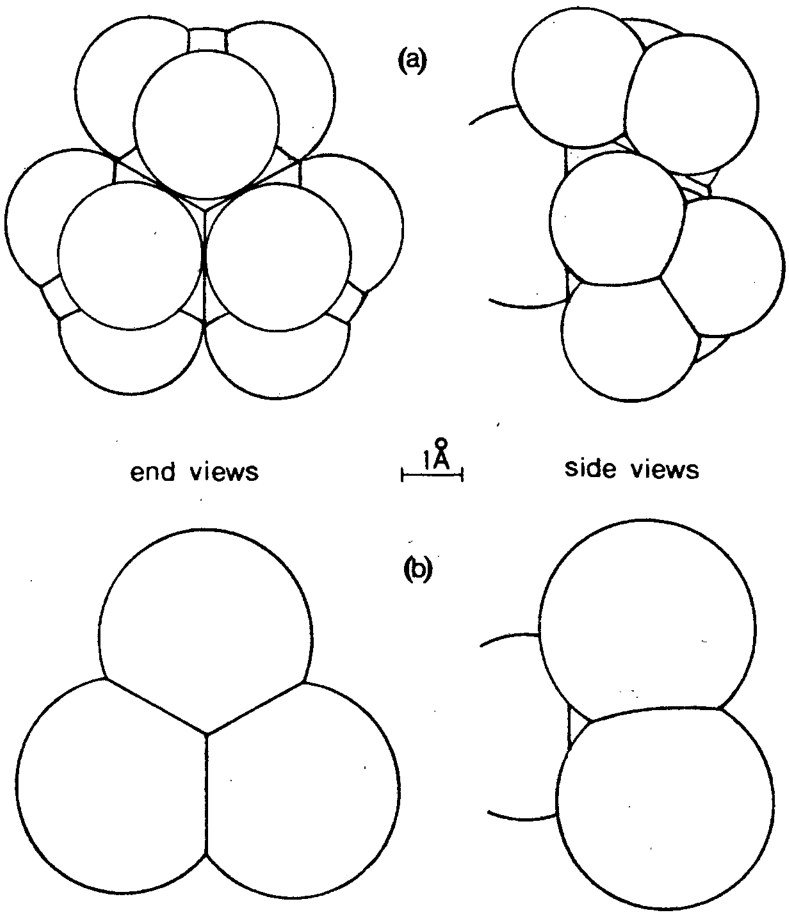

Figure 2.4. Relative sizes of (a) t-butyl and (b) CCl_3 *groups.*

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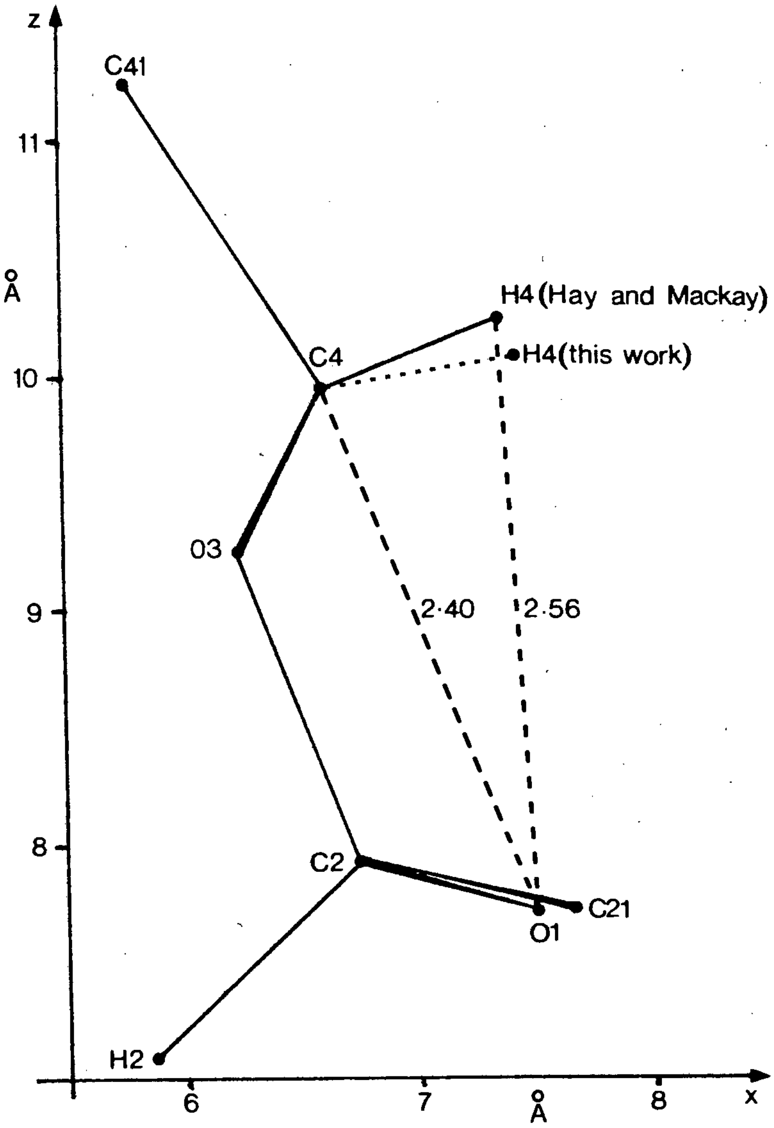

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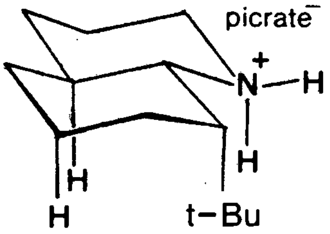

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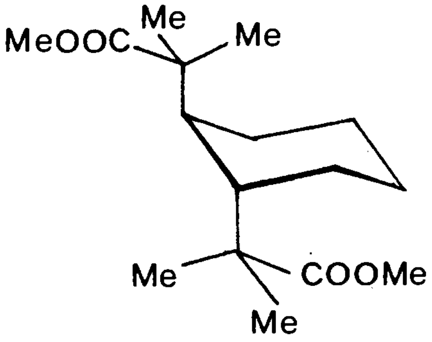


(2.24)

Thus, in α-parachloral, it is possible that in solution, chair and non-chair conformations are comparable in energy. Furthermore, it is difficult to assess the relative stabilities of boat and twist forms. Structurally, α-parachloral is far removed from the model compound cyclohexane, and the usual conformational energy scale has been severely upset. A number of attempts have been made in this work to establish the new energy order. The art of detecting non-chair forms and chair-twist equilibria has been much improved in recent years and the following methods in order of decreasing reliability, are in vogue: diffraction (electron and *X*-ray) and microwave techniques; nmr (especially ^{13}C) and other spectroscopy (especially infrared); ORD–CD, dipole moment measurements and kinetics.

2.6.1 Dipole moment studies

In an attempt to determine the conformation of α-parachloral, Novak and Whalley (1958) compared its experimentally observed dipole moment with values calculated for the possible conformers (2.4) and (2.5). Dipole moments were calculated by vector addition of individual bond moments, assuming $\mu_{CCl} = 1.57$, $\mu_{C-O} = 0.9$ and $\mu_{\overset{+}{C}-\overset{-}{H}} = 0.2$D, and tetrahedral angles throughout. Their results are given in Table 2.1 ($\mu_{calc,1}$). On these grounds they predicted the chair conformation for α-parachloral in solution. In the light of the crystal structure, their result carries no weight. Even if some chair conformer is present in solution, it is unlikely to be the dominant form. Furthermore, α-parachloral in solution probably exists as a mixture of conformers, so the measured dipole moment will be a weighted average of the dipole moments of individual conformers. Novak and Whalley did not consider the twist forms.

Although this method of calculating dipole moments was popular in the 1930s, its naivety has long been realised and it is seldom used nowadays. It cannot realistically be assumed that the electron distribution giving rise to a dipole moment in a molecule can be understood in terms of separate, non-interacting components. For example, the dipole of one bond may induce an opposing dipole in a neighbouring polarisable bond. A prime example of this is found in the chloromethanes. According to the method of vector addition of bond moments, the dipole moments of chloromethane and trichloromethane should be the same, 1.87D. However, while for the former the measured value is 1.85D, it is only 1.1D for the latter. This phenomenon is not due to deviation of valence angles from tetrahedral values (as electron diffraction measurements show), but to opposing moments induced by one C—Cl dipole in the other two, thus

Table 2.1

Dipole moment of α-parachloral.

Conformation	$\mu^{a}_{calc,1}$	$\mu^{b}_{calc,2}$	$\mu^{c}_{calc,3}$	μ^{d}_{obs}
Chair (2.4)	1.59	1.6	2.4	1.6 ± 0.1
Boat (2.5)	0.60	1.6	2.2	

a Novak and Whalley using $\mu_{CCl} = 1.57$, $\mu_{CO} = 0.9$, $\mu_{\overset{+}{C}\overset{-}{H}} = 0.2D$.

b Using $\mu_{CCl} = 1.57$, $\mu_{CO} = 0.9$, $\mu_{\overset{+}{C}\overset{-}{H}} = 0.2D$.

c Using $\mu_{CCl} = 1.5$, $\mu_{CO} = 0.7$, $\mu_{\overset{-}{C}\overset{+}{H}} = 0.4D$ (Moody and Thomas, 1971).

d Measured by Novak and Whalley - in cyclohexane at 25°C.

reducing the effective moment of each C—Cl bond (Smythe, 1929). Thus, molecules containing CCl_3 groups are prime victims of this failure of the method. Attempts have been made to calculate induced moments, but the improvements were not sufficient; other complicating factors remain (Moody and Thomas, 1971). Furthermore, the calculation of individual bond moments is a dubious affair. Various different tabulations of these have been produced. All bond moments in any given set are based upon the estimated bond moment of the C—H bond. There has been much discussion not only about the magnitude of the C—H moment, but also about its sense, so considerable care must be taken when deciding which bond moments to use (Moody and Thomas, 1971).

With these considerations in mind, Novak and Whalley's calculations were repeated, firstly using their bond moment values, and secondly, using more recent estimates (see Section 2.8.3). The assumption of tetrahedral angles throughout the molecule is acceptable, for the crystal structure shows that bond angles seldom deviate by 3° from 109.5°. This assumption will not be the grossest. The method of calculation is given in the Appendix and the results in Table 2.1, in the columns headed $\mu_{calc,2}$ and $\mu_{calc,3}$. It appears that Novak and Whalley must have miscalculated the dipole moment of the boat form of α-parachloral. According to present calculations, the dipole moments of chair and boat forms are not significantly different, so that no conclusion can be reached regarding the preferred conformation in solution.

An attempt was made to estimate a group moment for the CCl_3 group, to overcome the problem of dipole induction discussed earlier. The attempt was foiled, however, firstly by the lack of measured dipole moments of suitable CCl_3-containing compounds, and secondly by the wide scatter of results obtained.

Vectorial calculations of dipole moments have largely been replaced by quantum mechanical calculations, based on calculated molecular electron distributions. This is a more sophisticated and satisfactory approach. However, it is, in general, only applicable to small molecules since the commonly available programs cannot handle the large numbers of electrons that are present in a molecule such as parachloral.

2.6.2 Infrared spectroscopy

Infrared spectroscopy is potentially useful in determining whether the solid state and solution conformations of α-parachloral are different. Unfortunately, even if the chair is present in solution, spectra of the chair and boat forms are expected to be very similar, since their symmetries are the same (C_s). However, it was thought that if the intramolecular hydrogen bond could be detected by infrared spectroscopy, the C—H stretching region of the solution and solid state spectra should reveal any conformational differences, since the hydrogen bond cannot be present in the chair conformation. Spectra were run in carbon tetrachloride and as mulls in hexachlorobutadiene and nujol. The results are presented in Table 2.2. Novak and Whalley (1958) measured and assigned the infrared spectra of α- and β-parachloral. Only in the C—H stretching region do theirs and the present spectra differ significantly. As they pointed out, three C—H stretching vibrations are expected in the spectrum of α-parachloral, in accordance with its C_s symmetry. However, whereas they observed three bands in the 3000 cm^{-1} region, the present spectra show only two. The frequencies of their C—H bands differ by as much as 25 cm^{-1} from the present values.

The solution and solid state spectra of α-parachloral vary only slightly. Firstly, in the region of the C—H bends, 1325-1360 cm^{-1}, different

Table 2.2

Infrared spectra of the parachlorals.

α-Parachloral			β-Parachloral
Solution[a]	Solid[b]	Assignment[c]	Solution[a]
2946 m	2950 m	ν(C—H)	2926 w
2905 m	2907 m		2876 m
1391 w	1394 w		1411 m
1356 m	1357 s	δ(C—H)	1365 m
1337 m	1336 m		1328 s
1328 m,sh	1329 m,sh		
1309 s	1311 m		
1225 w	1230 w		1205 w
1165 vs	1167 vs	Skeletal stretching	1159 vs
1140 vs,sh	1150 vs,sh		1140 s,sh
	1140 vs,sh		
1079 m	1084 m		1075 m
1053 s	1052 s	Skeletal stretching	1037 s
1007 w	1003 w		
852 vs	851 vs		850 vs
820 s,sh	828 vs		835 s
812 s	811 vs		810 s

a In CCl_4.

b In HCBD and nujol.

c According to Novak and Whalley, 1958.

intensity patterns are observed in the two spectra. Secondly, the band at 828 cm^{-1} in the solid state spectrum appears to be shifted in the solution spectrum. The bands in this region are probably due to skeletal stretching vibrations (Novak and Whalley, 1958). These differences could constitute tenuous evidence for conformational differences. On the other hand, coupling interactions, present in the solid state but not in solution, could account for the differences.

On the formation of an A—H•••B hydrogen bond, three changes are normally observed in the A—H stretching band:

(i) its frequency shifts to a lower value;
(ii) it broadens; and
(iii) its intensity increases.

However, in C—H•••B systems, especially when B = oxygen, it has often been observed that the changes (i) and (ii) do not occur, presumably due to the weakness of the hydrogen bond (Pimentel and McClellan, 1960; Green, 1974). The intensity increase is considered to be the most sensitive indication of the presence of a hydrogen bond.

The C—H stretching bands are not noticeably broad in the solution or solid state spectra of α-parachloral. Neither can it be assessed whether the bands are shifted or more intense, since it is not possible to obtain a sample of α-parachloral which is free from hydrogen bonding. β-parachloral is not a suitable model compound since its symmetry is different. In fact, the C—H stretching frequencies are higher, and the bands only slightly more intense (relative to other spectral bands) in the α-isomer than in the β-isomer, but no unambiguous conclusion can be drawn from these findings. In short, infrared spectroscopy provides no convincing evidence, either for or against the existence of the chair form of α-parachloral in solution.

2.6.3 Nuclear magnetic resonance spectroscopy

Dynamic nmr spectroscopy (dnmr) has been used extensively to investigate conformational processes (Anet and Anet, 1975). One of the problems of this technique is that, although conformational processes are first order and thus relatively simple, the nmr spectrum of a cyclic compound is often very complex. For example, cyclohexane has a twelve proton system, giving rise to an enormously complicated ^{1}Hnmr spectrum. The problem may be simplified of course, by deuteration or by using ^{13}Cnmr. In the case of α-parachloral, the ^{1}H spectrum is very simple (Figure 2.7), two of the three protons being equivalent, with no observable coupling at 90 MHz. From that point of view, it is an ideal system for a dnmr experiment. Another requirement for a successful experiment, is that the frequency separation between lines that broaden and coalesce as the exchange rate increases, should be as great as possible. It is impossible to know whether this requirement is fulfilled in the case of α-parachloral, but from consideration of models, it is expected that the chemical shift of the unique proton (H_C) should differ considerably in chair and non-chair conformers.

The following nmr experiments were carried out:

(i) The ^{1}Hnmr spectrum of α-parachloral was measured in dichloromethane-d_2, at 20°C intervals, in the range 20°C to -80°C. The signal of the unique proton, H_C, was seen to shift steadily from δ 6.14 to δ 6.09 ppm, while that of the two equivalent protons ($H_{A,B}$) was invariant. Instrumental error is estimated to be better than 0.5 Hz, and the grossest possible uncertainty, including the measurement of chemical shifts, is estimated to be 1 Hz. Therefore, a shift of 0.05 ppm (5 Hz, measured at 100 MHz) is indeed a significant one, albeit small over such a wide temperature range.

(ii) The ^{1}Hnmr spectrum of α-parachloral was measured in dimethylsulphoxide-d_6, at 10°C intervals from 20°C to 120°C. Up to 70°C, there was no change in the spectrum. Above 70°C, the signal of H_C shifted from δ 6.08 to δ 6.11 ppm (3 Hz, measured at 90 MHz), while that of $H_{A,B}$ shifted from δ 6.20 to δ 6.15 ppm (5 Hz.)

(iii) The ^{1}Hnmr spectrum of α-parachloral was measured in acetone-d_6 at intervals from 20°C to -80°C. The spectral changes are depicted in Figure 2.6. The signal of H_C shifted by 4 Hz (measured at 100 MHz) and that of $H_{A,B}$ by 9 Hz.

(iv) The ^{1}Hnmr spectrum of α-parachloral was measured in solvents of varying donor strength at room temperature. The results are shown in Figure 2.7.

(v) The ^{13}Cnmr spectrum of α-parachloral was measured in chloroform-d, as shown in Figure 2.8.

The following description of the α-parachloral system is consistent with the above experimental observations:

(a) *The chair conformer is not present at temperatures below 70°C in any solvent.*

The change in the ^{1}Hnmr spectrum in dichloromethane-d_2 and dimethylsulphoxide-d_6 over the large temperature range from -80°C to 70°C is considered to be negligible. Even if some chair conformer were present

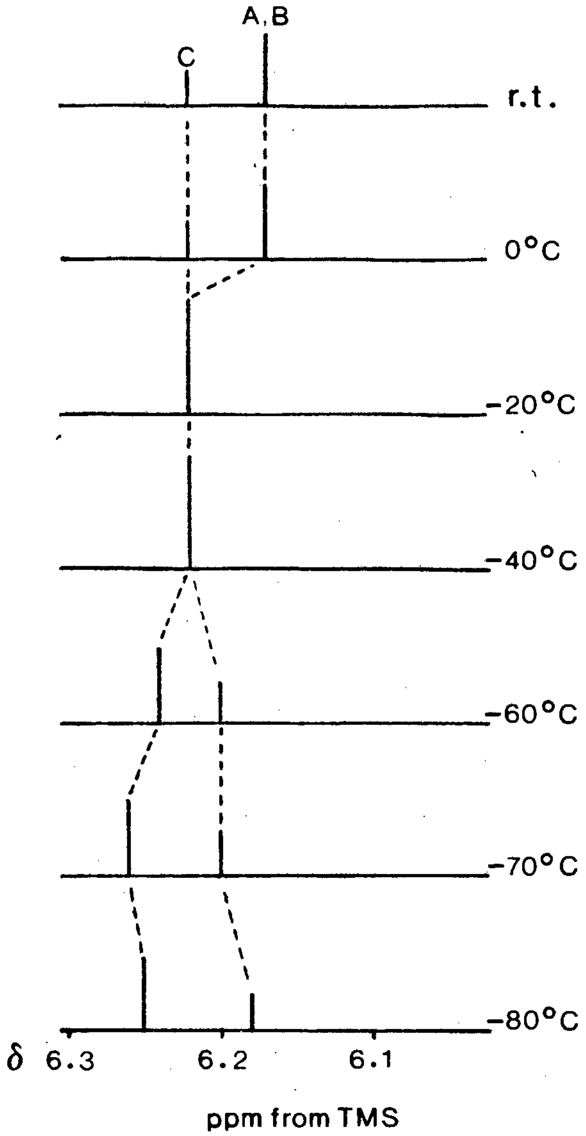


Figure 2.6. Temperature dependence of the ^{1}Hnmr spectrum of α-parachloral in acetone.

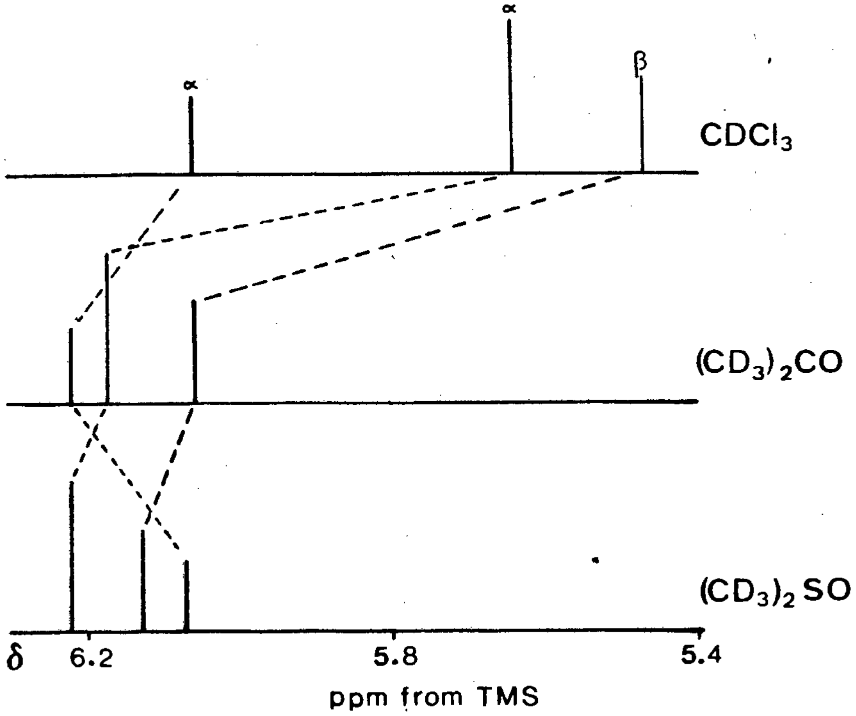


Figure 2.7. Solvent dependence of the ^{1}Hnmr spectra of α- and β-parachloral.

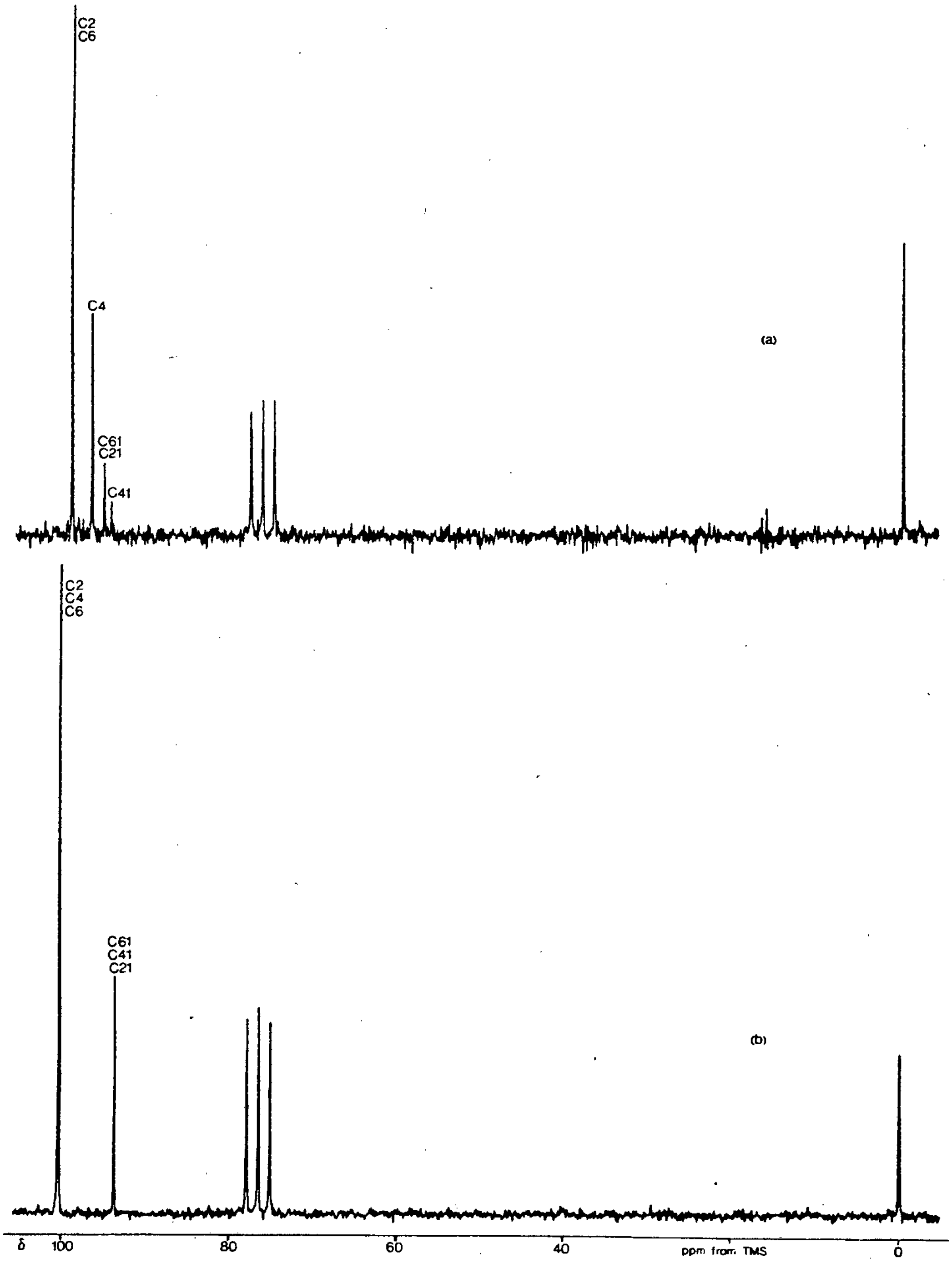


Figure 2.8. Broad-band decoupled ^{13}Cnmr spectra of (a) α-parachloral and (b) β-parachloral in $CDCl_3$.

it would certainly not be the predominant form, and the resulting chair—non-chair conformational equilibrium would have been manifested by a significant temperature dependence of the spectrum.

(b) *Some chair conformer may exist above 70°C.*
The temperature dependence of the ^{1}Hnmr spectrum of α-parachloral from 80°C to 120°C in dimethylsulphoxide-d_6, may indicate chair—non-chair equilibrium in this temperature range.

(c) *Below 70°C, only twist and boat conformers exist, and are in rapid equilibrium.*
The proposed system is depicted in Figures 2.9 and 2.10. In an important paper, Loomes and Robinson (1976) showed, *inter alia*, that the ^{13}C chemical shifts of ring carbon atoms in a large selection of six-membered carbocyclic and heterocyclic compounds, appear considerably upfield in twist conformers relative to those in diastereomeric chair conformers. The ^{13}Cnmr spectra of α- and β-parachloral are unambiguously assigned in Figure 2.8 (signals from ring carbon atoms are identifiable by nuclear overhauser enhancement effects). The ring carbon atoms in the α-isomer are shielded (by 1.1 and 3.5 ppm) relative to those of the β-isomer, which exists completely in the chair conformation. In view of the results of Loomes and Robinson, this provides good evidence for the predominance of non-chair conformers of α-parachloral.

If, at some temperature, the enantiomeric twist conformers were interconverting at a slow rate on the nmr time scale, then the protons H_A and H_B would be distinguishable (all three protons in either static twist conformer are non-equivalent), and the spectrum would have three lines. Since this is not observed at any temperature, it must be assumed that twist-twist interconversion, *via* the boat conformer, is very rapid.

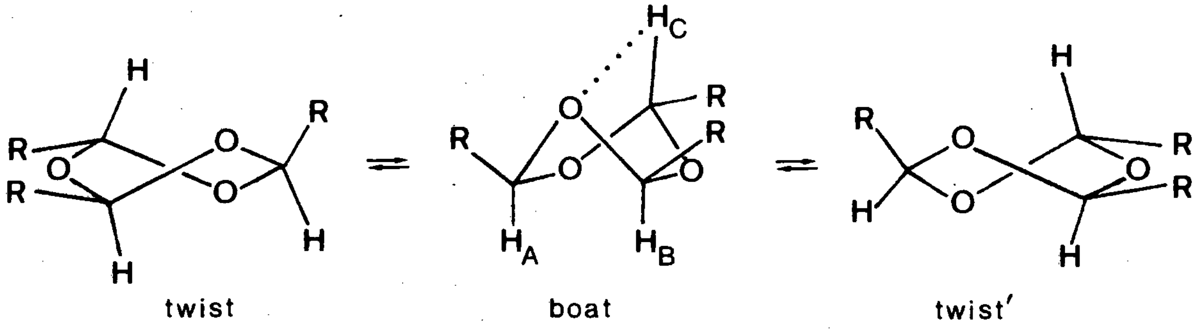


Figure 2.9. Conformers of α-parachloral (R = CCl_3) present in solution below 70°C.

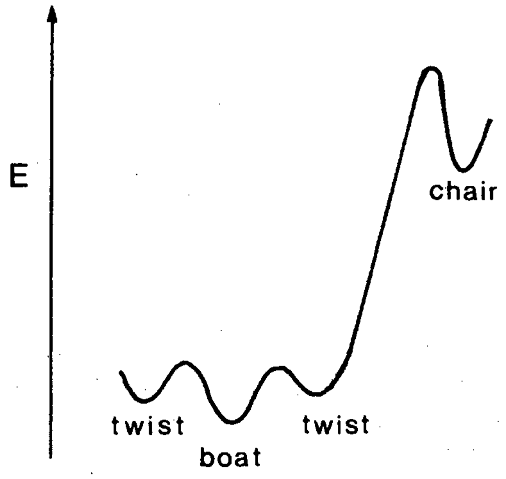


Figure 2.10. Proposed relative energies of conformations of α-parachloral.

Furthermore, the enthalpy difference between boat and twist forms is likely to be small, so that significant temperature effects are unlikely near room temperature (since the Boltzmann distribution curve will then be shallow in this region, and the populations of boat and twist states will be fairly constant).

(d) *The temperature dependence of the ^{1}Hnmr spectrum in acetone is due to competition between intra- and intermolecular hydrogen bonding.*
In general, the involvement of a proton in hydrogen bonding manifests as a downfield shift of its nmr signal (Joesten and Schaad, 1974). As discussed already, the hydrogens on the parachlorals are suitably "activated" to act as hydrogen bonding acids. The significant downfield shift of the ^{1}H signal from β-parachloral (Figure 2.7) on increasing solvent donor strength, is probably indicative of increasing involvement of the protons in intermolecular hydrogen bonding with the solvent. Likewise, the steady downfield shift of the signal due to H_A and H_B in the spectrum of α-parachloral (Figure 2.7) is considered to have the same cause. Proton H_C is the object of competition between intramolecular hydrogen bonding and intermolecular hydrogen bonding with the solvent. In dimethylsulphoxide the competition is likely to favour, almost exclusively, intermolecular hydrogen bonding, since that solvent is a very powerful donor. In acetone, the competition is probably more equal. On cooling, however, the hydrogen bonding donor capabilities of acetone will increase, precluding more and more, intramolecular hydrogen bonding. Hence the marked temperature dependence of α-parachloral in acetone (Figure 2.6). It is interesting that the pattern of signals is the same in acetone at low temperatures, as it is in dimethylsulphoxide. More explicitly, in non-donor solvents, H_C resonates downfield from $H_{A,B}$, whereas in strong donor mediums, this arrangement is inverted.

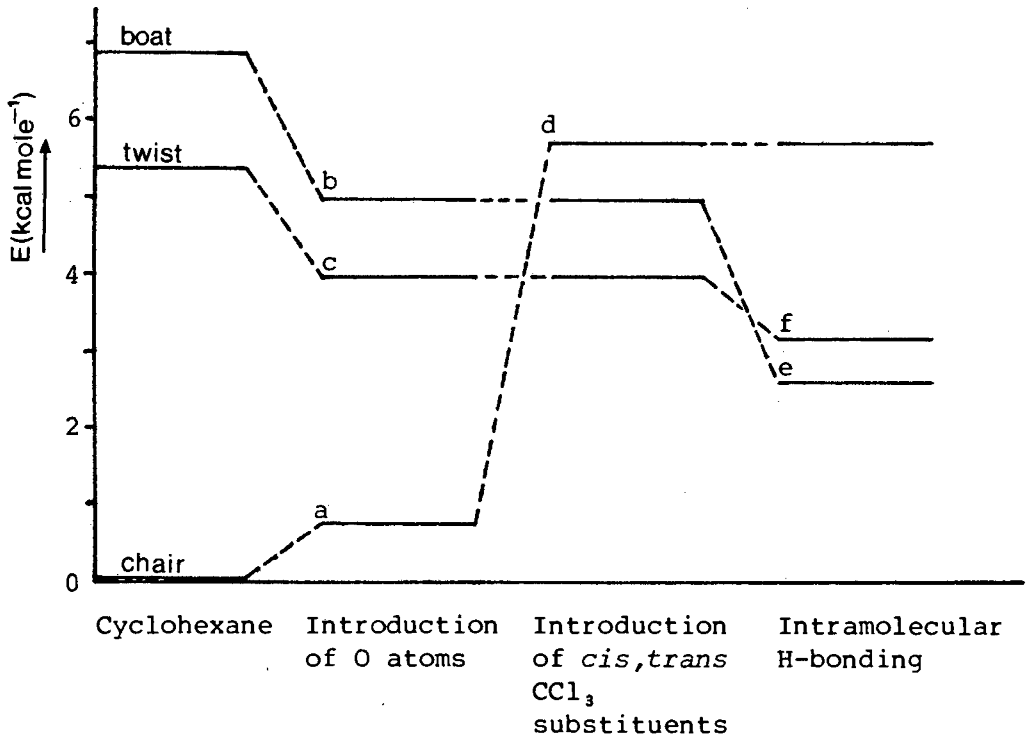
The idea of competition between intra- and intermolecular hydrogen bonding is not unprecedented. In orthonitro-anilines, for example, the hydrogen bonding in chloroform was found to be intramolecular, and in dimethylsulphoxide, intermolecular (Joesten and Schaad, 1974).

It may be expected that the signal from H_C should shift steadily downfield, as with $H_{A,B}$ on cooling in acetone, since the strength of its hydrogen bond is increasing. But there is another temperature-dependent factor which affects the chemical shift of H_C, namely, the influence of the neighbouring trichloromethyl groups. Whereas H_A and H_B are relatively remote from neighbouring CCl_3 groups, H_C falls under the powerful anisotropy of two such neighbours. Moreover, H_C experiences the effect of these CCl_3 groups more strongly in the twist than in the boat conformer. Since the rate of twist-boat-twist interconversion is temperature dependent, the influence of the neighbouring CCl_3 groups on H_C must also vary with temperature.

2.6.4 *Some simple energy considerations*

Cyclohexane, the most studied cyclic molecule, is a useful model compound in the conformational analysis of six-membered cyclic systems. The structures and energies of its conformations are well known (Eliel *et al.*, 1967). Conceivably, the relative energies of conformations of α-parachloral could be estimated by extrapolation from those of cyclohexane. Figure 2.11 represents an attempt in this direction. The diagram shows how the energies of conformations of α-parachloral may be affected by a hypothetical stepwise conversion of cyclohexane into α-parachloral. A complete inversion of the energy order is suggested, a prediction supported both by nmr studies and the consideration of molecular models.

Figure 2.11. Estimation of energies of conformations of α-parachloral by extrapolation from cyclohexane.



a The chair is slightly destabilised by shortening of the ring bonds leading to increased *syn*-axial interactions. However, they are now present on one side of the ring only. The distance between *syn*-axial hydrogen atoms in β-parachloral is 2.30 Å, about the van der Waals distance.

b The boat experiences the lifting of much of its strain. The removal of hydrogen atoms from the 1,3,5-positions reduces the torsional strain of eclipsed bonds. The ring bonds are still eclipsed, however. The serious steric compression of the flagpole hydrogen atoms has been removed.

c The same stresses which are reduced in the boat are reduced in the twist, but to a smaller extent. Lowered rotational energies about ring bonds tend to reduce the pseudorotation barrier.

d The conformational energy of an axial t-butyl group has been estimated to be ∼ 5 kcal mol^{-1} (Eliel *et al.*, 1967). It has been assumed here that CCl$_3$ groups in unhindered positions (eq, ψ_{eq} or I_C) exert a similar influence on the energies of chair and non-chair conformations.

e ΔH for a hydrogen bond between chloroform and an ether is about -2.5 kcal mol^{-1} (Joesten and Schaad, 1974).

f Although no hydrogen bonding can be present in the twist, some stabilisation may result from close approaches of hydrogen to oxygen atoms.

2.7 *CONCLUSION*

That α-parachloral chooses a boat conformation in the solid state constitutes, perhaps, the strongest evidence against the existence of the chair form in solution. It is likely, in view of the crystal structure, that the boat is the most stable conformation of all. In solution, however, with solvent interference in the trans-annular hydrogen bond, which stabilises the boat form, the twist conformer probably also becomes important. Examples of similar systems are found in (2.8), (2.19) and (2.21). The boat conformer of (2.8) is preferred in the solid state and in solution. In (2.19) also, in solution, intramolecular hydrogen bonding stabilises non-chair conformations to the practical exclusion of the already burdened chair. Although a non-chair conformation of (2.21) is important in solution, the chair form is not strained enough to prevent its equal importance, as borne out by its appearance in the crystal structure. An nmr temperature study (preferably ^{13}C) on α-parachloral above 120°C may yield more positive evidence of the existence of its chair conformer.

2.8 *APPENDIX*

2.8.1 *Preparation and characterisation of the parachlorals*

A mixture of the parachlorals was prepared by Professor H. Irving according to the method of Chattaway and Kellett (1928). The isomers were separated by dry-column chromatography using deactivated Merck silica gel 60 (containing 20% m/m water). 3 g of parachloral and 3 g of silica gel were ground together and 30 ml of chloroform added. The solvent was removed on a rotary evaporator and the parachloral sample, now adsorbed onto silica gel, was added to a 45 mm diameter column, Nmr spectra were measured on a Varian XL100 100 MHz spectrometer and a Bruker WH90 90 MHz FT spectrometer.

2.8.3 *Dipole moment calculations*

(i) α-*Parachloral, chair conformer.*

The molecule is aligned with the cartesian co-ordinate system as shown in Figure 2.12. Tetrahedral angles are assumed throughout. Simple considerations show that C–CCl_3 reduces vectorially to C–Cl.

Then, if μ_x, μ_y and μ_z are the components of the molecular dipole parallel to x, y and z respectively, after cancellation of equal and opposite dipole components,

$$\begin{aligned} \mu_x &= 2\mu_{CO} - \mu_{CH} + (2\mu_{CH} - 4\mu_{CO} - 3\mu_{CCl})B_x \\ \mu_y &= -2\mu_{CH}B_y - 4\mu_{CO}C_y \\ \text{and} \quad \mu_z &= 0 \end{aligned}$$

where μ_{AB} is the magnitude of the A–B bond moment,

$$\begin{aligned} B_x &= \cos 70.5° \\ B_y &= \sin 70.5° \\ \text{and} \quad C_y &= \sin 70.5° \cos 60°. \end{aligned}$$

Substituting $\mu_{CO} = 0.9$, $\mu_{\overset{+}{C}\overset{-}{H}} = 0.2$ and $\mu_{CCl} = 1.57D$ (Novak and Whalley, 1958), the resultant is

$$\mu_{calc,2} = 1.6D$$

Substituting $\mu_{CO} = 0.7$, $\mu_{\overset{-}{C}\overset{+}{H}} = 0.4$ and $\mu_{CCl} = 1.5$ D (Moody and Thomas, 1971),

$$\mu_{calc,3} = 2.4 \text{ D}$$

in the direction shown in Figure 2.12.

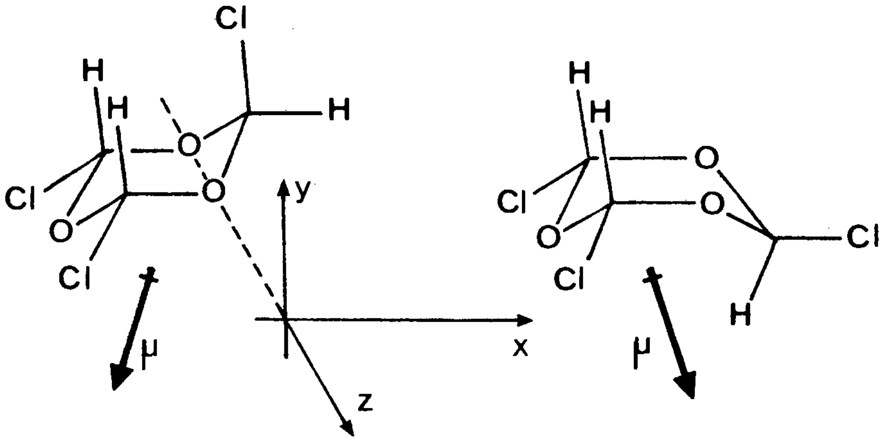


Figure 2.12. Models used for calculation of dipole moment of α-parachloral.

(ii) *α-Parachloral, boat conformer.*

If the molecule is aligned as Figure 2.12 shows, then

$$\mu_x = 2\mu_{CO} + \mu_{CCl} + (3\mu_{CH} - 4\mu_{CO} - 2\mu_{CCl})B_x$$

$$\mu_y = -\mu_{CH}B_y - 2\mu_{CCl}C_y$$

and $\mu_z = 0$.

The resultants are

$$\mu_{calc,2} = 1.6D$$

and $\mu_{calc,3} = 2.2D$

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3

AN UNUSUAL KIND OF ISOMERISM IN PARABUTYLCHLORAL, 2,4,6-TRIS(1',1',2'-TRICHLOROPROPYL)-1,3,5-TRIOXANE

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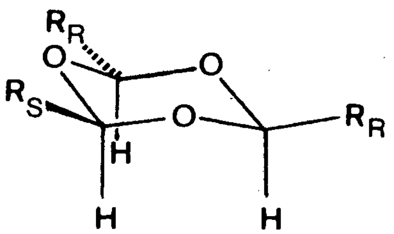
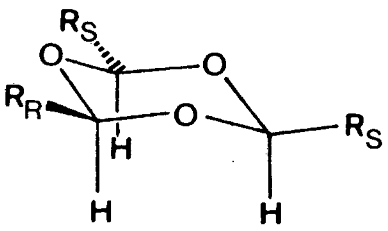
3.1 INTRODUCTION

During their work on polymers of aliphatic chloroaldehydes, Chattaway and Kellett (1928) isolated two forms of the cyclic trimer of butylchloral (2,3,3-trichlorobutanal), presuming them to be *cis,cis* and *cis,trans* isomers by analogy with their work on α- and β-parachloral (Section 2.1). The ^{1}Hnmr spectrum of the more soluble β-isomer shows the equivalence of the three ring protons and of the three side-chains, pointing to the expected C_{3v} symmetry in solution (Baron and Hollis, 1964). In the spectrum of the α-isomer however, non-equivalence of all three ring protons and of all three side-chains was observed by these workers. They rationalised this unexpected behaviour in terms of a *cis,trans*-chair form with restricted rotation about the bond joining the axial $CCl_2CHClCH_3$ group to the ring. This would remove the imagined mirror plane from the molecule. However, they observed no significant changes in the spectrum at elevated temperatures.

In a later paper, Baron (1967) re-examined the ^{1}Hnmr spectrum of α-parabutylchloral and proposed that the chiral carbon atoms β to the trioxane ring cause magnetic non-equivalence of the ring protons. He showed that the spectrum can be explained if α-parabutylchloral is considered to be a racemate of the two structures (3.1) and (3.2) where R_S and R_R are the two enantiomeric forms of the $CCl_2CHClCH_3$ side-chain.



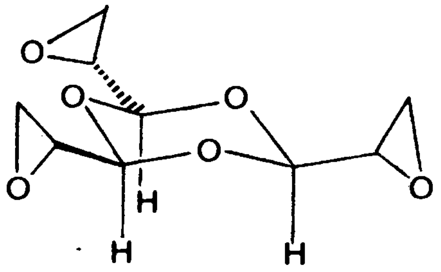
(3.1)



(3.2)

The two enantiomers (3.1) and (3.2) (which may be called the RRS and RSS isomers respectively) are, of course, indistinguishable by nmr. The non-equivalence of the ring protons arises from the fact that the molecules possess no elements of symmetry. In a similar manner, β-parabutylchloral was envisaged as a racemate of the two compounds with substituents either *all* R_S or *all* R_R (the SSS and RRR isomers respectively).

This proposition was made following the initiative of Jungnickel and Reilly (1965) who demonstrated a similar situation with the cyclic trimer of glycidaldehyde (3.3). The chiral centre in the epoxide substituent leads to the existence of RRR-SSS and RRS-RSS racemates. The ^{1}Hnmr spectra of glycidaldehyde trimers were readily interpreted in this light.



(3.3)

Baron's hypothesis has now been tested by determining the crystal structures of both isomers of parabutylchloral. Their ^{13}Cnmr spectra are also discussed.

3.2 PREPARATION OF PARABUTYLCHLORAL

Butylchloral hydrate was prepared from crotonaldehyde through α-chlorocrotonaldehyde following a standard method (Ropp *et al.*, 1963). Trimerisation was carried out following the method of Chattaway and

Kellett (1928). The isomers were separated initially by fractional crystallisation, but more effectively by silica gel column chromatography. The compounds were identified and characterised by microanalysis, melting point, ^{1}Hnmr and mass spectrometry. The ^{1}Hnmr spectra (Figure 3.1) are identical to those reported by Baron and Hollis (1964). Numerical chemical shift data are given in Table 3.1. The melting points are slightly higher than those determined by Chattaway and Kellett (1928). Difficulties were experienced during separation by fractional crystallisation in the present work, and a large number of crystallisations were necessary to achieve chromatographic purity. It is possible that the early workers, with their tedious technique alone, did not reach this standard.

3.3 MASS SPECTROMETRY OF TRIOXANES

The mass spectra of α-parachloral and α-parabutylchloral are shown in Figures 3.2 and 3.3. In both cases, the molecular ion was not observed until the electron beam energy was lowered to 11 eV, indicating facile ring-cleavage. Even so, under these low energy conditions, it is the M+1 ion and not the molecular ion which is observed. The molecular ion evidently combines with a hydrogen atom in the source. The assignment of peaks in the mass spectra of these trioxanes, and the deduction of cracking patterns, is assisted by chlorine isotopic patterns. The patterns are often slightly distorted in the final mass spectrum, but are nonetheless of great help in determining the number of chlorine atoms in each fragment. Fragmentation patterns are suggested in Schemes 3.1 and 3.2.

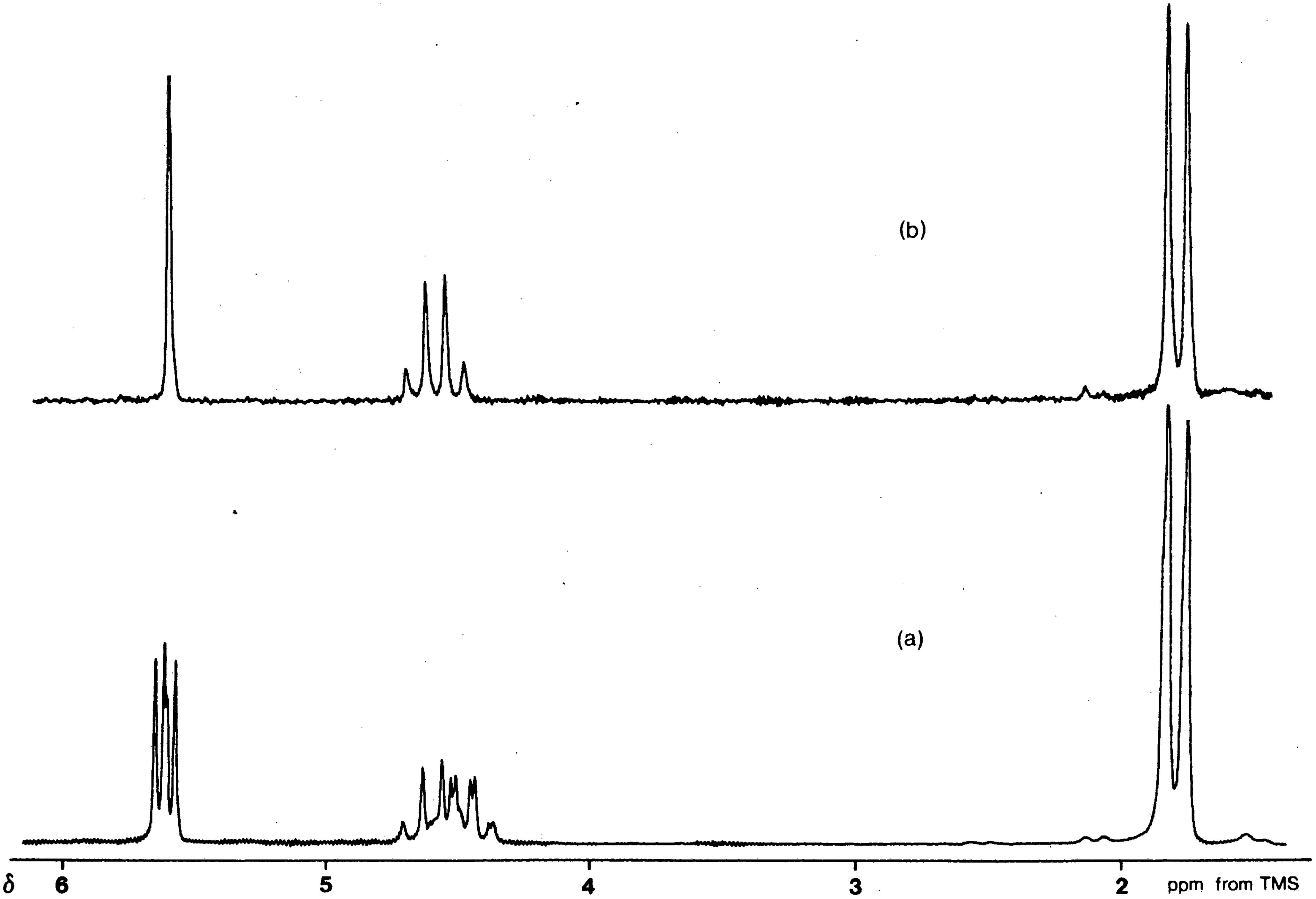


Figure 3.1. ^{1}*Hnmr spectra of (a) α-parabutylchloral and (b) β-parabutylchloral in* $CDCl_3$.

Table 3.1

^{1}H chemical shifts (ppm from TMS) and coupling constants (Hz) for α- and β-parabutylchloral in $CDCl_3$.

	Ring H	CHCl	CH_3	^3J
α-parabutylchloral	5.66(s) 5.62(s) 5.58(s)	4.60(q) 4.50(q) 4.48(q)	1.82(d)	6.3
β-parabutylchloral	5.61(s)	4.61(q)	1.81(d)	6.3

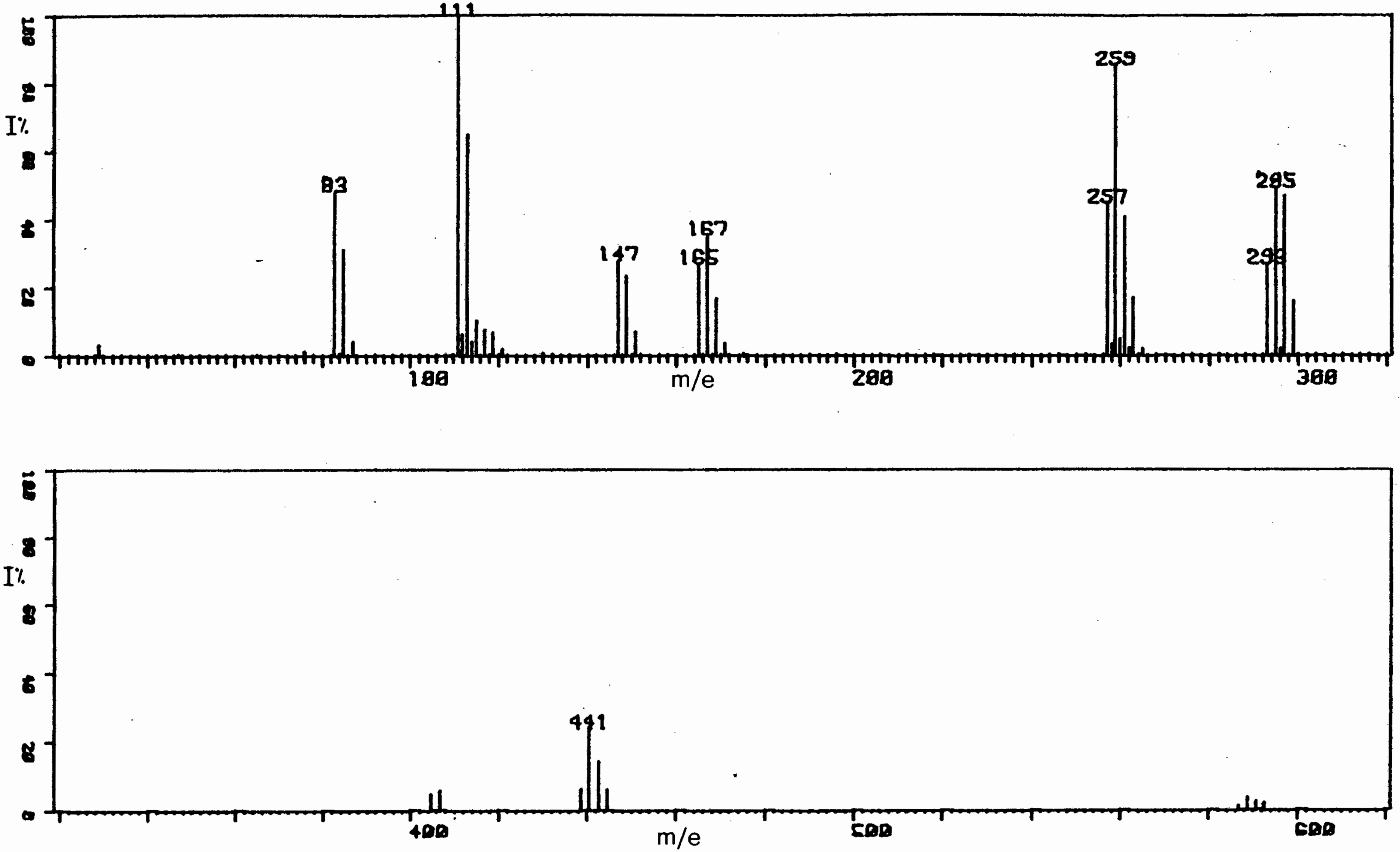


Figure 3.2 11eV mass spectrum of α-parachloral.

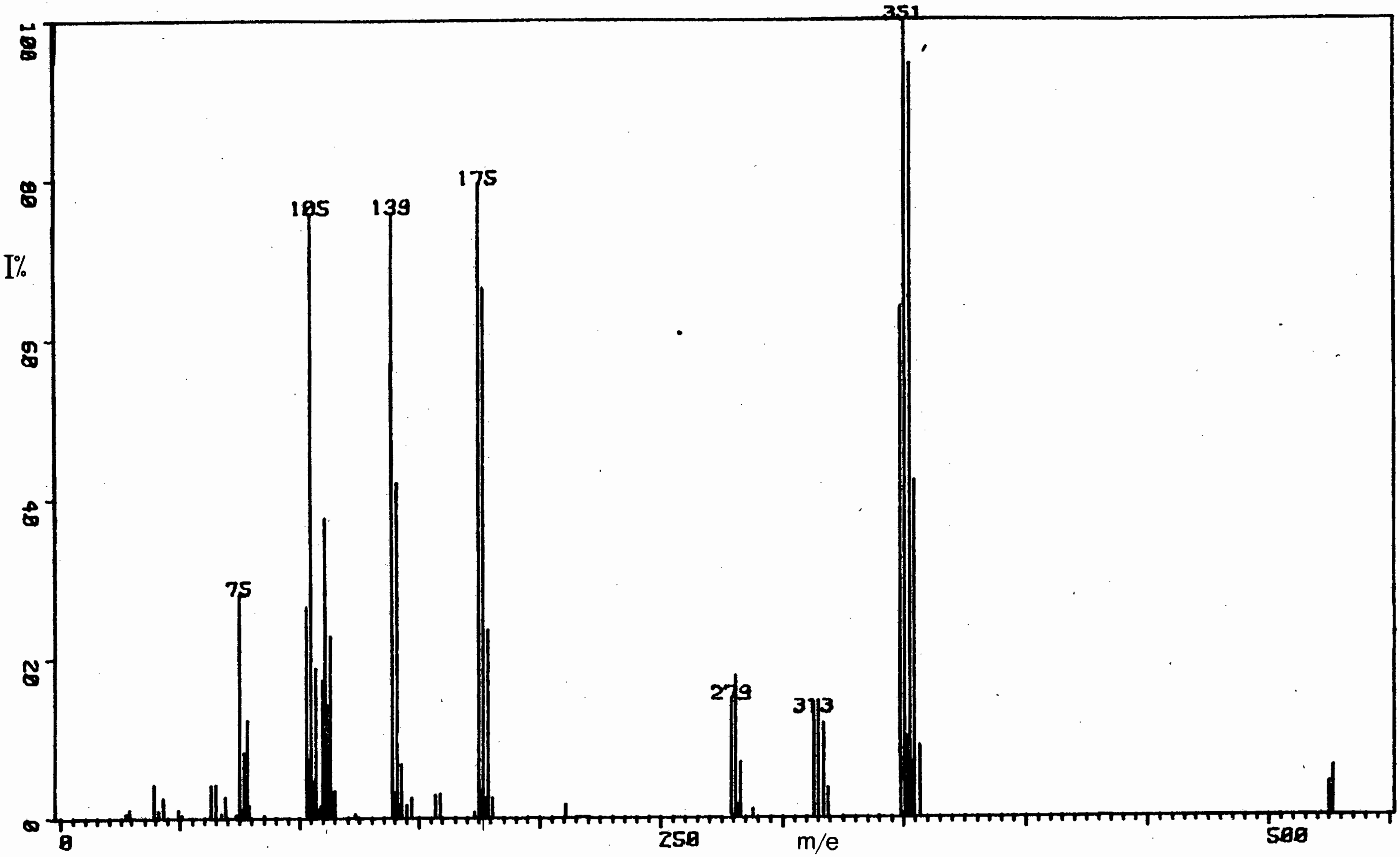
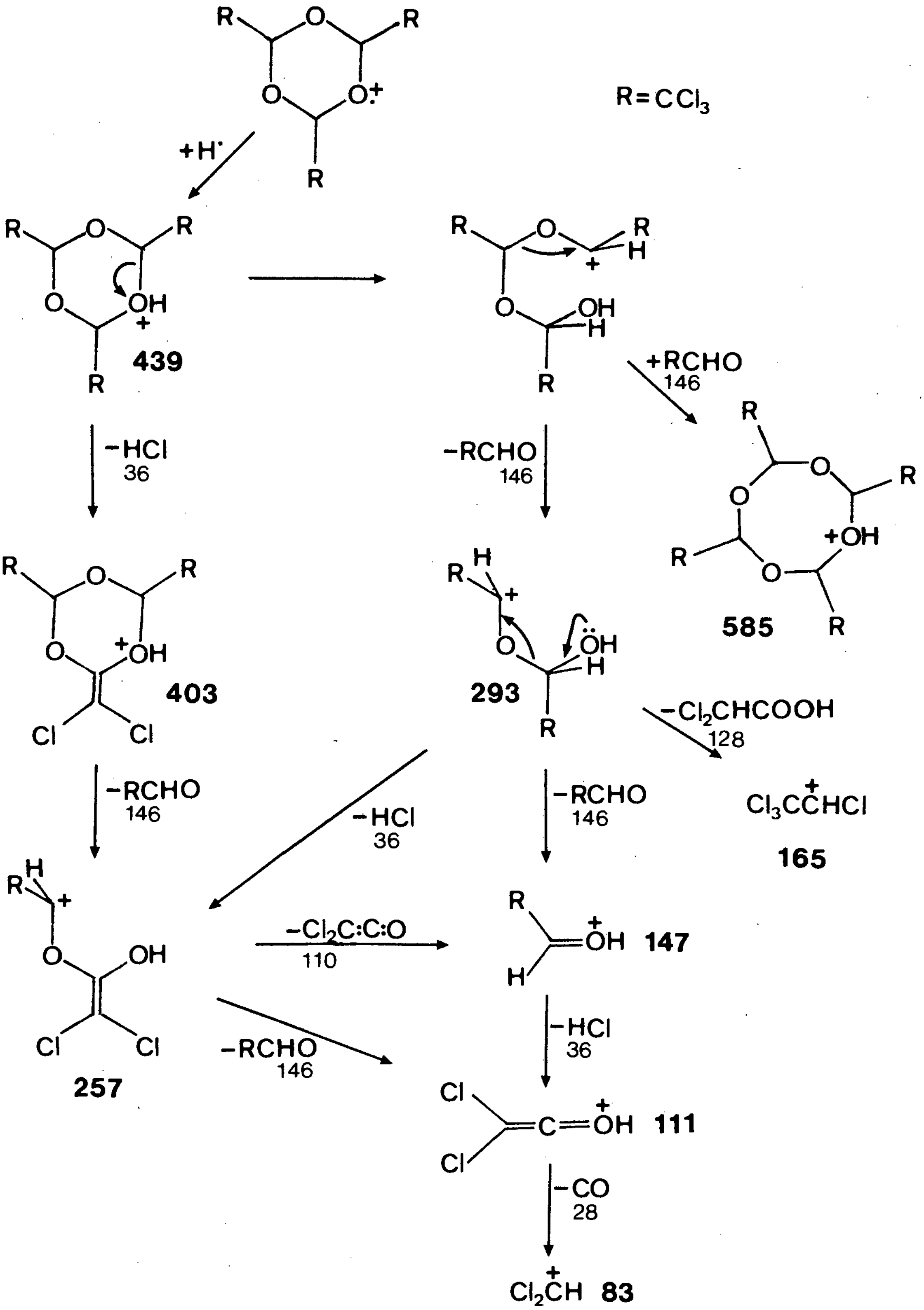
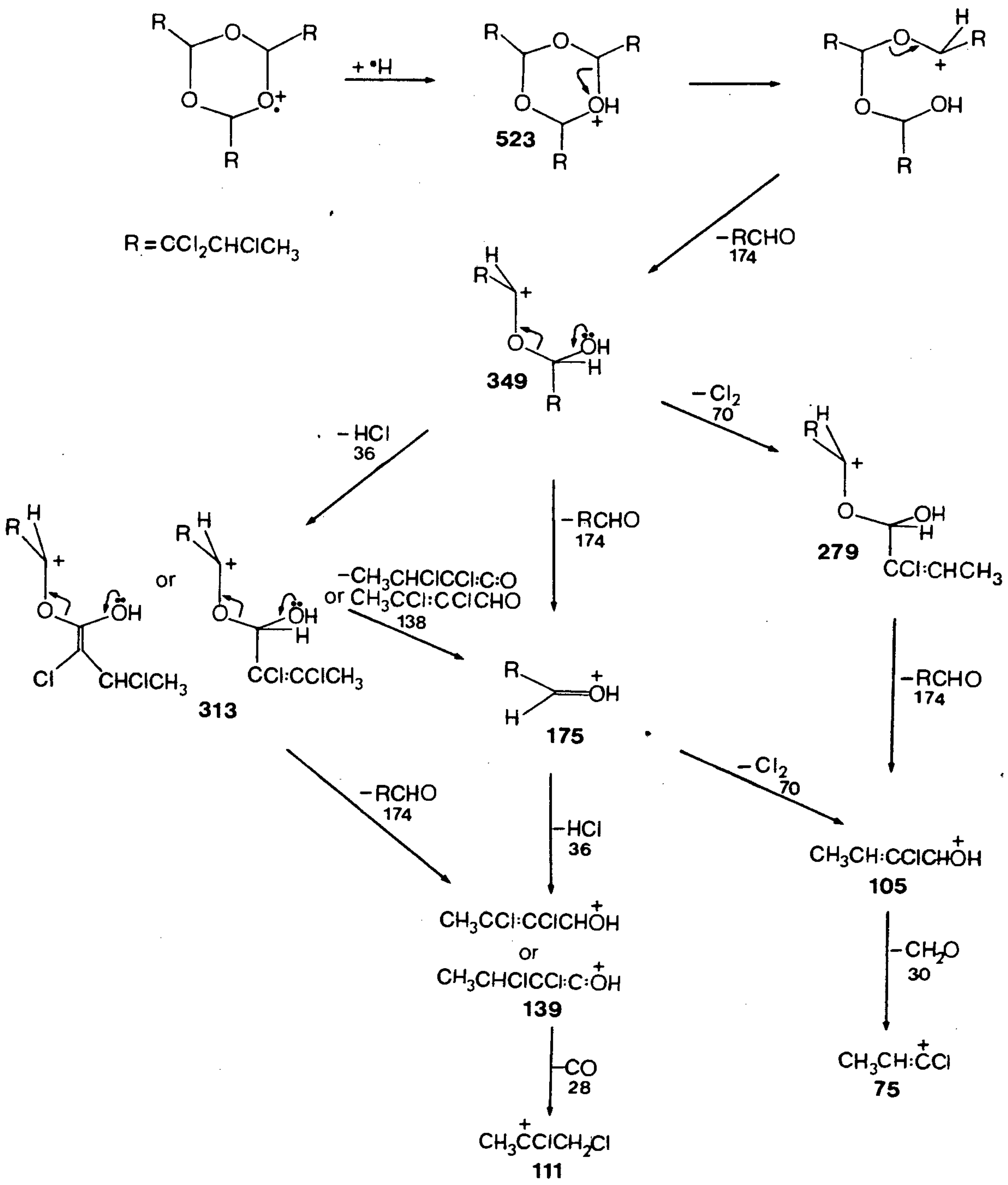


Figure 3.3 11eV mass spectrum of α-parabutylchloral.



Scheme 3.1. Mass spectral fragmentation pattern of α-parachloral.

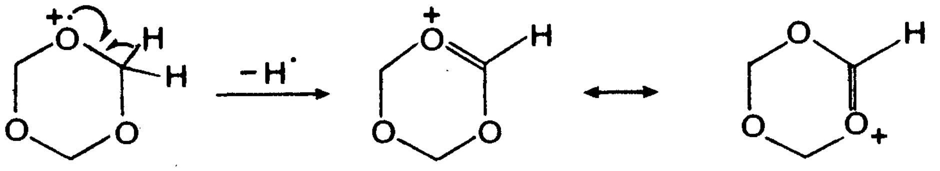


Scheme 3.2. Mass spectral fragmentation pattern of α-parabutylchloral.

It is satisfying to see the parallel that runs between the fragmentation patterns of the two trioxanes. In both cases, depolymerisation occurs, making the dimer and the monomer important fragments. Both molecules lose HCl at various stages of their fragmentation, and in the parabutylchloral molecule there are two possible sites for its loss. Hence two structures each are suggested for fragments of mass 139 and 313. It could be argued by analogy with parachloral, that of the two ions of mass 139, the ketene derivative is more stable, but in the other ion, an α,β-unsaturated system, the positive charge can be stabilised by delocalisation.

A fragment of mass 585, corresponding to the tetramer of chloral, appears in the spectrum of parachloral. This species could not have resulted from the polymerisation of chloral in the source of the mass spectrometer, since the mass spectrum of chloral hydrate contains no polymer peaks. The tetramer could possibly be formed by the incorporation of a chloral molecule into the trioxane ring, or by the combination of two dimer molecules.

The mass spectrum of paraldehyde, 2,4,6-trimethyl-1,3,5-trioxane displays similar characteristics to those of parachloral and parabutylchloral, in that the monomer and dimer feature in the spectrum and the molecular ion is not observed at 70 eV (J. Collin, 1960). In the spectra of 1,3-dioxane and 1,3,5-trioxane however, although the molecular ion is observed under ordinary conditions, it is dwarfed by the M-1 ion, due to the extensive charge delocalisation which is possible in the latter species (3.4) (Elad and Youssefyeh, 1964; Condé-Caprace and Collin, 1969).



(3.4)

3.4 ^{13}C NUCLEAR MAGNETIC RESONANCE OF PARABUTYLCHLORAL

The fully ^{1}H-coupled, 22.63 MHz ^{13}Cnmr spectrum (obtained by a gated Overhauser-enhanced experiment) of α-parabutylchloral is shown in Figure 3.4a; the ^{1}H-decoupled spectrum is shown in Figure 3.4b. The same absence of symmetry manifested in the ^{1}Hnmr spectrum, is mirrored here. The lowest field resonances, a group of closely spaced signals (Figure 3.4b) are assigned to the ring carbon atoms - each considerably deshielded by two flanking oxygen atoms, and each showing only $^1J_{^1H-^{13}C}$ coupling resolved. The singlet at δ 90.50 ppm may be assigned to the α-carbon atoms (each lacking a hydrogen atom). This signal does not show the asymmetry of the molecule. The β-carbon atoms resonate in a closely spaced group (Figure 3.4c) again with only $^1J_{^1H-^{13}C}$ coupling resolved.

Finally, the carbon atom of the methyl group is found to resonate at δ 19.8 ppm.

The ^{13}Cnmr spectra of β-parabutylchloral are shown in Figure 3.5. It is evident that the ^{13}C chemical shifts of the β-isomer are very similar to those of the α-isomer, and the expected magnetic equivalence of the ring carbons in the symmetrical β-isomer is clearly evident. Table 3.2 lists the measured ^{13}Cnmr parameters for both isomers.

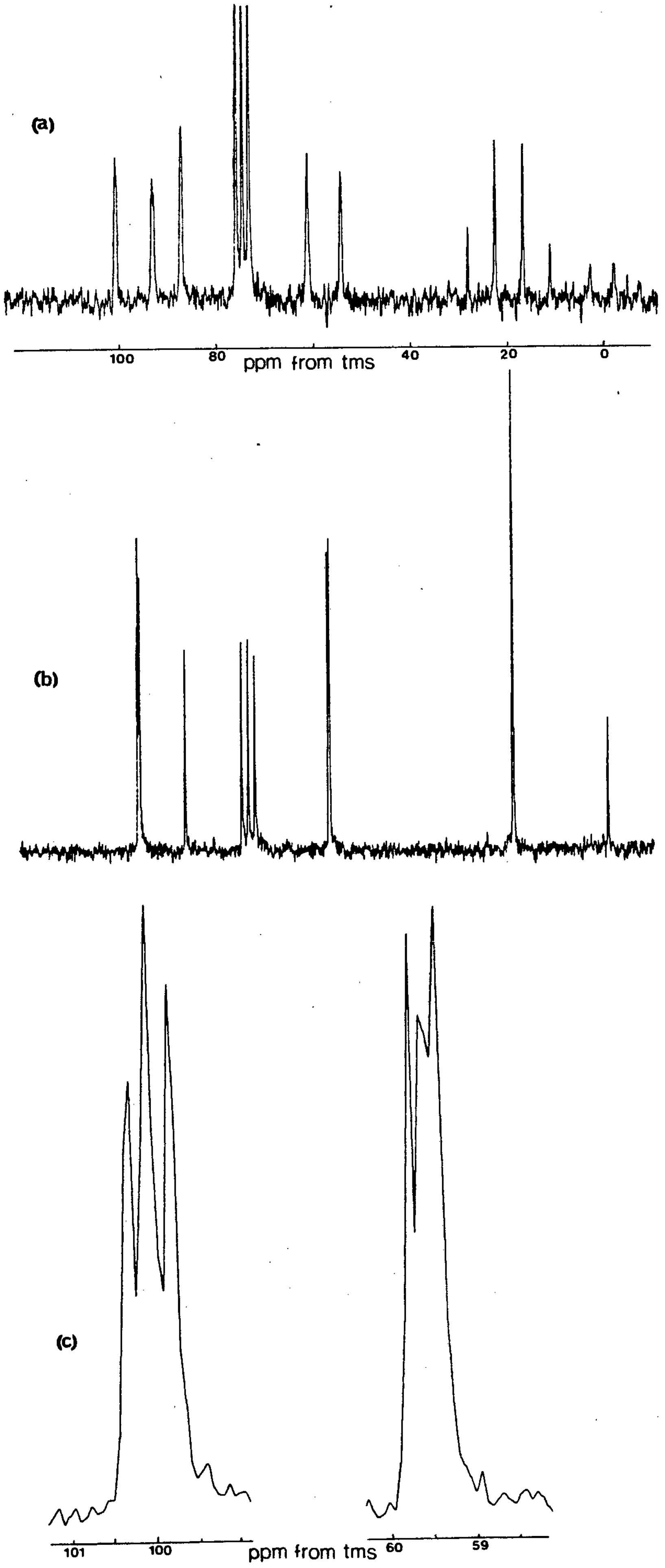


Figure 3.4. (a) Fully ^{1}H-coupled ^{13}Cnmr spectrum of α-parabutylchloral.
(b) Broad band decoupled ^{13}Cnmr spectrum of α-parabutylchloral.
(c) 18-fold expansion of the decoupled signals due to the ring carbon atoms and the β-carbon atoms respectively.

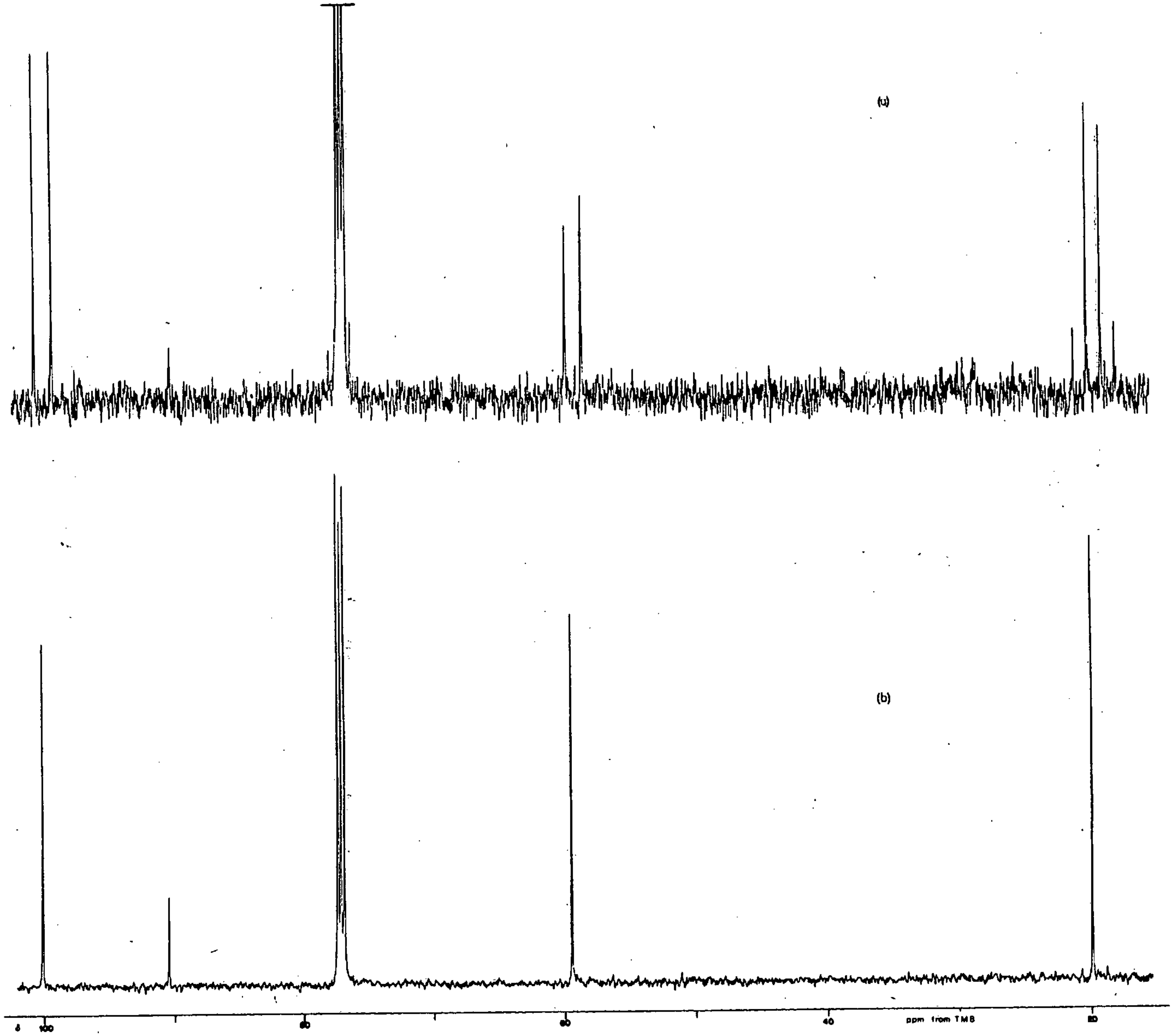


Figure 3.5. (a) Fully ^{1}H-coupled ^{13}Cnmr spectrum and (b) broad-band decoupled spectrum

3.5 X-RAY CRYSTALLOGRAPHY

The crystal structures of α- and β-parabutylchloral were determined to establish the nature of their isomerism. As discussed in Section 3.1, nmr results are ambiguous leaving *x*-ray crystallography as the only method for solving the problem.

α- and β-parabutylchloral crystallise in the non-centrosymmetric space groups $P2_12_12_1$ and $Pna2_1$ respectively. Since bulk samples of either isomer display no optical activity, spontaneous resolution of their racemic mixtures must occur on crystal formation. Other examples of this phenomenon have been observed (McCallum *et al.*, 1980).

As shown in Figure 3.6a, α-parabutylchloral exists in the chair conformation and the *cis,cis*-configuration. Two of the side chains have the same chirality at the β-carbon atoms, while that of the other is inverted: the RRS isomer or its enantiomer. The crystal structure thus verifies Baron's proposal (Section 3.1). Figure 3.6b shows the molecular structure of β-parabutylchloral. The ring is also in the chair form with all side chains equatorial. The unsymmetrical β-carbon atoms all have the same chirality: the SSS isomer or its enantiomer.

Torsion angles in the rings of both isomers (Figures 3.7 and 3.8) are all within 5% of 60°. The planes defined by O1•••O3•••O5 and C2•••C4•••C6 are inclined at 0.5° to each other in α-parabutylchloral and at 1.8° to each other in the β-isomer. In both isomers, the mean interplanar distance in the region of the rings is 0.46 Å. The sets of atoms C2•••C4•••C6 and O1•••O3•••O5 in both compounds form near perfect equilateral triangles (with all sides in the range 2.29-2.33 Å). The

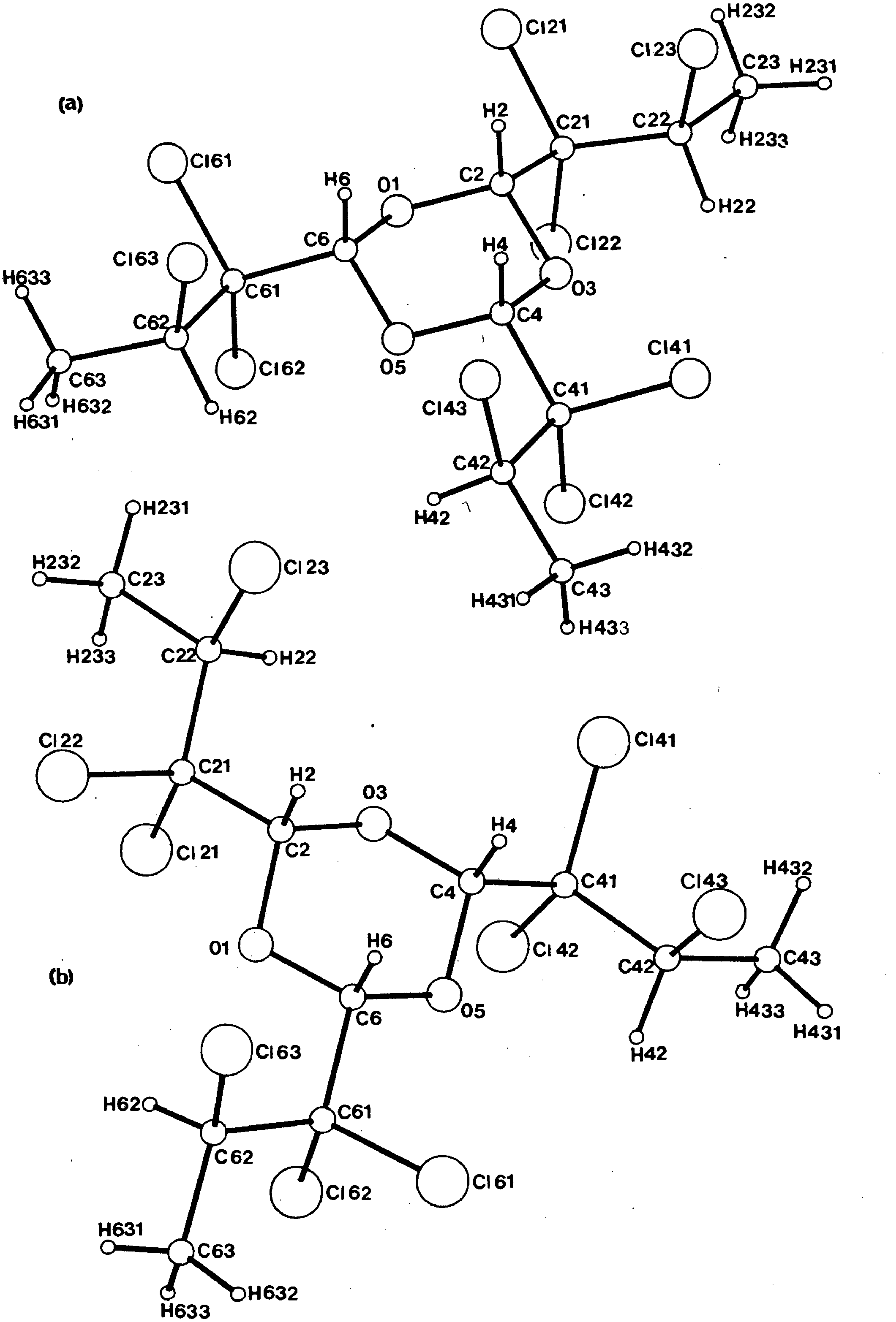


Figure 3.6. Molecular structure of (a) α-parabutylchloral and (b) β-parabutylchloral.

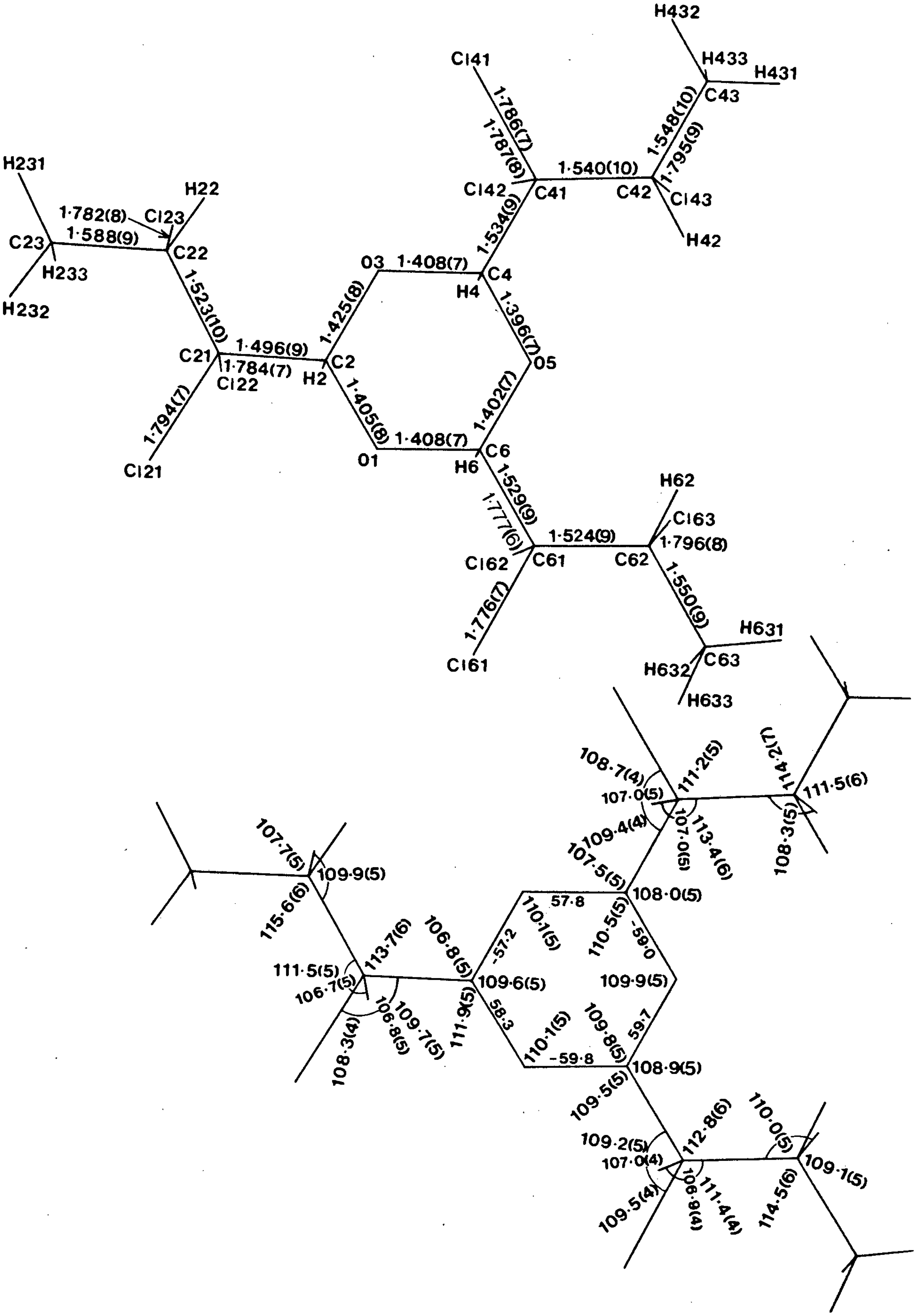


Figure 3.7. Bond lengths (Å), bond angles (°) and endocyclic torsion angles (°) in α-parabutylchloral.

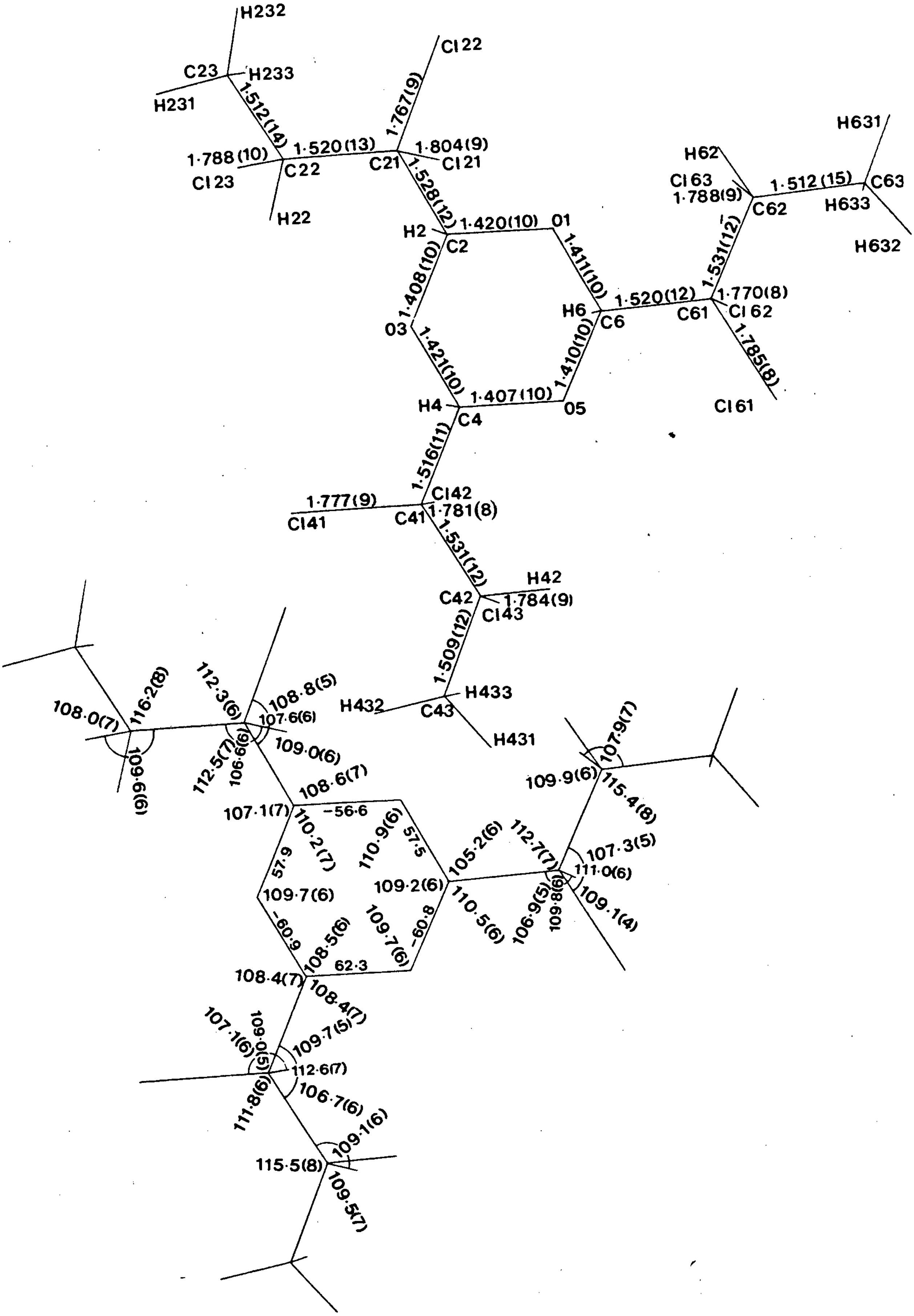


Figure 3.8. Bond lengths (Å), bond angles (°) and endocyclic torsion angles (°) in β-parabutylchloral.

mean values of the endocyclic bond lengths and angles and the carbon-chlorine distances compare favourably with those for β-parachloral (Hay and Mackay, 1980).

In both isomers the molecules are oriented with the mean ring plane almost parallel to the (100) plane. Viewed down a (Figure 3.9) the trioxane rings do not overlap and there are no close approaches in the a direction. The packing is apparently determined by the bulk of the chlorinated side-chains.

As Figure 3.10 illustrates, the conformation of side-chains in α- and β-parabutylchloral appears to depend upon the configuration at the β-carbon atom. More explicitly, in the β-isomer, the side-chains all have the same configuration and conformation so that the molecule has a pseudo-three-fold axis passing through the centre of the ring. In the α-isomer, however, the β-carbon configuration and the conformation of one side-chain differ from those of the other two so that the molecule has no pseudo-symmetry. Two structural features help to understand this dependence of conformation on configuration. Firstly, in each isomer, all carbon-carbon bonds are staggered so that the back-bones of the side-chains are sandwiched between the planes defined by O1•••O3•••O5 and C2•••C4•••C6. Hence there are only two reasonable conformations which the side-chains may adopt. Secondly, as Figure 3.6 shows, in both isomers, the carbon-chlorine bonds at the chiral centres are all axially directed. Since adjacent molecules are separated in the a direction by the translation a ≈ 12 Å, intermolecular non-bonded interactions cannot account for the orientation of these carbon-chlorine bonds, so the cause must be intramolecular.

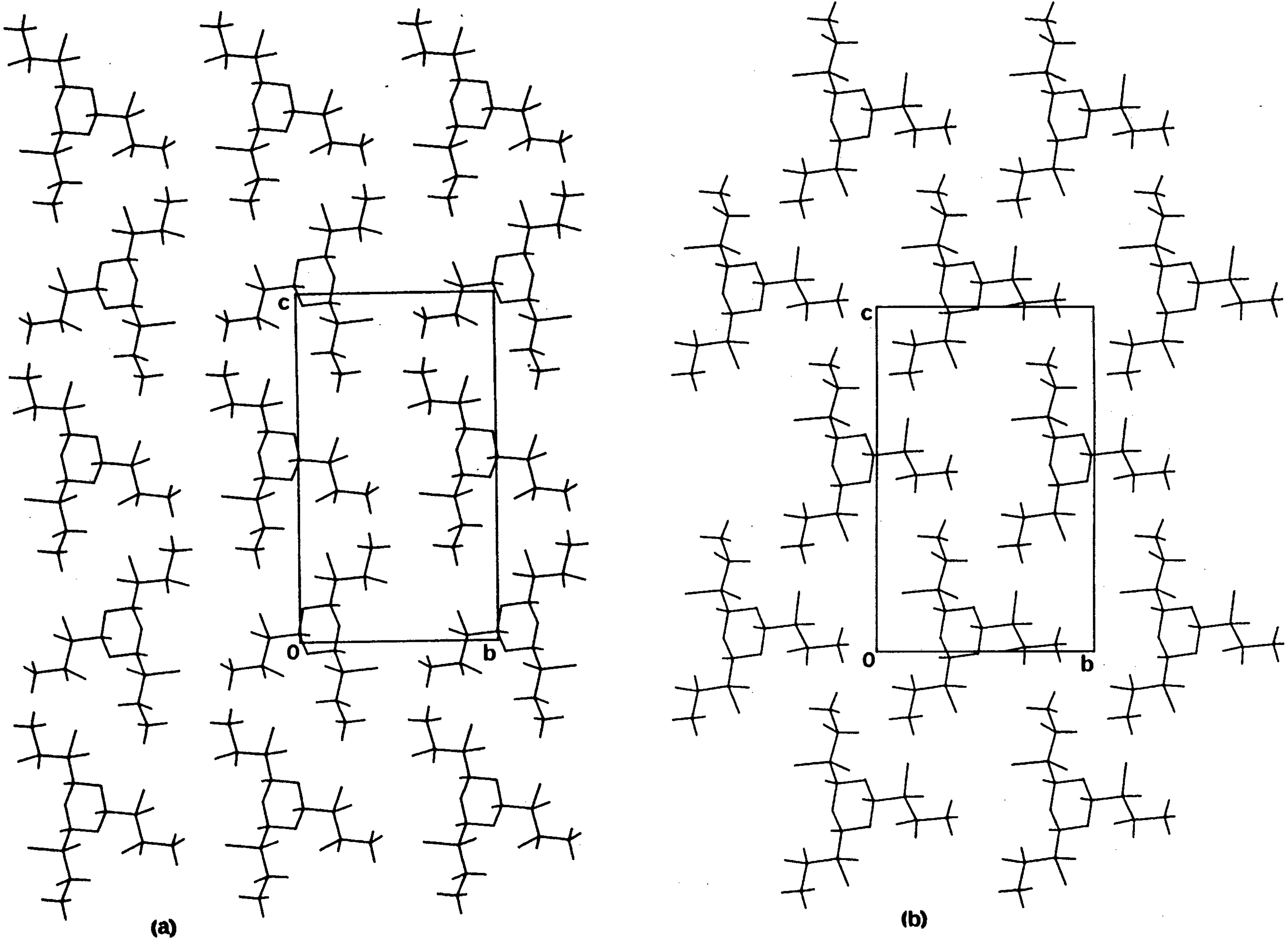


Figure 3.9. Crystal structures of (a) α-parabutylchloral and (b) β-parabutylchloral viewed down a.

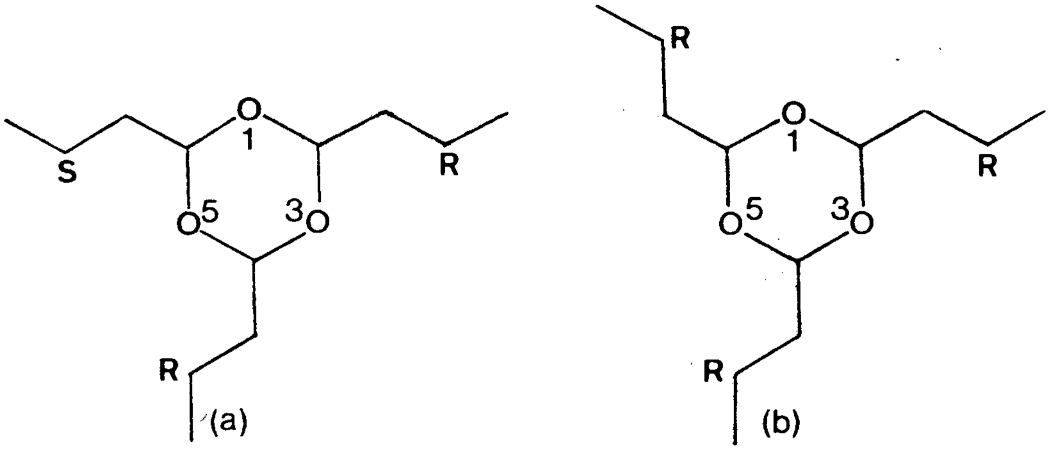


Figure 3.10. Skeletal structures of (a) α-parabutylchloral and (b) β-parabutylchloral.

A study of models reveals that a β-chlorine atom lying in the plane of the molecule would seriously interact with the equatorial lone-pair on the nearby ring oxygen atom. Thus, side-chains will prefer to adopt that conformation in which this lone-pair—lone-pair interaction is avoided, that is, one in which the β-carbon—chlorine bond is axially directed. Since there are only two reasonable conformations, a side-chain with S-configuration will prefer the alternative conformation to that assumed by a side-chain with R-configuration.

3.6 *EXPERIMENTAL DETAILS*

3.6.1 *Separation of α- and β-parabutylchlorals*

The isomers were separated initially by fractional crystallisation, as described by Chattaway and Kellett, but more effectively by dry-packed column chromatography on deactivated silica gel (Section 2.8.1), eluting with 2% ethyl acetate in petroleum ether (60-80°C). The separation was monitored by tlc of the effluent fractions. Spots were visualised by spraying the plates with ethanolic fluorescein and viewing under UV light. R_f values on silica gel tlc plates using the above solvent system are: β-isomer, 0.55; α-isomer, 0.45. The α-isomer melted at 180-185°C (180°C, Chattaway and Kellet, 1928) (Found: C 27.4, H 2.8%. Calc. for $C_{12}H_{15}Cl_9O_3$: C 27.38, H 2.87%) and the β-isomer at 161-166°C (157°C, Chattaway and Kellett, 1928) (Found: C 27.3, H 2.9%).

3.6.2 *Instrumental details*

The mass spectra of the trioxanes were measured on a V.G. Micromass 16F spectrometer. The ^{13}Cnmr spectra of α-parabutylchloral were recorded at 22.63 MHz using a Bruker WH90 FT spectrometer, and those of the β-isomer were obtained at 125.76 MHz on a Bruker WM500 superconducting instrument; the small amount of sample available necessitated the use of a higher sensitivity instrument.

3.6.3 X-ray crystallography

Beautiful rhombic crystals of α-parabutylchloral were obtained by slow cooling of a saturated solution in glacial acetic acid. Prismatic crystals of the β-isomer were grown from ethanol.

Preliminary photography revealed space group symmetry and initial cell dimensions. Accurate lattice constants were obtained from a least-squares analysis of the settings of 25 high order reflections measured on a Phillips PW 1100 four-circle diffractometer using graphite-monochromated Mo *K*α radiation ($\lambda = 0.7107$ Å). Crystal stability was checked by periodically monitoring three reference reflections during data collection. Intensities were collected by the ω-2θ scan technique. Corrections were made for Lorentz and polarisation effects, but not for absorption. Table 3.3 gives details of crystal and data collection parameters.

The structure of the α-isomer was solved by direct methods using the multi-solution tangent refinement procedures of SHELX (Sheldrick, 1978). Using reflections with normalised structure factors $E \geqslant 1.2$, a starting set of eight reflections (with three used for origin definition) was allowed to generate 256 permutations. Of the 12 E-maps obtained, the second (reliability index $R_A = 0.138$) gave 18 of the 24 non-hydrogen atoms, which yielded sufficient phase information to locate all the non-hydrogen atoms in subsequent weighted difference syntheses. The structure of the β-isomer was solved by the fully automatic direct

Table 3.3

Crystal data and experimental and refinement parameters.

	α-parabutylchloral	β-parabutylchloral
Space group	$P2_12_12_1$ (no. 19)	$Pna2_1$ (no. 33)
a (Å)	12.165(6)	12.387(6)
b (Å)	9.964(5)	10.488(5)
c (Å)	17.433(9)	16.605(8)
M_r	526.3	526.3
V (Å^3)	2113	2157
D_c (Mg m^{-3})	1.65	1.62
F(000)	1056	1056
μ(Mo *K*α) (mm^{-1})	1.11	1.09
Crystal dimensions (mm)	0.5 x 0.5 x 0.3	0.5 x 0.4 x 0.4
Scan mode	ω-2θ	ω-2θ
Scan width (°θ)	1.2	1.22
Scan speed (°θ s^{-1})	0.040	0.049
Range scanned (2θ) (°)	6-46	6-46

continued/...

Table 3.3 (continued)

	α-parabutylchloral	β-parabutylchloral
Stability of 3 standard reflections (%)	1.8, 0.5, 0.4	0.7, 0.5, 0.4
Number of reflections collected	1699	1564
Number of observed reflections	1667	1417 with $I_{(rel)} > 2\sigma I_{(rel)}$
Number of variables	228	152
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.048	0.047
$R_w = \sum w^{\frac{1}{2}}\|\|F_o\| - \|F_c\|\|/\sum w^{\frac{1}{2}}\|F_o\|$	0.049	0.053
Weighting scheme w	$(\sigma^2F + 0.001F^2)^{-1}$	$(\sigma^2F)^{-1}$
U_{iso} of methine H atoms (Å²)	0.046(8)	0.029(8)
U_{iso} of methyl H atoms (Å²)	0.067(8)	0.051(8)

methods program SHELX84 (Sheldrick, 1984) which yielded 19 non-hydrogen atoms. In both structures, methine hydrogen atoms were placed at 1.00 Å from their parent carbon atoms, their positions being dictated by the geometry of the molecules, while methyl hydrogen atoms were treated as rigid groups. In the final refinements, the heavy atoms were treated anisotropically. The isotropic temperature factors of each type of hydrogen atom were treated as single parameters. Table 3.3 gives details of the final refinement, and the final atomic parameters are listed in Tables 3.4 and 3.5.

Structure factors, analyses of variance, hydrogen atom co-ordinates, anisotropic temperature factors and torsion angles of α- and β-parabutylchloral are given in Tables 3.6 to 3.15. All calculations were performed at the University of Cape Town Computer Centre on a Univac 1100/81 computer using SHELX, SHELX84, XANADU (molecular geometry) and PLUTO (illustrations) (Roberts and Sheldrick, 1975; Motherwell, 1975).

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Table 3.4

Fractional atomic co-ordinates ($\times 10^4$) *and thermal parameters* ($Å^2 \times 10^3$) *for non-H atoms in α-parabutylchloral.*

U(equiv) = $\frac{1}{3}$ (trace of the orthogonalised U_{ij} matrix)

Atom	x/a	y/b	z/c	U(equiv)
O(1)	3607(3)	0170(4)	0969(2)	36(2)
C(2)	3390(5)	1546(6)	1062(3)	37(3)
O(3)	2672(4)	1992(4)	0469(2)	37(2)
C(4)	3139(5)	1725(6)	-0254(3)	31(3)
O(5)	3357(3)	0357(4)	-0334(2)	33(2)
C(6)	4079(5)	-0066(6)	0244(3)	33(3)
C(21)	2826(5)	1832(6)	1807(4)	37(3)
C(22)	2425(6)	3274(7)	1882(4)	49(4)
C(23)	1914(5)	3663(6)	2690(3)	37(3)
CL(21)	3779(2)	1410(2)	2555(1)	59(1)
CL(22)	1646(1)	0782(2)	1902(2)	52(1)
CL(23)	3533(2)	4397(2)	1696(2)	101(2)
C(41)	2290(6)	2120(6)	-0864(4)	44(4)
C(42)	2649(6)	1770(7)	-1688(4)	51(4)
C(43)	1830(8)	2226(9)	-2315(4)	66(5)
CL(41)	2050(2)	3880(2)	-0761(1)	59(1)
CL(42)	1033(1)	1247(2)	-0687(1)	59(1)
CL(43)	3993(2)	2458(3)	-1846(1)	74(1)
C(61)	4297(5)	-1569(6)	0147(4)	33(3)
C(62)	4660(6)	-1936(6)	-0662(4)	41(3)
C(63)	4994(6)	-3425(7)	-0767(4)	48(4)
CL(61)	5309(2)	-2017(2)	0835(1)	55(1)
CL(62)	3065(1)	-2470(2)	0332(1)	59(1)
CL(63)	5782(2)	-0882(2)	-0954(1)	71(1)

Table 3.5

Fractional atomic co-ordinates (x10^4) and thermal parameters ($\AA^2$ x10^3) for non-H atoms in β-parabutylchloral.

Atom	x/a	y/b	z/c	U(equiv)
O(1)	0292(5)	-2055(5)	-0398(4)	44(2)
C(2)	0704(7)	-1835(8)	-1184(6)	44(2)
O(3)	0954(4)	-0535(5)	-1284(4)	42(1)
C(4)	1714(6)	-0152(7)	-0691(6)	38(2)
O(5)	1250(4)	-0333(5)	0074(4)	39(1)
C(6)	1028(7)	-1639(8)	0194(5)	40(2)
C(21)	-0173(7)	-2161(8)	-1797(6)	46(2)
C(22)	0139(7)	-1791(9)	-2651(6)	48(2)
C(23)	-0645(8)	-2169(9)	-3307(7)	58(3)
CL(21)	-1378(2)	-1273(3)	-1556(3)	71(1)
CL(22)	-0454(3)	-3807(2)	-1706(3)	76(2)
CL(23)	1428(2)	-2459(4)	-2891(2)	87(2)
C(41)	1942(6)	1257(7)	-0800(6)	37(2)
C(42)	2615(7)	1814(8)	-0112(6)	44(2)
C(43)	2905(8)	3205(9)	-0195(7)	55(3)
CL(41)	2596(2)	1438(2)	-1746(2)	52(1)
CL(42)	0703(2)	2120(2)	-0817(3)	62(1)
CL(43)	3818(2)	0895(2)	0000(0)	60(1)
C(61)	0454(6)	-1843(8)	0992(5)	37(2)
C(62)	0108(7)	-3230(8)	1120(6)	47(2)
C(63)	-0412(9)	-3514(9)	1924(7)	66(3)
CL(61)	1360(2)	-1339(2)	1765(2)	58(2)
CL(62)	-0726(2)	-0895(2)	1030(2)	56(1)
CL(63)	1247(2)	-4262(3)	1010(3)	86(2)

Table 3.6

Observed and calculated structure factors for α-parabutylchloral.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	138	137	6	3	0	9	8	9	6	0	8	7	3	0	1	61	66	12	2	1	9	8
4	0	0	100	110	7	3	0	57	57	10	6	0	15	15	4	0	1	100	99	13	2	1	19	20
6	0	0	9	9	8	3	0	16	16	11	6	0	7	4	5	0	1	7	10	0	3	1	110	111
8	0	0	11	10	10	3	0	14	15	1	7	0	6	6	6	0	1	6	7	1	3	1	95	98
10	0	0	33	33	11	3	0	6	7	2	7	0	50	54	7	0	1	25	25	2	3	1	93	88
12	0	0	7	8	12	3	0	15	15	3	7	0	76	77	8	0	1	18	19	3	3	1	22	23
2	1	0	30	36	0	4	0	54	50	4	7	0	76	79	9	0	1	32	33	4	3	1	40	34
3	1	0	57	51	1	4	0	29	31	6	7	0	36	35	10	0	1	16	17	5	3	1	109	109
4	1	0	116	112	2	4	0	7	6	7	7	0	27	27	11	0	1	27	29	6	3	1	82	82
5	1	0	76	71	3	4	0	97	102	8	7	0	8	7	12	0	1	9	8	7	3	1	32	32
6	1	0	54	54	4	4	0	22	23	9	7	0	10	10	13	0	1	16	15	8	3	1	22	22
7	1	0	22	22	5	4	0	17	18	10	7	0	6	5	2	1	1	161	161	9	3	1	21	21
8	1	0	15	14	6	4	0	23	24	0	8	0	8	7	3	1	1	31	29	10	3	1	13	13
9	1	0	13	15	7	4	0	11	12	1	8	0	47	47	4	1	1	81	84	11	3	1	17	17
10	1	0	31	32	8	4	0	10	10	2	8	0	8	8	5	1	1	37	37	12	3	1	14	15
12	1	0	11	13	11	4	0	14	16	3	8	0	18	18	6	1	1	44	43	0	4	1	52	50
13	1	0	15	16	1	5	0	89	88	4	8	0	27	29	7	1	1	50	49	1	4	1	37	39
0	2	0	154	152	2	5	0	34	37	5	8	0	8	8	8	1	1	57	57	2	4	1	125	128
1	2	0	70	77	3	5	0	40	38	6	8	0	9	10	9	1	1	47	49	3	4	1	57	55
2	2	0	21	20	4	5	0	55	54	7	8	0	21	22	10	1	1	11	12	4	4	1	49	47
3	2	0	71	66	5	5	0	27	25	8	8	0	8	10	11	1	1	5	7	5	4	1	66	65
4	2	0	112	110	6	5	0	32	31	9	8	0	7	10	12	1	1	12	12	6	4	1	5	4
5	2	0	101	97	7	5	0	13	12	2	9	0	6	4	13	1	1	8	9	8	4	1	42	43
6	2	0	35	36	8	5	0	13	13	3	9	0	15	15	0	2	1	25	27	9	4	1	35	36
8	2	0	5	4	9	5	0	29	28	4	9	0	9	8	1	2	1	68	69	10	4	1	9	11
9	2	0	32	34	0	6	0	27	30	5	9	0	12	11	2	2	1	23	24	11	4	1	14	15
10	2	0	33	33	1	6	0	33	35	6	9	0	33	33	3	2	1	69	68	12	4	1	22	22
11	2	0	14	15	2	6	0	19	19	7	9	0	23	23	4	2	1	65	61	0	5	1	15	16
12	2	0	21	21	3	6	0	8	9	1	10	0	16	16	5	2	1	62	60	1	5	1	64	62
13	2	0	8	6	4	6	0	30	31	2	10	0	10	9	6	2	1	39	39	2	5	1	39	39
1	3	0	58	67	5	6	0	53	54	3	10	0	23	23	7	2	1	21	22	3	5	1	17	17
3	3	0	21	20	6	6	0	8	7	4	10	0	26	25	8	2	1	47	48	4	5	1	64	64
4	3	0	17	18	7	6	0	7	6	5	10	0	6	1	9	2	1	18	19	5	5	1	18	19
5	3	0	8	9	8	6	0	25	25	2	0	1	58	58	10	2	1	17	18	6	5	1	9	8
7	5	1	36	36	6	8	1	8	9	9	1	2	18	17	4	4	2	7	6	2	7	2	36	37
8	5	1	20	21	7	8	1	6	5	10	1	2	16	16	5	4	2	22	22	3	7	2	18	18
9	5	1	10	8	8	8	1	15	16	12	1	2	17	17	6	4	2	54	51	4	7	2	34	33
10	5	1	32	32	1	9	1	13	12	13	1	2	10	12	7	4	2	19	17	5	7	2	6	5
11	5	1	14	14	2	9	1	37	38	0	2	2	18	19	8	4	2	20	20	6	7	2	14	13
0	6	1	45	48	4	9	1	17	17	1	2	2	93	91	9	4	2	17	16	7	7	2	30	30
1	6	1	52	52	5	9	1	17	18	2	2	2	51	51	10	4	2	11	11	8	7	2	11	10
2	6	1	25	27	6	9	1	6	6	3	2	2	115	115	11	4	2	25	26	9	7	2	15	16
3	6	1	43	41	7	9	1	11	11	4	2	2	81	79	12	4	2	7	9	0	8	2	22	23
4	6	1	15	16	0	10	1	7	6	5	2	2	84	84	0	5	2	37	37	1	8	2	31	31
5	6	1	36	35	1	10	1	8	7	6	2	2	48	47	1	5	2	65	63	2	8	2	32	33
6	6	1	13	13	2	10	1	26	25	7	2	2	23	22	2	5	2	73	72	3	8	2	17	17
7	6	1	27	26	3	10	1	16	15	8	2	2	26	27	3	5	2	24	23	4	8	2	9	7
8	6	1	11	10	4	10	1	12	12	9	2	2	37	38	4	5	2	34	32	5	8	2	19	19
9	6	1	13	13	5	10	1	8	9	10	2	2	28	29	5	5	2	21	18	6	8	2	14	12
10	6	1	11	10	2	0	2	62	56	12	2	2	15	16	6	5	2	36	36	7	8	2	18	17
11	6	1	7	4	3	0	2	10	8	13	2	2	15	16	7	5	2	7	6	8	8	2	16	15
0	7	1	13	14	4	0	2	87	87	0	3	2	26	26	8	5	2	14	14	9	8	2	12	13
1	7	1	42	42	5	0	2	75	75	1	3	2	119	126	9	5	2	10	10	0	9	2	19	18
2	7	1	65	68	6	0	2	18	18	2	3	2	29	27	10	5	2	6	6	1	9	2	10	10
3	7	1	39	42	7	0	2	21	21	3	3	2	44	44	11	5	2	27	27	2	9	2	36	37
4	7	1	17	15	8	0	2	49	52	4	3	2	56	53	0	6	2	15	15	4	9	2	8	7
5	7	1	12	11	10	0	2	26	26	5	3	2	51	50	1	6	2	24	24	5	9	2	9	10
6	7	1	32	31	11	0	2	50	52	6	3	2	48	45	2	6	2	30	31	6	9	2	10	9
7	7	1	12	10	13	0	2	9	11	7	3	2	29	29	3	6	2	53	50	7	9	2	23	23
8	7	1	27	27	0	1	2	4	5	8	3	2	20	21	4	6	2	29	29	0	10	2	17	15
9	7	1	21	22	1	1	2	28	25	9	3	2	30	31	5	6	2	29	28	1	10	2	16	15
10	7	1	11	10	2	1	2	96	96	10	3	2	34	33	6	6	2	50	49	2	10	2	14	15
0	8	1	10	8	3	1	2	37	37	11	3	2	17	16	7	6	2	32	32	3	10	2	13	13
1	8	1	8	7	4	1	2	51	50	12	3	2	7	6	9	6	2	6	6	4	10	2	7	6
2	8	1	10	11	5	1	2	5	7	0	4	2	45	40	10	6	2	22	22	5	10	2	7	5
3	8	1	26	28	6	1	2	62	60	1	4	2	69	71	11	6	2	11	11	0	0	3	4	0
4	8	1	11	12	7	1	2	22	20	2	4	2	109	108	0	7	2	14	14	1	0	3	50	49
5	8	1	20	19	8	1	2	52	52	3	4	2	52	54	1	7	2	12	11	2	0	3	21	18

continued/......

Table 3.6 (continued)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
3	0	3	95	89	1	3	3	112	115	10	5	3	22	22	6	9	3	18	19	0	2	4	51	53
4	0	3	55	54	2	3	3	59	54	11	5	3	23	23	7	9	3	19	17	1	2	4	112	115
5	0	3	72	74	3	3	3	85	87	0	6	3	8	7	1	10	3	10	10	2	2	4	97	91
6	0	3	59	61	4	3	3	15	15	1	6	3	16	16	2	10	3	14	15	3	2	4	34	31
7	0	3	26	27	5	3	3	15	15	2	6	3	17	18	4	10	3	10	10	4	2	4	35	34
8	0	3	30	30	6	3	3	46	45	3	6	3	20	21	5	10	3	7	6	5	2	4	77	75
9	0	3	15	15	7	3	3	16	16	4	6	3	67	66	0	0	4	29	24	6	2	4	46	46
10	0	3	33	35	8	3	3	30	31	6	6	3	37	37	1	0	4	68	73	7	2	4	9	8
13	0	3	11	11	9	3	3	9	9	7	6	3	13	13	2	0	4	75	66	8	2	4	37	38
1	1	3	138	139	10	3	3	41	41	8	6	3	37	39	3	0	4	19	19	9	2	4	26	27
2	1	3	60	61	11	3	3	12	12	9	6	3	16	18	4	0	4	42	42	10	2	4	17	16
3	1	3	94	94	12	3	3	15	15	10	6	3	10	8	5	0	4	20	21	11	2	4	8	8
4	1	3	70	67	0	4	3	52	54	0	7	3	11	10	6	0	4	13	11	12	2	4	11	12
5	1	3	49	48	1	4	3	41	43	1	7	3	51	53	7	0	4	55	57	0	3	4	30	30
6	1	3	46	44	2	4	3	54	53	2	7	3	15	16	8	0	4	14	12	1	3	4	58	60
7	1	3	45	47	3	4	3	36	31	3	7	3	32	32	9	0	4	37	37	2	3	4	19	19
8	1	3	21	22	4	4	3	46	42	4	7	3	26	26	10	0	4	20	20	3	3	4	53	50
9	1	3	55	56	5	4	3	25	23	5	7	3	16	16	11	0	4	7	8	4	3	4	73	69
10	1	3	18	20	6	4	3	38	36	6	7	3	18	18	12	0	4	9	9	5	3	4	52	50
12	1	3	5	5	7	4	3	20	20	7	7	3	22	22	13	0	4	8	11	6	3	4	19	19
13	1	3	8	8	8	4	3	11	11	8	7	3	22	22	0	1	4	10	12	7	3	4	21	21
0	2	3	20	22	9	4	3	9	10	9	7	3	12	11	1	1	4	88	95	8	3	4	6	5
1	2	3	40	38	10	4	3	13	12	10	7	3	14	13	2	1	4	42	39	9	3	4	14	15
2	2	3	90	80	11	4	3	11	12	0	8	3	22	22	3	1	4	65	63	10	3	4	20	21
4	2	3	77	74	12	4	3	17	18	1	8	3	23	24	4	1	4	50	45	11	3	4	22	22
5	2	3	23	23	0	5	3	72	76	3	8	3	29	31	5	1	4	68	66	12	3	4	17	17
6	2	3	31	31	1	5	3	22	20	4	8	3	14	13	6	1	4	53	52	0	4	4	15	15
7	2	3	34	35	2	5	3	35	36	5	8	3	15	15	7	1	4	14	16	1	4	4	92	94
8	2	3	47	46	3	5	3	40	39	6	8	3	18	19	8	1	4	26	26	2	4	4	23	24
9	2	3	12	11	4	5	3	84	82	7	8	3	17	18	9	1	4	37	40	3	4	4	21	21
10	2	3	11	10	5	5	3	15	15	8	8	3	8	7	10	1	4	24	26	4	4	4	63	62
11	2	3	10	11	6	5	3	25	25	1	9	3	15	17	11	1	4	10	8	5	4	4	27	27
12	2	3	6	6	7	5	3	37	37	3	9	3	11	11	12	1	4	19	19	6	4	4	41	40
0	3	3	35	32	8	5	3	28	29	4	9	3	17	17	13	1	4	14	16	7	4	4	23	22
8	4	4	35	34	0	8	4	28	28	4	1	5	23	22	1	4	5	15	16	2	7	5	30	31
9	4	4	36	36	1	8	4	30	29	5	1	5	45	43	2	4	5	14	13	3	7	5	18	19
10	4	4	23	24	2	8	4	6	6	6	1	5	55	55	3	4	5	33	33	4	7	5	52	49
11	4	4	26	26	3	8	4	23	24	7	1	5	30	31	4	4	5	9	8	5	7	5	22	21
12	4	4	8	8	5	8	4	19	17	8	1	5	21	22	5	4	5	43	40	6	7	5	17	16
0	5	4	60	61	7	8	4	26	26	9	1	5	50	52	6	4	5	15	14	8	7	5	6	6
1	5	4	22	21	8	8	4	17	17	10	1	5	11	11	7	4	5	38	39	9	7	5	10	8
2	5	4	61	60	0	9	4	8	8	11	1	5	8	8	8	4	5	21	22	1	8	5	32	33
3	5	4	23	24	1	9	4	5	6	12	1	5	12	11	9	4	5	21	19	2	8	5	14	13
4	5	4	30	29	2	9	4	13	12	0	2	5	10	13	10	4	5	10	9	3	8	5	36	34
5	5	4	29	29	3	9	4	20	19	1	2	5	56	59	11	4	5	14	14	4	8	5	16	15
6	5	4	18	17	4	9	4	21	20	2	2	5	68	66	0	5	5	60	61	5	8	5	21	20
7	5	4	22	20	5	9	4	23	24	3	2	5	128	122	1	5	5	50	51	8	8	5	17	17
8	5	4	17	15	6	9	4	16	16	4	2	5	25	22	2	5	5	33	31	0	9	5	51	54
10	5	4	11	10	7	9	4	12	12	5	2	5	43	41	4	5	5	64	63	1	9	5	9	10
11	5	4	10	9	0	10	4	23	24	6	2	5	22	21	5	5	5	40	38	3	9	5	8	8
0	6	4	17	18	1	10	4	14	14	7	2	5	41	40	6	5	5	18	17	4	9	5	11	10
1	6	4	11	10	2	10	4	6	6	8	2	5	26	27	7	5	5	37	39	5	9	5	22	22
2	6	4	22	24	4	10	4	18	19	9	2	5	9	11	8	5	5	24	25	6	9	5	13	13
3	6	4	19	18	1	0	5	94	95	10	2	5	17	16	9	5	5	11	10	0	10	5	9	9
4	6	4	22	22	2	0	5	126	130	12	2	5	14	16	11	5	5	8	7	4	10	5	6	8
5	6	4	42	41	3	0	5	63	60	1	3	5	34	39	0	6	5	11	10	0	0	6	127	122
6	6	4	51	50	4	0	5	60	62	2	3	5	41	37	1	6	5	9	8	1	0	6	15	14
8	6	4	19	18	5	0	5	26	25	3	3	5	49	48	2	6	5	29	28	2	0	6	72	73
9	6	4	28	28	6	0	5	62	58	4	3	5	17	17	3	6	5	26	25	3	0	6	85	85
10	6	4	13	13	7	0	5	49	49	5	3	5	19	17	4	6	5	14	14	4	0	6	8	6
1	7	4	37	39	8	0	5	75	76	6	3	5	45	44	5	6	5	49	48	5	0	6	25	23
2	7	4	8	9	9	0	5	47	46	7	3	5	17	16	6	6	5	22	21	6	0	6	8	11
3	7	4	24	24	10	0	5	10	11	8	3	5	36	36	7	6	5	18	17	7	0	6	8	9
4	7	4	16	14	12	0	5	24	24	9	3	5	22	23	8	6	5	24	21	8	0	6	21	21
5	7	4	21	21	0	1	5	88	94	10	3	5	22	23	9	6	5	9	9	10	0	6	19	21
6	7	4	17	18	1	1	5	82	89	11	3	5	8	8	10	6	5	8	10	11	0	6	6	5
7	7	4	20	20	2	1	5	114	110	12	3	5	18	19	0	7	5	28	29	12	0	6	22	24
8	7	4	15	15	3	1	5	84	81	0	4	5	16	18	1	7	5	43	44	0	1	6	18	17

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Table 3.6 (continued)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	1	6	38	39	11	3	6	11	10	8	6	6	13	13	6	0	7	24	25	4	3	7	12	13
2	1	6	16	17	12	3	6	13	13	10	6	6	11	10	7	0	7	63	63	5	3	7	28	27
3	1	6	63	63	0	4	6	94	97	0	7	6	22	23	8	0	7	14	13	6	3	7	24	24
4	1	6	56	52	1	4	6	39	42	1	7	6	13	13	10	0	7	8	8	7	3	7	24	24
5	1	6	57	54	2	4	6	20	21	2	7	6	22	22	11	0	7	8	7	8	3	7	12	11
6	1	6	11	11	3	4	6	34	33	3	7	6	31	31	12	0	7	11	10	9	3	7	24	25
7	1	6	42	41	4	4	6	59	57	4	7	6	14	13	0	1	7	19	22	10	3	7	7	6
8	1	6	52	51	5	4	6	56	54	5	7	6	6	6	1	1	7	37	37	11	3	7	6	9
9	1	6	41	42	6	4	6	27	26	7	7	6	10	10	2	1	7	138	138	0	4	7	27	29
11	1	6	16	16	7	4	6	12	12	8	7	6	13	13	3	1	7	68	64	1	4	7	13	13
12	1	6	10	10	8	4	6	11	11	9	7	6	11	12	4	1	7	58	53	2	4	7	52	55
0	2	6	28	27	9	4	6	25	25	0	8	6	33	33	5	1	7	39	38	3	4	7	38	36
1	2	6	30	31	10	4	6	40	41	1	8	6	34	34	6	1	7	48	48	4	4	7	16	15
2	2	6	50	49	11	4	6	25	25	2	8	6	37	39	7	1	7	11	12	5	4	7	44	43
3	2	6	105	102	0	5	6	28	25	3	8	6	12	12	8	1	7	34	34	6	4	7	21	20
4	2	6	69	65	1	5	6	45	46	4	8	6	22	21	9	1	7	16	17	7	4	7	7	5
5	2	6	33	33	2	5	6	18	18	5	8	6	16	14	10	1	7	21	21	8	4	7	23	23
6	2	6	53	52	3	5	6	53	50	6	8	6	15	15	11	1	7	28	30	11	4	7	11	10
7	2	6	40	41	4	5	6	21	22	7	8	6	19	17	12	1	7	11	11	1	5	7	31	31
8	2	6	27	29	5	5	6	13	14	8	8	6	8	7	0	2	7	73	81	2	5	7	30	31
9	2	6	11	11	6	5	6	42	42	0	9	6	7	8	1	2	7	49	51	3	5	7	30	29
10	2	6	22	21	7	5	6	13	13	1	9	6	11	10	2	2	7	15	14	4	5	7	20	21
11	2	6	7	6	8	5	6	17	16	2	9	6	10	11	3	2	7	82	81	5	5	7	23	22
0	3	6	6	4	9	5	6	15	14	3	9	6	10	11	4	2	7	61	60	6	5	7	17	17
1	3	6	9	7	10	5	6	13	12	4	9	6	16	13	5	2	7	60	60	7	5	7	25	23
2	3	6	34	31	11	5	6	23	23	5	9	6	9	8	6	2	7	37	36	8	5	7	7	5
3	3	6	28	27	0	6	6	23	24	6	9	6	6	7	7	2	7	12	12	9	5	7	15	15
4	3	6	43	42	1	6	6	34	36	0	10	6	30	30	8	2	7	15	15	10	5	7	6	5
5	3	6	23	21	2	6	6	18	19	3	10	6	7	7	9	2	7	21	21	0	6	7	21	22
6	3	6	31	30	3	6	6	16	15	1	0	7	52	55	10	2	7	11	10	1	6	7	30	31
7	3	6	53	53	4	6	6	40	39	2	0	7	109	114	0	3	7	29	31	2	6	7	15	15
8	3	6	14	12	5	6	6	63	60	3	0	7	59	56	1	3	7	47	55	3	6	7	29	28
9	3	6	31	31	6	6	6	46	44	4	0	7	4	6	2	3	7	15	12	4	6	7	31	29
10	3	6	22	21	7	6	6	40	38	5	0	7	10	9	3	3	7	56	54	5	6	7	14	14
6	6	7	15	13	8	0	8	10	10	8	3	8	20	20	3	7	8	7	6	7	1	9	74	73
7	6	7	21	21	10	0	8	10	9	9	3	8	10	10	4	7	8	12	10	8	1	9	17	17
9	6	7	8	10	11	0	8	35	36	10	3	8	15	15	5	7	8	14	15	9	1	9	14	14
10	6	7	7	4	12	0	8	6	5	2	4	8	22	23	6	7	8	14	13	10	1	9	12	12
0	7	7	42	44	0	1	8	37	40	3	4	8	37	37	7	7	8	24	25	11	1	9	10	11
1	7	7	32	33	1	1	8	36	35	4	4	8	35	34	8	7	8	10	11	0	2	9	18	17
2	7	7	16	17	2	1	8	56	55	5	4	8	22	21	0	8	8	17	18	1	2	9	6	6
3	7	7	24	25	3	1	8	73	70	6	4	8	36	35	1	8	8	21	20	2	2	9	49	49
5	7	7	13	13	4	1	8	23	23	7	4	8	14	14	2	8	8	23	23	3	2	9	45	44
6	7	7	10	10	6	1	8	69	69	8	4	8	9	6	3	8	8	12	14	4	2	9	12	11
7	7	7	10	10	7	1	8	44	42	9	4	8	12	11	4	8	8	7	7	5	2	9	9	9
9	7	7	14	14	8	1	8	11	10	10	4	8	8	8	5	8	8	9	9	6	2	9	31	31
0	8	7	38	39	9	1	8	7	8	0	5	8	20	22	6	8	8	11	9	7	2	9	29	28
1	8	7	7	3	10	1	8	13	14	2	5	8	63	64	0	9	8	17	17	8	2	9	58	58
2	8	7	16	16	11	1	8	25	28	3	5	8	33	33	1	9	8	14	14	9	2	9	15	16
3	8	7	7	7	12	1	8	6	7	4	5	8	23	23	2	9	8	9	8	10	2	9	10	9
4	8	7	12	11	0	2	8	36	37	5	5	8	16	15	3	9	8	19	20	0	3	9	57	56
5	8	7	28	28	1	2	8	79	84	6	5	8	35	33	4	9	8	11	10	1	3	9	21	22
6	8	7	18	17	2	2	8	22	21	7	5	8	18	17	5	9	8	20	20	2	3	9	37	40
7	8	7	10	9	3	2	8	48	46	8	5	8	18	17	1	0	9	30	32	3	3	9	26	24
0	9	7	11	11	4	2	8	28	28	10	5	8	20	21	2	0	9	13	14	4	3	9	21	21
1	9	7	48	49	5	2	8	51	52	0	6	8	47	48	3	0	9	21	24	5	3	9	40	38
2	9	7	23	23	6	2	8	38	38	1	6	8	25	24	5	0	9	48	47	6	3	9	13	13
3	9	7	13	12	7	2	8	52	52	2	6	8	37	38	6	0	9	14	13	7	3	9	11	11
4	9	7	15	13	8	2	8	28	27	3	6	8	42	42	7	0	9	7	5	8	3	9	28	29
5	9	7	26	24	10	2	8	8	9	4	6	8	54	51	10	0	9	7	7	9	3	9	21	21
0	0	8	143	152	11	2	8	11	11	5	6	8	41	39	11	0	9	22	21	10	3	9	12	13
1	0	8	62	63	0	3	8	5	4	6	6	8	20	21	0	1	9	70	72	11	3	9	30	32
2	0	8	33	33	1	3	8	28	29	7	6	8	16	15	1	1	9	40	41	0	4	9	75	78
3	0	8	36	34	2	3	8	77	80	8	6	8	16	16	2	1	9	25	25	1	4	9	24	25
4	0	8	22	19	3	3	8	31	30	9	6	8	20	20	3	1	9	33	33	2	4	9	30	29
5	0	8	18	16	4	3	8	36	35	0	7	8	10	11	4	1	9	18	18	3	4	9	30	30
6	0	8	16	16	5	3	8	22	21	1	7	8	24	26	5	1	9	35	35	4	4	9	17	16
7	0	8	21	21	7	3	8	19	18	2	7	8	26	26	6	1	9	40	40	5	4	9	22	21

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Table 3.6 (continued)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
6	4	9	12	13	3	8	9	8	8	7	2	10	17	16	0	6	10	18	18	0	1	11	36	37
7	4	9	41	41	5	8	9	13	13	8	2	10	13	11	1	6	10	16	16	1	1	11	19	21
8	4	9	19	20	6	8	9	6	7	9	2	10	7	7	2	6	10	9	9	2	1	11	51	51
9	4	9	13	13	1	9	9	6	6	10	2	10	11	10	3	6	10	24	25	3	1	11	30	29
10	4	9	13	13	2	9	9	11	11	0	3	10	11	11	4	6	10	21	20	4	1	11	32	32
0	5	9	8	6	3	9	9	18	18	1	3	10	56	59	5	6	10	18	18	5	1	11	8	7
1	5	9	38	41	4	9	9	18	18	2	3	10	30	29	6	6	10	36	34	6	1	11	29	29
2	5	9	13	13	0	0	10	26	28	3	3	10	15	15	7	6	10	7	4	7	1	11	28	28
4	5	9	70	68	1	0	10	16	18	4	3	10	35	33	8	6	10	11	11	9	1	11	10	10
5	5	9	40	40	2	0	10	30	29	5	3	10	34	34	0	7	10	9	10	10	1	11	6	8
6	5	9	11	11	3	0	10	29	26	6	3	10	20	19	1	7	10	8	8	1	2	11	6	8
7	5	9	21	22	5	0	10	74	75	7	3	10	13	14	2	7	10	14	15	2	2	11	26	29
8	5	9	6	6	6	0	10	6	3	8	3	10	24	23	5	7	10	19	18	3	2	11	37	36
10	5	9	8	11	7	0	10	15	13	9	3	10	27	26	7	7	10	18	17	4	2	11	10	9
1	6	9	16	16	8	0	10	8	7	0	4	10	6	7	0	8	10	15	15	5	2	11	27	27
2	6	9	28	28	9	0	10	20	20	1	4	10	9	10	1	8	10	32	32	6	2	11	20	19
3	6	9	45	45	10	0	10	10	10	2	4	10	37	40	2	8	10	15	17	8	2	11	17	16
4	6	9	43	41	11	0	10	29	28	3	4	10	18	18	3	8	10	6	7	9	2	11	16	18
5	6	9	21	21	1	1	10	5	5	4	4	10	23	23	4	8	10	15	17	10	2	11	23	22
6	6	9	6	6	2	1	10	24	27	5	4	10	8	6	5	8	10	19	17	0	3	11	14	13
7	6	9	9	10	3	1	10	42	43	6	4	10	24	24	0	9	10	10	8	1	3	11	39	41
8	6	9	11	10	4	1	10	28	28	7	4	10	6	6	1	9	10	11	11	2	3	11	29	29
9	6	9	24	24	6	1	10	41	42	8	4	10	35	33	2	9	10	7	6	3	3	11	13	13
0	7	9	8	9	7	1	10	29	29	9	4	10	16	16	3	9	10	7	6	4	3	11	9	8
1	7	9	30	30	8	1	10	14	14	10	4	10	15	14	1	0	11	42	45	5	3	11	10	12
2	7	9	16	16	9	1	10	16	17	1	5	10	19	20	2	0	11	12	11	6	3	11	57	56
3	7	9	18	20	10	1	10	12	13	2	5	10	31	32	3	0	11	51	52	7	3	11	6	7
4	7	9	17	17	11	1	10	15	13	3	5	10	30	30	4	0	11	23	23	8	3	11	20	21
5	7	9	11	11	0	2	10	17	18	4	5	10	21	21	5	0	11	14	15	9	3	11	11	10
6	7	9	14	12	1	2	10	58	60	5	5	10	13	14	6	0	11	56	57	10	3	11	16	15
7	7	9	11	11	2	2	10	24	23	6	5	10	11	13	7	0	11	6	4	0	4	11	18	19
8	7	9	23	20	3	2	10	27	29	7	5	10	20	19	8	0	11	10	10	1	4	11	27	30
1	8	9	8	8	4	2	10	34	34	8	5	10	19	19	9	0	11	8	7	2	4	11	20	20
2	8	9	15	15	5	2	10	10	10	9	5	10	15	16	10	0	11	11	10	3	4	11	32	33
4	4	11	22	20	2	0	12	30	31	5	3	12	26	25	1	8	12	17	17	5	3	13	15	14
5	4	11	13	14	3	0	12	22	24	6	3	12	26	27	2	8	12	16	17	6	3	13	30	29
6	4	11	11	9	4	0	12	12	11	7	3	12	23	22	3	8	12	8	9	7	3	13	11	10
7	4	11	18	18	5	0	12	8	7	8	3	12	7	8	1	0	13	16	16	8	3	13	11	11
8	4	11	13	12	6	0	12	16	17	9	3	12	8	9	2	0	13	57	60	9	3	13	15	15
9	4	11	22	23	7	0	12	12	13	0	4	12	42	44	3	0	13	7	5	0	4	13	16	17
0	5	11	10	11	8	0	12	20	21	1	4	12	31	33	4	0	13	7	7	1	4	13	19	18
1	5	11	19	19	9	0	12	6	4	2	4	12	23	24	5	0	13	13	12	2	4	13	11	10
2	5	11	19	20	10	0	12	7	7	3	4	12	29	29	6	0	13	6	5	4	4	13	22	21
3	5	11	10	10	0	1	12	19	20	4	4	12	20	20	7	0	13	28	26	6	4	13	13	13
4	5	11	24	26	1	1	12	40	42	5	4	12	21	21	8	0	13	26	24	7	4	13	24	23
5	5	11	7	5	2	1	12	25	25	6	4	12	8	8	9	0	13	8	8	8	4	13	7	9
6	5	11	12	13	3	1	12	26	27	7	4	12	18	17	0	1	13	34	36	1	5	13	12	14
7	5	11	27	27	4	1	12	36	37	8	4	12	10	8	1	1	13	9	9	2	5	13	9	9
8	5	11	9	7	5	1	12	12	11	0	5	12	8	8	2	1	13	30	30	3	5	13	38	39
9	5	11	7	8	6	1	12	14	13	1	5	12	10	10	3	1	13	14	12	4	5	13	17	17
0	6	11	9	9	7	1	12	25	25	2	5	12	14	14	4	1	13	18	16	5	5	13	17	16
1	6	11	13	13	8	1	12	15	14	3	5	12	29	30	5	1	13	29	27	6	5	13	11	10
2	6	11	20	20	9	1	12	14	14	4	5	12	16	14	6	1	13	8	7	7	5	13	15	15
4	6	11	15	16	0	2	12	7	9	5	5	12	9	9	7	1	13	10	9	0	6	13	30	31
5	6	11	14	14	1	2	12	15	15	6	5	12	12	13	8	1	13	19	19	1	6	13	23	24
6	6	11	9	7	2	2	12	37	39	7	5	12	10	9	9	1	13	21	21	5	6	13	22	21
7	6	11	14	13	3	2	12	33	34	0	6	12	6	7	0	2	13	17	18	0	7	13	29	30
0	7	11	25	26	4	2	12	30	30	1	6	12	25	27	1	2	13	29	30	1	7	13	17	18
1	7	11	14	14	5	2	12	13	13	2	6	12	9	11	2	2	13	33	33	2	7	13	18	17
3	7	11	33	34	6	2	12	6	6	4	6	12	17	17	3	2	13	21	20	3	7	13	10	9
4	7	11	11	12	7	2	12	23	22	5	6	12	18	17	4	2	13	39	39	4	7	13	16	16
6	7	11	8	9	8	2	12	6	4	6	6	12	16	16	5	2	13	29	30	0	0	14	51	52
0	8	11	9	7	9	2	12	11	10	7	6	12	20	20	6	2	13	21	21	1	0	14	31	32
2	8	11	10	11	10	2	12	16	18	0	7	12	9	9	7	2	13	21	20	2	0	14	25	26
3	8	11	13	12	1	3	12	17	16	1	7	12	17	17	1	3	13	23	24	3	0	14	42	41
4	8	11	18	17	2	3	12	15	15	2	7	12	9	11	2	3	13	23	22	4	0	14	36	36
0	0	12	81	82	3	3	12	16	14	3	7	12	25	25	3	3	13	16	17	7	0	14	26	27
1	0	12	72	73	4	3	12	14	15	4	7	12	17	17	4	3	13	13	13	8	0	14	7	4

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Table 3.6 (continued)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
9	0	14	18	17	7	4	14	9	10	1	3	15	25	24	0	2	16	11	11	3	1	17	16	18
0	1	14	8	10	0	5	14	20	20	2	3	15	22	24	1	2	16	8	7	4	1	17	15	16
1	1	14	33	34	1	5	14	20	19	3	3	15	28	30	2	2	16	8	9	5	1	17	10	7
2	1	14	42	43	2	5	14	32	33	5	3	15	10	10	3	2	16	11	11	6	1	17	17	16
3	1	14	26	25	3	5	14	23	21	6	3	15	17	15	4	2	16	26	25	0	2	17	8	6
4	1	14	14	12	4	5	14	20	20	0	4	15	29	31	5	2	16	11	10	2	2	17	21	19
5	1	14	17	17	5	5	14	12	13	1	4	15	20	21	6	2	16	22	21	3	2	17	12	12
6	1	14	18	16	6	5	14	7	8	2	4	15	8	7	0	3	16	8	5	4	2	17	10	11
7	1	14	10	10	2	6	14	21	22	3	4	15	10	12	1	3	16	14	14	0	3	17	19	19
8	1	14	22	22	5	6	14	25	26	4	4	15	13	13	2	3	16	34	34	1	3	17	7	7
9	1	14	6	3	0	7	14	19	20	5	4	15	18	17	3	3	16	23	25	3	3	17	11	9
0	2	14	6	6	1	7	14	10	11	6	4	15	6	7	4	3	16	10	11	4	3	17	6	8
1	2	14	24	24	2	7	14	15	15	1	5	15	16	15	5	3	16	7	8	0	4	17	17	17
2	2	14	26	26	3	7	14	7	7	3	5	15	15	15	0	4	16	27	28	1	4	17	18	17
3	2	14	9	10	1	0	15	23	22	4	5	15	14	14	2	4	16	9	9	2	4	17	10	10
4	2	14	6	5	2	0	15	36	35	5	5	15	13	15	3	4	16	10	10	3	4	17	16	16
5	2	14	27	27	4	0	15	37	36	0	6	15	14	15	4	4	16	10	11	0	5	17	10	12
6	2	14	17	15	5	0	15	10	9	1	6	15	10	10	5	4	16	8	6	0	0	18	45	44
8	2	14	18	18	0	1	15	16	16	2	6	15	7	7	0	5	16	10	8	1	0	18	28	26
1	3	14	23	23	1	1	15	36	38	3	6	15	17	17	1	5	16	16	17	3	0	18	16	14
2	3	14	28	29	3	1	15	22	20	0	0	16	7	6	2	5	16	21	20	4	0	18	10	10
3	3	14	12	11	4	1	15	15	15	1	0	16	14	13	3	5	16	7	8	1	1	18	12	11
4	3	14	11	11	5	1	15	15	14	3	0	16	10	9	4	5	16	8	7	2	1	18	10	10
5	3	14	18	18	6	1	15	12	11	4	0	16	18	18	1	0	17	9	10	3	1	18	9	8
6	3	14	13	11	7	1	15	11	11	5	0	16	14	14	2	0	17	8	7	4	1	18	19	18
8	3	14	10	10	0	2	15	32	33	6	0	16	18	17	3	0	17	9	9	0	2	18	6	3
0	4	14	23	24	1	2	15	14	15	7	0	16	9	8	4	0	17	16	17	1	2	18	10	9
1	4	14	28	29	2	2	15	15	15	0	1	16	19	17	5	0	17	16	16	2	2	18	9	10
2	4	14	12	11	3	2	15	26	26	1	1	16	8	8	6	0	17	17	18	3	2	18	9	7
3	4	14	11	10	5	2	15	21	20	2	1	16	6	6	0	1	17	19	19	0	3	18	7	7
4	4	14	17	17	6	2	15	16	16	3	1	16	16	16	1	1	17	21	22	2	3	18	10	7
5	4	14	21	20	7	2	15	11	13	4	1	16	6	6	2	1	17	9	10	1	1	19	10	8
6	4	14	6	6	0	3	15	24	24	6	1	16	11	10										

Table 3.7

Analyses of variance for α-parabutylchloral.

	GGG	UGG	GUG	UUG	GGU	UGU	GUU	UUU	ALL
N	228	199	196	178	198	176	178	170	1523
V	123	120	128	117	138	121	121	115	123

SIN THETA	0.00 -	.17 -	.22 -	.26 -	.28 -	.30 -	.33 -	.35 -	.36 -	.38 - .40
N	154	166	191	116	136	220	156	90	192	102
V	195	148	108	97	105	107	99	113	106	122

SQRT(F/FMAX)	0.00 -	.23 -	.26 -	.29 -	.32 -	.35 -	.38 -	.43 -	.48 -	.58 - 1.00
N	182	157	127	170	142	155	163	129	151	147
V	139	131	114	119	118	115	131	116	117	126

ABS(H)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	134	159	160	156	155	144	134	120	108	85	76	47	33	12	0
V	167	131	133	122	122	124	112	99	110	103	107	109	97	141	0

ABS(K)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	178	199	189	185	176	156	137	117	92	65	29	0	0	0	0
V	155	133	121	131	121	112	108	105	111	94	105	0	0	0	0

ABS(L)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	101	118	118	111	115	104	110	99	95	90	85	76	73	58	170
V	143	120	119	138	136	138	119	136	119	102	123	117	98	109	112

Table 3.8

Hydrogen atom co-ordinates ($x10^4$) for α-parabutylchloral.

Atom	x/a	y/b	z/c
H(2)	4115(5)	2018(6)	1048(3)
H(22)	1817(6)	3351(7)	1499(4)
H(231)	1571(5)	4572(6)	2734(3)
H(232)	2484(5)	3554(6)	3099(3)
H(233)	1335(5)	2959(6)	2754(3)
H(4)	3841(5)	2239(6)	-0311(3)
H(42)	2663(6)	0770(7)	-1733(4)
H(431)	2162(8)	2039(9)	-2829(4)
H(432)	1731(8)	3215(9)	-2250(4)
H(433)	1099(8)	1771(9)	-2278(4)
H(6)	4784(5)	0444(6)	0206(3)
H(62)	3999(5)	-1789(6)	-0993(4)
H(631)	5158(6)	-3631(7)	-1316(4)
H(632)	4379(6)	-4010(7)	-0585(4)
H(633)	5664(6)	-3598(7)	-0449(4)

Table 3.9

Anisotropic temperature factors ($x10^3$ Å^2) for α-parabutylchloral.

ATOM	U11	U22	U33	U23	U13	U12
O(1)	039(2)	034(2)	036(2)	003(2)	000(2)	009(2)
C(2)	036(3)	036(3)	038(4)	001(3)	-003(3)	-001(3)
O(3)	042(2)	037(2)	031(2)	002(2)	-002(2)	009(2)
C(4)	033(3)	028(3)	030(2)	-002(3)	002(3)	010(3)
O(5)	039(2)	034(2)	027(2)	-002(3)	-001(2)	014(2)
C(6)	029(3)	037(3)	034(3)	-004(3)	-009(3)	004(3)
C(21)	035(3)	042(4)	034(3)	-006(3)	001(3)	-002(3)
C(22)	050(4)	048(4)	049(4)	-001(4)	004(4)	002(4)
C(23)	047(4)	026(3)	037(3)	-012(3)	025(3)	005(3)
CL(21)	063(1)	070(1)	042(1)	-007(1)	-019(1)	002(1)
CL(22)	048(1)	052(1)	056(1)	-001(1)	006(1)	-012(1)
CL(23)	107(2)	056(1)	141(3)	-027(2)	053(2)	-022(1)
C(41)	050(4)	037(4)	046(4)	008(3)	007(3)	015(3)
C(42)	068(5)	031(4)	052(4)	002(3)	-011(4)	017(4)
C(43)	098(7)	065(5)	036(4)	008(4)	-022(4)	019(5)
CL(41)	080(1)	040(1)	058(1)	006(1)	008(1)	027(1)
CL(42)	039(1)	068(1)	072(1)	014(1)	-008(1)	-001(1)
CL(43)	071(1)	090(2)	063(1)	018(1)	023(1)	010(1)
C(61)	023(3)	035(3)	042(4)	-003(3)	-003(3)	004(3)
C(62)	038(4)	037(4)	049(4)	-005(3)	-012(3)	016(3)
C(63)	050(4)	042(4)	054(4)	-018(4)	-012(4)	018(3)
CL(61)	059(1)	053(1)	054(1)	004(1)	-024(1)	018(1)
CL(62)	044(1)	043(1)	089(1)	-001(1)	006(1)	-009(1)
CL(63)	068(1)	066(1)	079(1)	007(1)	028(1)	012(1)

Table 3.10

Torsion angles (°) in α-parabutylchloral.

C(6) -- O(1) -- C(2) -- H(2)	-63.3
C(6) -- O(1) -- C(2) -- O(3)	58.3
C(6) -- O(1) -- C(2) -- C(21)	176.6
C(2) -- O(1) -- C(6) -- O(5)	-59.8
C(2) -- O(1) -- C(6) -- H(6)	60.3
C(2) -- O(1) -- C(6) -- C(61)	180.0
O(1) -- C(2) -- O(3) -- C(4)	-57.3
H(2) -- C(2) -- O(3) -- C(4)	61.2
C(21) -- C(2) -- O(3) -- C(4)	-178.7
O(1) -- C(2) -- C(21) -- C(22)	-171.5
O(1) -- C(2) -- C(21) -- CL(21)	65.1
O(1) -- C(2) -- C(21) -- CL(22)	-52.1
H(2) -- C(2) -- C(21) -- C(22)	70.0
H(2) -- C(2) -- C(21) -- CL(21)	-53.4
H(2) -- C(2) -- C(21) -- CL(22)	-170.6
O(3) -- C(2) -- C(21) -- C(22)	-51.6
O(3) -- C(2) -- C(21) -- CL(21)	-175.0
O(3) -- C(2) -- C(21) -- CL(22)	67.8
C(2) -- O(3) -- C(4) -- H(4)	-62.6
C(2) -- O(3) -- C(4) -- O(5)	57.8
C(2) -- O(3) -- C(4) -- C(41)	175.4
O(3) -- C(4) -- O(5) -- C(6)	-59.0
H(4) -- C(4) -- O(5) -- C(6)	61.7
C(41) -- C(4) -- O(5) -- C(6)	-176.3
O(3) -- C(4) -- C(41) -- C(42)	-175.0
O(3) -- C(4) -- C(41) -- CL(41)	61.9
O(3) -- C(4) -- C(41) -- CL(42)	-55.6
H(4) -- C(4) -- C(41) -- C(42)	64.5
H(4) -- C(4) -- C(41) -- CL(41)	-58.6
H(4) -- C(4) -- C(41) -- CL(42)	-176.1
O(5) -- C(4) -- C(41) -- C(42)	-55.8
O(5) -- C(4) -- C(41) -- CL(41)	-178.8
O(5) -- C(4) -- C(41) -- CL(42)	63.6
C(4) -- O(5) -- C(6) -- O(1)	59.7
C(4) -- O(5) -- C(6) -- H(6)	-60.0
C(4) -- O(5) -- C(6) -- C(61)	180.0
O(1) -- C(6) -- C(61) -- C(62)	172.1
O(1) -- C(6) -- C(61) -- CL(61)	-65.2
O(1) -- C(6) -- C(61) -- CL(62)	53.3
O(5) -- C(6) -- C(61) -- C(62)	51.9
O(5) -- C(6) -- C(61) -- CL(61)	174.7
O(5) -- C(6) -- C(61) -- CL(62)	-66.8
H(6) -- C(6) -- C(61) -- C(62)	-68.2
H(6) -- C(6) -- C(61) -- CL(61)	54.6
H(6) -- C(6) -- C(61) -- CL(62)	173.1
C(2) -- C(21) -- C(22) -- H(22)	68.3
C(2) -- C(21) -- C(22) -- C(23)	-174.9
C(2) -- C(21) -- C(22) -- CL(23)	-53.0
CL(21)-- C(21) -- C(22) -- H(22)	-170.8
CL(21)-- C(21) -- C(22) -- C(23)	-54.1

continued/......

Table 3.10 (continued)

CL(21)-- C(21) -- C(22) -- CL(23)	67.8
CL(22)-- C(21) -- C(22) -- H(22)	-52.8
CL(22)-- C(21) -- C(22) -- C(23)	64.0
CL(22)-- C(21) -- C(22) -- CL(23)	-174.1
C(21) -- C(22) -- C(23) -- H(231)	-173.5
C(21) -- C(22) -- C(23) -- H(232)	61.3
C(21) -- C(22) -- C(23) -- H(233)	-54.4
H(22) -- C(22) -- C(23) -- H(231)	-57.8
H(22) -- C(22) -- C(23) -- H(232)	177.1
H(22) -- C(22) -- C(23) -- H(233)	61.3
CL(23)-- C(22) -- C(23) -- H(231)	63.6
CL(23)-- C(22) -- C(23) -- H(232)	-61.5
CL(23)-- C(22) -- C(23) -- H(233)	-177.3
C(4) -- C(41) -- C(42) -- H(42)	67.6
C(4) -- C(41) -- C(42) -- C(43)	-177.1
C(4) -- C(41) -- C(42) -- CL(43)	-52.2
CL(41)-- C(41) -- C(42) -- H(42)	-171.7
CL(41)-- C(41) -- C(42) -- C(43)	-56.4
CL(41)-- C(41) -- C(42) -- CL(43)	68.5
CL(42)-- C(41) -- C(42) -- H(42)	-53.1
CL(42)-- C(41) -- C(42) -- C(43)	62.2
CL(42)-- C(41) -- C(42) -- CL(43)	-172.9
C(41) -- C(42) -- C(43) -- H(431)	174.5
C(41) -- C(42) -- C(43) -- H(432)	56.7
C(41) -- C(42) -- C(43) -- H(433)	-63.7
H(42) -- C(42) -- C(43) -- H(431)	-68.1
H(42) -- C(42) -- C(43) -- H(432)	174.0
H(42) -- C(42) -- C(43) -- H(433)	53.6
CL(43)-- C(42) -- C(43) -- H(431)	51.3
CL(43)-- C(42) -- C(43) -- H(432)	-66.5
CL(43)-- C(42) -- C(43) -- H(433)	173.0
C(6) -- C(61) -- C(62) -- H(62)	-68.8
C(6) -- C(61) -- C(62) -- C(63)	174.6
C(6) -- C(61) -- C(62) -- CL(63)	51.3
CL(61)-- C(61) -- C(62) -- H(62)	170.9
CL(61)-- C(61) -- C(62) -- C(63)	54.3
CL(61)-- C(61) -- C(62) -- CL(63)	-69.0
CL(62)-- C(61) -- C(62) -- H(62)	51.3
CL(62)-- C(61) -- C(62) -- C(63)	-65.4
CL(62)-- C(61) -- C(62) -- CL(63)	171.3
C(61) -- C(62) -- C(63) -- H(631)	174.7
C(61) -- C(62) -- C(63) -- H(632)	54.0
C(61) -- C(62) -- C(63) -- H(633)	-65.0
H(62) -- C(62) -- C(63) -- H(631)	58.7
H(62) -- C(62) -- C(63) -- H(632)	-62.1
H(62) -- C(62) -- C(63) -- H(633)	179.0
CL(63)-- C(62) -- C(63) -- H(631)	-61.5
CL(63)-- C(62) -- C(63) -- H(632)	177.8
CL(63)-- C(62) -- C(63) -- H(633)	58.8

Table 3.11

Observed and calculated structure factors for β-parabutylchloral.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	134	145	5	3	0	23	24	5	6	0	28	28	3	11	0	21	20	2	3	1	49	47
4	0	0	143	147	6	3	0	73	75	6	6	0	12	10	4	11	0	14	12	3	3	1	61	60
6	0	0	58	57	7	3	0	16	13	7	6	0	14	17	2	0	1	75	76	4	3	1	69	70
8	0	0	66	65	8	3	0	43	46	8	6	0	7	6	4	0	1	51	51	5	3	1	112	115
10	0	0	54	47	9	3	0	12	15	9	6	0	9	9	6	0	1	32	31	6	3	1	35	36
12	0	0	13	14	10	3	0	22	20	10	6	0	8	8	8	0	1	25	24	8	3	1	33	31
2	1	0	72	75	12	3	0	14	14	1	7	0	24	24	10	0	1	58	58	9	3	1	15	14
3	1	0	61	62	1	4	0	29	30	2	7	0	36	33	12	0	1	13	12	10	3	1	23	21
4	1	0	104	104	2	4	0	19	18	3	7	0	82	84	2	1	1	137	145	11	3	1	20	20
5	1	0	22	22	3	4	0	74	75	4	7	0	32	34	3	1	1	35	34	12	3	1	13	11
6	1	0	81	79	4	4	0	7	9	5	7	0	20	19	4	1	1	49	48	13	3	1	13	12
7	1	0	11	10	5	4	0	39	37	6	7	0	39	39	5	1	1	82	81	1	4	1	46	47
8	1	0	15	13	6	4	0	20	22	7	7	0	70	70	6	1	1	73	73	2	4	1	130	136
9	1	0	32	33	7	4	0	6	5	9	7	0	34	32	7	1	1	17	17	3	4	1	57	57
10	1	0	66	65	8	4	0	36	37	10	7	0	9	8	8	1	1	16	16	4	4	1	58	55
11	1	0	12	11	9	4	0	6	5	1	8	0	41	40	9	1	1	25	23	5	4	1	51	52
12	1	0	11	11	10	4	0	16	15	2	8	0	28	30	10	1	1	7	5	6	4	1	45	45
13	1	0	19	17	11	4	0	22	20	3	8	0	83	82	11	1	1	16	16	7	4	1	29	30
1	2	0	96	103	12	4	0	15	16	4	8	0	8	8	12	1	1	13	13	8	4	1	28	27
2	2	0	55	58	1	5	0	106	105	5	8	0	12	13	13	1	1	15	15	9	4	1	6	6
3	2	0	28	31	2	5	0	64	60	6	8	0	18	19	1	2	1	69	72	10	4	1	26	28
4	2	0	81	84	3	5	0	19	19	7	8	0	13	14	2	2	1	40	41	11	4	1	12	12
5	2	0	14	14	4	5	0	6	7	9	8	0	20	18	3	2	1	57	57	12	4	1	31	26
6	2	0	5	7	6	5	0	52	49	1	9	0	12	10	4	2	1	96	98	0	5	1	56	52
7	2	0	78	76	7	5	0	5	2	2	9	0	8	6	5	2	1	74	75	1	5	1	31	32
8	2	0	17	19	8	5	0	17	16	3	9	0	9	9	6	2	1	56	55	2	5	1	62	62
9	2	0	9	7	10	5	0	15	15	5	9	0	6	5	7	2	1	43	39	3	5	1	56	56
10	2	0	30	29	11	5	0	10	10	0	10	0	15	15	8	2	1	16	17	4	5	1	25	26
11	2	0	15	17	12	5	0	11	9	1	10	0	14	14	9	2	1	40	38	5	5	1	51	50
12	2	0	9	11	0	6	0	17	20	2	10	0	32	29	10	2	1	24	24	6	5	1	11	10
13	2	0	9	9	1	6	0	31	30	3	10	0	24	22	11	2	1	15	16	7	5	1	7	9
1	3	0	90	93	2	6	0	34	33	5	10	0	12	14	12	2	1	12	12	8	5	1	27	26
2	3	0	47	48	3	6	0	41	42	1	11	0	10	8	0	3	1	143	151	9	5	1	13	13
3	3	0	38	34	4	6	0	79	77	2	11	0	26	22	1	3	1	40	43	10	5	1	10	11
11	5	1	33	32	8	9	1	15	15	5	2	2	46	47	3	5	2	75	74	3	8	2	21	20
1	6	1	48	49	1	10	1	19	19	6	2	2	55	53	4	5	2	20	19	4	8	2	12	13
2	6	1	41	42	2	10	1	18	15	7	2	2	15	14	5	5	2	43	41	6	8	2	12	13
3	6	1	26	27	3	10	1	15	15	8	2	2	43	43	6	5	2	16	16	7	8	2	25	24
4	6	1	30	30	5	10	1	13	11	9	2	2	43	41	7	5	2	46	46	8	8	2	15	13
5	6	1	28	29	6	10	1	16	17	11	2	2	10	10	8	5	2	16	15	9	8	2	16	17
6	6	1	10	6	0	11	1	21	18	12	2	2	10	9	9	5	2	23	22	1	9	2	15	17
7	6	1	7	9	1	11	1	10	8	13	2	2	9	11	10	5	2	14	15	2	9	2	19	19
8	6	1	10	10	3	11	1	12	14	1	3	2	15	14	11	5	2	13	15	3	9	2	17	15
11	6	1	7	10	4	11	1	10	12	2	3	2	98	99	12	5	2	11	8	4	9	2	13	15
0	7	1	19	18	2	0	2	62	63	3	3	2	50	50	0	6	2	47	48	5	9	2	11	12
1	7	1	23	23	4	0	2	99	96	4	3	2	52	51	1	6	2	48	51	6	9	2	13	11
2	7	1	13	12	6	0	2	65	63	5	3	2	16	13	2	6	2	27	27	7	9	2	10	8
3	7	1	54	55	8	0	2	28	28	6	3	2	75	76	3	6	2	36	36	0	10	2	23	24
4	7	1	23	27	10	0	2	40	39	7	3	2	55	55	4	6	2	29	31	1	10	2	27	26
5	7	1	37	37	12	0	2	16	17	8	3	2	35	37	5	6	2	45	45	2	10	2	12	13
6	7	1	15	15	1	1	2	23	23	9	3	2	9	10	6	6	2	33	33	3	10	2	15	14
7	7	1	7	4	2	1	2	115	115	10	3	2	42	44	7	6	2	33	32	5	10	2	14	14
8	7	1	14	14	3	1	2	77	77	11	3	2	7	8	8	6	2	12	13	6	10	2	17	17
10	7	1	19	19	4	1	2	38	38	12	3	2	7	8	9	6	2	24	25	1	11	2	10	8
1	8	1	14	14	5	1	2	37	37	0	4	2	36	38	10	6	2	14	12	3	11	2	10	9
2	8	1	32	32	6	1	2	49	50	1	4	2	89	87	11	6	2	21	21	2	0	3	33	35
3	8	1	22	21	7	1	2	61	60	2	4	2	52	50	1	7	2	35	35	4	0	3	84	85
4	8	1	32	35	8	1	2	45	44	3	4	2	76	76	2	7	2	31	32	6	0	3	85	86
6	8	1	8	8	9	1	2	30	29	4	4	2	44	44	3	7	2	13	14	8	0	3	53	55
7	8	1	21	20	10	1	2	26	28	5	4	2	21	20	4	7	2	17	17	10	0	3	60	62
8	8	1	8	6	11	1	2	9	9	6	4	2	10	7	5	7	2	22	21	12	0	3	19	17
0	9	1	8	8	12	1	2	23	23	7	4	2	26	25	6	7	2	8	9	0	1	3	191	208
1	9	1	8	9	13	1	2	10	11	8	4	2	20	18	7	7	2	6	1	1	1	3	87	88
2	9	1	19	18	0	2	2	88	86	10	4	2	24	23	8	7	2	13	15	2	1	3	72	71
3	9	1	12	12	1	2	2	64	64	11	4	2	27	25	9	7	2	19	19	3	1	3	103	102
4	9	1	31	31	2	2	2	21	23	12	4	2	14	11	10	7	2	9	10	4	1	3	58	58
5	9	1	13	12	3	2	2	123	123	1	5	2	81	80	0	8	2	66	66	5	1	3	77	80
7	9	1	19	20	4	2	2	80	78	2	5	2	35	34	1	8	2	40	40	6	1	3	19	20

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Table 3.11 (continued)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
7	1	3	27	27	4	4	3	42	41	1	7	3	53	53	1	11	3	22	22	1	3	4	54	53
8	1	3	23	21	5	4	3	21	21	2	7	3	25	24	3	11	3	10	10	2	3	4	35	38
9	1	3	22	23	6	4	3	62	60	3	7	3	50	52	0	0	4	115	110	3	3	4	40	39
11	1	3	18	18	7	4	3	27	25	4	7	3	37	37	2	0	4	78	79	4	3	4	66	66
12	1	3	21	19	8	4	3	11	11	5	7	3	30	29	4	0	4	60	60	5	3	4	43	40
13	1	3	8	9	9	4	3	17	19	6	7	3	11	10	6	0	4	58	59	6	3	4	16	15
1	2	3	51	49	10	4	3	16	12	7	7	3	19	19	8	0	4	60	60	7	3	4	22	22
2	2	3	33	32	11	4	3	14	14	8	7	3	20	21	10	0	4	25	24	8	3	4	8	8
3	2	3	91	90	12	4	3	11	10	9	7	3	24	22	12	0	4	15	17	9	3	4	15	14
4	2	3	43	43	0	5	3	58	59	1	8	3	24	26	1	1	4	71	68	10	3	4	27	27
5	2	3	14	14	1	5	3	18	17	2	8	3	28	28	2	1	4	115	117	11	3	4	20	20
6	2	3	28	27	2	5	3	19	20	3	8	3	14	15	3	1	4	37	36	12	3	4	15	14
7	2	3	55	53	3	5	3	23	24	4	8	3	16	17	4	1	4	40	39	0	4	4	127	128
8	2	3	19	17	4	5	3	59	60	5	8	3	11	13	5	1	4	55	54	1	4	4	12	10
9	2	3	28	27	5	5	3	37	37	6	8	3	14	13	6	1	4	41	41	2	4	4	11	12
10	2	3	17	16	6	5	3	42	44	7	8	3	27	27	7	1	4	23	24	3	4	4	52	53
11	2	3	18	17	7	5	3	25	28	8	8	3	6	4	8	1	4	49	51	4	4	4	21	20
13	2	3	23	25	8	5	3	15	12	9	8	3	15	15	9	1	4	11	11	5	4	4	7	4
0	3	3	173	179	9	5	3	14	13	0	9	3	45	44	10	1	4	29	31	6	4	4	37	36
1	3	3	60	59	10	5	3	30	26	1	9	3	11	8	11	1	4	8	7	7	4	4	12	12
2	3	3	66	63	11	5	3	11	9	2	9	3	21	21	12	1	4	8	6	8	4	4	9	9
3	3	3	28	26	12	5	3	19	17	3	9	3	9	8	0	2	4	116	111	9	4	4	28	29
4	3	3	108	108	1	6	3	7	9	4	9	3	12	11	1	2	4	115	114	10	4	4	36	35
5	3	3	39	42	2	6	3	21	22	5	9	3	12	14	2	2	4	51	51	11	4	4	23	23
6	3	3	13	12	3	6	3	55	55	6	9	3	20	18	3	2	4	14	15	12	4	4	13	13
7	3	3	7	5	4	6	3	34	35	7	9	3	7	10	4	2	4	52	52	1	5	4	32	32
8	3	3	21	21	5	6	3	10	10	8	9	3	16	16	5	2	4	39	39	2	5	4	34	36
9	3	3	16	16	6	6	3	43	43	1	10	3	7	5	6	2	4	22	21	3	5	4	25	25
10	3	3	18	18	7	6	3	33	30	2	10	3	15	17	7	2	4	41	41	4	5	4	17	20
11	3	3	14	14	8	6	3	20	21	3	10	3	20	21	8	2	4	7	9	5	5	4	19	19
12	3	3	22	22	9	6	3	18	17	4	10	3	14	14	9	2	4	50	49	6	5	4	27	28
1	4	3	39	37	10	6	3	18	16	5	10	3	9	9	10	2	4	13	13	7	5	4	26	27
2	4	3	26	23	11	6	3	19	19	6	10	3	10	10	11	2	4	10	10	8	5	4	10	8
3	4	3	54	53	0	7	3	52	53	0	11	3	11	9	13	2	4	7	7	9	5	4	30	30
11	5	4	13	11	4	9	4	10	9	6	2	5	31	29	2	5	5	24	23	7	8	5	8	6
0	6	4	26	25	6	9	4	24	22	7	2	5	59	61	3	5	5	86	85	8	8	5	7	7
1	6	4	35	34	7	9	4	15	13	8	2	5	10	10	4	5	5	76	76	9	8	5	7	10
2	6	4	22	22	2	10	4	14	15	9	2	5	50	51	5	5	5	47	49	0	9	5	51	48
3	6	4	23	23	3	10	4	15	16	10	2	5	11	10	6	5	5	18	22	1	9	5	17	17
4	6	4	12	11	4	10	4	9	6	11	2	5	19	18	7	5	5	22	24	2	9	5	22	23
5	6	4	8	7	5	10	4	15	16	12	2	5	23	23	8	5	5	14	13	3	9	5	9	9
6	6	4	21	22	6	10	4	15	15	0	3	5	58	60	10	5	5	6	4	4	9	5	32	33
7	6	4	38	36	1	11	4	13	12	1	3	5	37	34	11	5	5	12	10	5	9	5	7	5
8	6	4	11	14	2	11	4	17	16	2	3	5	37	35	1	6	5	33	34	6	9	5	11	8
9	6	4	12	10	2	0	5	177	181	3	3	5	58	55	2	6	5	38	41	7	9	5	10	8
10	6	4	8	6	4	0	5	9	11	4	3	5	27	25	3	6	5	41	41	2	10	5	12	11
11	6	4	20	21	6	0	5	20	18	5	3	5	38	39	4	6	5	21	22	4	10	5	13	12
1	7	4	21	21	8	0	5	53	57	6	3	5	66	66	5	6	5	24	24	5	10	5	7	4
2	7	4	43	43	10	0	5	35	37	7	3	5	26	26	6	6	5	67	66	0	11	5	30	30
3	7	4	21	21	12	0	5	26	24	8	3	5	11	11	7	6	5	20	21	0	0	6	139	137
4	7	4	38	36	0	1	5	95	90	9	3	5	26	27	9	6	5	13	12	2	0	6	62	64
5	7	4	27	25	1	1	5	103	100	10	3	5	16	17	10	6	5	29	28	4	0	6	102	101
6	7	4	11	9	2	1	5	71	68	11	3	5	9	6	11	6	5	6	7	6	0	6	17	17
7	7	4	35	35	3	1	5	89	90	12	3	5	13	14	0	7	5	8	9	8	0	6	91	93
8	7	4	10	10	4	1	5	36	37	1	4	5	12	11	1	7	5	6	4	10	0	6	23	24
10	7	4	10	9	5	1	5	55	57	2	4	5	42	48	2	7	5	14	13	12	0	6	28	28
1	8	4	17	17	6	1	5	34	33	3	4	5	51	50	3	7	5	11	11	1	1	6	43	40
2	8	4	17	19	7	1	5	55	55	4	4	5	18	17	4	7	5	45	44	2	1	6	63	61
3	8	4	15	15	8	1	5	48	48	5	4	5	19	17	5	7	5	56	55	3	1	6	68	67
4	8	4	33	33	9	1	5	32	34	6	4	5	25	25	6	7	5	17	17	4	1	6	19	18
5	8	4	21	21	10	1	5	10	13	7	4	5	43	42	8	7	5	7	8	5	1	6	40	37
6	8	4	18	18	11	1	5	7	9	8	4	5	8	10	9	7	5	8	7	6	1	6	33	34
7	8	4	16	14	13	1	5	10	10	9	4	5	18	20	1	8	5	7	8	7	1	6	67	67
8	8	4	9	10	1	2	5	23	21	10	4	5	33	34	2	8	5	41	42	8	1	6	46	48
9	8	4	15	15	2	2	5	64	61	11	4	5	16	16	3	8	5	7	10	9	1	6	26	27
1	9	4	23	23	3	2	5	119	115	12	4	5	15	15	4	8	5	9	9	10	1	6	16	17
2	9	4	23	24	4	2	5	54	54	0	5	5	49	50	5	8	5	9	9	11	1	6	12	12
3	9	4	14	15	5	2	5	34	32	1	5	5	55	56	6	8	5	15	16	12	1	6	12	13

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Table 3.11 (continued)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	2	6	32	29	1	5	6	22	22	8	8	6	12	13	5	2	7	37	36	4	5	7	6	5
1	2	6	47	47	2	5	6	20	21	1	9	6	26	27	6	2	7	25	26	5	5	7	29	31
2	2	6	48	46	3	5	6	22	20	2	9	6	8	10	7	2	7	51	48	6	5	7	20	18
3	2	6	100	98	4	5	6	41	42	4	9	6	20	20	8	2	7	25	27	7	5	7	12	11
4	2	6	58	57	5	5	6	8	10	5	9	6	12	12	9	2	7	24	25	8	5	7	21	22
5	2	6	18	19	7	5	6	20	21	6	9	6	11	10	10	2	7	11	11	9	5	7	14	13
6	2	6	11	12	8	5	6	10	9	7	9	6	11	10	11	2	7	13	12	10	5	7	12	13
7	2	6	42	43	9	5	6	17	17	0	10	6	26	26	12	2	7	7	7	1	6	7	33	35
8	2	6	7	4	10	5	6	9	10	2	10	6	13	11	0	3	7	40	40	2	6	7	12	13
9	2	6	35	36	11	5	6	12	11	3	10	6	17	17	1	3	7	10	12	3	6	7	27	29
10	2	6	14	15	0	6	6	28	30	4	10	6	9	7	2	3	7	12	14	4	6	7	33	35
11	2	6	9	8	1	6	6	15	15	5	10	6	9	8	3	3	7	58	53	5	6	7	25	23
12	2	6	6	6	2	6	6	35	35	2	0	7	119	117	4	3	7	41	42	6	6	7	24	28
1	3	6	30	27	3	6	6	16	14	4	0	7	39	41	5	3	7	47	46	7	6	7	17	18
2	3	6	29	27	4	6	6	13	15	6	0	7	20	23	6	3	7	14	13	8	6	7	7	7
3	3	6	49	49	5	6	6	14	14	8	0	7	31	31	7	3	7	10	11	9	6	7	17	18
4	3	6	43	41	6	6	6	35	34	10	0	7	11	13	8	3	7	15	16	10	6	7	14	15
5	3	6	7	4	7	6	6	33	33	12	0	7	24	24	9	3	7	10	10	0	7	7	40	37
6	3	6	36	37	8	6	6	11	7	0	1	7	85	81	11	3	7	9	9	1	7	7	25	27
7	3	6	54	54	10	6	6	10	10	1	1	7	60	56	1	4	7	20	18	2	7	7	18	18
8	3	6	23	26	1	7	6	23	22	2	1	7	110	102	2	4	7	76	76	3	7	7	11	11
10	3	6	17	15	2	7	6	8	10	3	1	7	104	98	3	4	7	19	18	4	7	7	16	15
12	3	6	9	10	3	7	6	16	16	4	1	7	53	53	4	4	7	21	22	5	7	7	43	43
0	4	6	109	112	5	7	6	30	30	5	1	7	49	48	5	4	7	21	21	6	7	7	18	17
1	4	6	24	22	6	7	6	9	11	6	1	7	26	25	6	4	7	32	34	7	7	7	12	13
2	4	6	21	21	7	7	6	8	8	7	1	7	40	42	7	4	7	22	21	8	7	7	7	8
3	4	6	30	34	8	7	6	13	12	8	1	7	34	32	8	4	7	8	8	9	7	7	12	11
4	4	6	27	26	0	8	6	51	52	10	1	7	14	15	9	4	7	23	24	1	8	7	26	27
5	4	6	22	24	1	8	6	6	8	11	1	7	14	14	10	4	7	31	32	2	8	7	25	25
6	4	6	17	16	2	8	6	22	23	12	1	7	9	9	11	4	7	14	15	3	8	7	10	9
7	4	6	7	7	3	8	6	12	11	1	2	7	76	74	0	5	7	59	56	5	8	7	17	15
8	4	6	29	29	4	8	6	11	11	2	2	7	22	23	1	5	7	25	21	6	8	7	8	7
9	4	6	19	19	5	8	6	31	33	3	2	7	64	62	2	5	7	23	24	7	8	7	11	11
10	4	6	29	29	6	8	6	14	12	4	2	7	36	35	3	5	7	40	39	8	8	7	13	12
0	9	7	46	47	9	2	8	26	28	0	6	8	36	34	4	0	9	18	18	8	3	9	24	22
1	9	7	13	13	10	2	8	11	9	1	6	8	26	26	6	0	9	20	21	9	3	9	18	19
2	9	7	7	6	11	2	8	14	14	2	6	8	20	19	8	0	9	7	10	11	3	9	9	9
3	9	7	10	10	1	3	8	15	15	3	6	8	62	62	10	0	9	25	25	1	4	9	41	39
4	9	7	19	21	2	3	8	74	76	4	6	8	46	46	0	1	9	72	72	2	4	9	15	15
6	9	7	7	6	3	3	8	20	20	5	6	8	8	4	1	1	9	39	38	3	4	9	10	10
2	10	7	14	14	4	3	8	38	38	6	6	8	10	11	2	1	9	33	30	6	4	9	27	25
4	10	7	13	13	5	3	8	16	16	8	6	8	6	6	3	1	9	10	8	7	4	9	9	10
0	0	8	143	142	6	3	8	30	30	10	6	8	8	6	4	1	9	38	37	8	4	9	14	13
2	0	8	36	32	7	3	8	34	35	1	7	8	18	17	5	1	9	38	38	9	4	9	12	14
4	0	8	48	46	8	3	8	23	23	2	7	8	16	17	6	1	9	55	55	10	4	9	6	3
6	0	8	15	15	9	3	8	11	11	3	7	8	14	13	7	1	9	21	22	0	5	9	27	27
8	0	8	37	40	10	3	8	21	21	4	7	8	21	22	8	1	9	26	28	1	5	9	10	10
10	0	8	33	37	0	4	8	48	50	5	7	8	16	18	10	1	9	14	14	2	5	9	26	28
12	0	8	12	11	1	4	8	28	28	6	7	8	16	17	11	1	9	18	19	3	5	9	15	15
1	1	8	21	18	2	4	8	28	28	7	7	8	11	9	1	2	9	54	52	4	5	9	37	35
2	1	8	42	37	3	4	8	53	51	8	7	8	9	11	2	2	9	36	37	5	5	9	31	30
3	1	8	48	46	4	4	8	24	23	9	7	8	7	6	3	2	9	39	38	6	5	9	20	20
4	1	8	46	46	5	4	8	25	23	0	8	8	55	54	4	2	9	11	13	7	5	9	6	5
5	1	8	8	6	6	4	8	32	34	1	8	8	18	20	5	2	9	36	36	8	5	9	17	16
6	1	8	38	38	7	4	8	12	12	3	8	8	7	6	6	2	9	23	24	9	5	9	10	13
7	1	8	31	34	8	4	8	12	14	6	8	8	8	9	7	2	9	46	48	10	5	9	13	15
8	1	8	12	11	9	4	8	11	12	7	8	8	17	19	8	2	9	17	18	2	6	9	24	23
9	1	8	12	13	10	4	8	12	14	1	9	8	16	17	9	2	9	14	15	3	6	9	44	45
12	1	8	8	9	1	5	8	7	7	2	9	8	23	24	10	2	9	9	12	4	6	9	27	25
0	2	8	64	63	2	5	8	52	54	3	9	8	12	13	11	2	9	13	15	5	6	9	17	17
1	2	8	58	57	3	5	8	41	41	4	9	8	10	10	0	3	9	45	43	7	6	9	23	21
2	2	8	32	31	4	5	8	12	11	5	9	8	13	13	1	3	9	34	35	8	6	9	15	13
3	2	8	59	61	5	5	8	42	40	6	9	8	14	14	2	3	9	23	23	9	6	9	10	10
4	2	8	42	42	6	5	8	48	50	0	10	8	11	11	3	3	9	8	7	0	7	9	37	36
5	2	8	51	52	7	5	8	28	29	1	10	8	7	8	4	3	9	28	30	1	7	9	17	19
6	2	8	43	45	8	5	8	15	17	2	10	8	14	14	5	3	9	22	21	2	7	9	22	22
7	2	8	46	49	9	5	8	22	22	3	10	8	16	14	6	3	9	11	12	3	7	9	20	21
8	2	8	26	29	10	5	8	12	12	2	0	9	44	44	7	3	9	16	15	4	7	9	18	20

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Table 3.11 (continued)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
7	7	9	8	9	4	2	10	12	12	7	5	10	19	19	4	1	11	22	24	8	4	11	8	10
8	7	9	17	17	5	2	10	22	22	8	5	10	21	19	5	1	11	16	16	9	4	11	16	16
1	8	9	20	19	6	2	10	12	14	9	5	10	7	7	6	1	11	28	30	0	5	11	8	11
2	8	9	9	11	7	2	10	18	18	0	6	10	30	31	7	1	11	12	13	1	5	11	18	18
4	8	9	8	6	8	2	10	10	10	1	6	10	25	24	8	1	11	6	2	2	5	11	34	34
5	8	9	7	7	9	2	10	18	18	3	6	10	28	29	9	1	11	23	26	3	5	11	17	17
6	8	9	18	18	10	2	10	9	10	4	6	10	31	32	1	2	11	10	10	4	5	11	18	18
7	8	9	13	15	11	2	10	7	9	5	6	10	28	29	2	2	11	29	28	5	5	11	15	17
0	9	9	11	12	1	3	10	17	17	6	6	10	11	12	3	2	11	31	30	7	5	11	8	9
2	9	9	21	23	2	3	10	37	37	7	6	10	15	15	4	2	11	27	25	8	5	11	12	12
3	9	9	15	15	3	3	10	15	14	8	6	10	10	9	5	2	11	15	15	9	5	11	15	16
4	9	9	18	18	5	3	10	8	7	1	7	10	11	14	6	2	11	17	19	1	6	11	9	11
5	9	9	13	13	6	3	10	32	33	2	7	10	9	10	7	2	11	13	15	2	6	11	22	23
1	10	9	7	6	7	3	10	26	27	3	7	10	9	8	8	2	11	15	16	3	6	11	14	14
0	0	10	120	114	8	3	10	11	11	4	7	10	8	9	9	2	11	18	19	4	6	11	12	12
2	0	10	13	14	9	3	10	8	7	5	7	10	7	7	10	2	11	11	14	5	6	11	22	21
4	0	10	54	53	10	3	10	25	25	6	7	10	12	12	0	3	11	55	56	0	7	11	7	8
6	0	10	33	33	0	4	10	14	13	7	7	10	9	8	1	3	11	43	45	1	7	11	28	28
8	0	10	8	9	1	4	10	24	28	0	8	10	28	30	2	3	11	37	36	2	7	11	11	13
10	0	10	15	14	2	4	10	13	10	1	8	10	18	19	3	3	11	14	11	5	7	11	13	14
1	1	10	19	17	3	4	10	32	31	2	8	10	10	8	4	3	11	28	28	6	7	11	10	12
2	1	10	51	52	4	4	10	41	42	3	8	10	33	32	5	3	11	36	35	1	8	11	6	4
3	1	10	24	24	5	4	10	17	19	4	8	10	11	11	6	3	11	9	9	2	8	11	14	16
4	1	10	35	33	6	4	10	27	28	5	8	10	8	7	7	3	11	11	12	3	8	11	8	6
6	1	10	45	46	7	4	10	14	13	6	8	10	13	11	8	3	11	18	18	4	8	11	9	10
7	1	10	32	34	8	4	10	6	8	4	9	10	11	8	9	3	11	16	18	0	9	11	13	13
8	1	10	8	9	9	4	10	7	8	2	0	11	49	48	10	3	11	13	14	2	9	11	7	9
9	1	10	17	16	10	4	10	8	11	4	0	11	28	31	1	4	11	18	17	0	0	12	98	97
10	1	10	23	23	1	5	10	25	24	6	0	11	33	34	2	4	11	26	25	2	0	12	22	25
11	1	10	12	12	2	5	10	21	20	8	0	11	23	25	3	4	11	7	6	4	0	12	63	64
0	2	10	16	18	3	5	10	29	29	10	0	11	7	6	4	4	11	20	22	6	0	12	22	21
1	2	10	60	59	4	5	10	20	20	1	1	11	40	39	5	4	11	18	16	8	0	12	12	12
2	2	10	15	14	5	5	10	19	17	2	1	11	38	37	6	4	11	14	14	10	0	12	9	10
3	2	10	23	24	6	5	10	16	16	3	1	11	24	23	7	4	11	10	11	1	1	12	29	29
2	1	12	32	31	7	4	12	11	12	8	1	13	18	18	4	6	13	8	9	7	3	14	11	11
3	1	12	26	25	8	4	12	19	21	9	1	13	8	7	6	6	13	18	16	8	3	14	14	12
4	1	12	28	28	1	5	12	27	26	1	2	13	44	41	0	7	13	15	14	0	4	14	49	49
5	1	12	17	19	2	5	12	6	8	2	2	13	11	13	1	7	13	11	10	1	4	14	9	11
6	1	12	15	15	3	5	12	15	16	3	2	13	25	24	2	7	13	8	9	2	4	14	7	5
7	1	12	17	18	4	5	12	14	13	4	2	13	6	6	3	7	13	20	21	3	4	14	22	21
8	1	12	16	15	5	5	12	9	8	5	2	13	18	18	4	7	13	17	18	4	4	14	8	8
9	1	12	12	12	7	5	12	10	10	6	2	13	9	8	1	8	13	8	10	5	4	14	14	14
10	1	12	17	16	0	6	12	10	12	7	2	13	23	23	0	0	14	35	34	6	4	14	8	8
0	2	12	32	30	2	6	12	21	20	8	2	13	10	10	2	0	14	27	28	1	5	14	7	4
1	2	12	31	31	3	6	12	31	32	9	2	13	19	18	4	0	14	41	42	2	5	14	27	29
2	2	12	7	6	4	6	12	7	6	0	3	13	17	14	6	0	14	16	15	3	5	14	17	17
3	2	12	21	21	5	6	12	16	15	1	3	13	13	13	1	1	14	20	20	4	5	14	11	10
4	2	12	21	22	6	6	12	16	17	3	3	13	21	19	2	1	14	23	21	5	5	14	19	18
5	2	12	10	11	7	6	12	13	13	4	3	13	16	16	3	1	14	8	10	6	5	14	13	13
6	2	12	24	24	1	7	12	11	10	5	3	13	28	28	4	1	14	16	17	0	6	14	9	11
7	2	12	27	28	2	7	12	12	13	6	3	13	20	20	5	1	14	15	16	1	6	14	11	8
8	2	12	17	17	3	7	12	21	23	8	3	13	6	3	6	1	14	6	4	2	6	14	12	10
9	2	12	12	11	5	7	12	7	3	1	4	13	17	17	7	1	14	8	9	3	6	14	20	22
1	3	12	11	11	0	8	12	22	21	2	4	13	28	28	8	1	14	12	12	4	6	14	7	5
2	3	12	33	34	1	8	12	15	16	3	4	13	7	11	0	2	14	17	17	5	6	14	25	26
3	3	12	17	19	2	8	12	7	5	5	4	13	8	9	1	2	14	22	20	1	7	14	11	11
4	3	12	13	13	3	8	12	25	24	6	4	13	21	20	2	2	14	10	10	2	7	14	7	8
5	3	12	21	23	2	0	13	70	68	7	4	13	7	7	3	2	14	29	28	2	0	15	9	10
6	3	12	24	25	4	0	13	8	8	0	5	13	6	7	4	2	14	18	15	4	0	15	12	11
7	3	12	11	11	6	0	13	25	25	1	5	13	10	11	5	2	14	23	22	6	0	15	18	19
9	3	12	7	4	8	0	13	12	13	2	5	13	17	21	6	2	14	9	8	0	1	15	32	29
0	4	12	64	64	0	1	13	77	76	3	5	13	17	17	7	2	14	10	9	1	1	15	14	13
1	4	12	14	13	1	1	13	11	11	4	5	13	20	21	1	3	14	17	16	2	1	15	24	23
2	4	12	16	19	2	1	13	40	40	5	5	13	19	18	2	3	14	17	16	3	1	15	22	21
3	4	12	12	14	3	1	13	10	10	6	5	13	10	8	3	3	14	16	18	4	1	15	27	26
4	4	12	31	32	4	1	13	22	21	7	5	13	9	9	4	3	14	33	31	5	1	15	12	13
5	4	12	24	25	5	1	13	35	35	1	6	13	19	19	5	3	14	12	10	6	1	15	14	15
6	4	12	9	10	6	1	13	14	15	3	6	13	8	9	6	3	14	18	17	7	1	15	11	11
2	2	15	25	23	1	4	15	18	19	1	1	16	19	18	3	3	16	9	9	3	1	17	12	12
3	2	15	15	15	3	4	15	17	16	2	1	16	14	12	4	3	16	8	6	4	1	17	16	16
4	2	15	7	7	4	4	15	13	10	6	1	16	9	10	3	4	16	9	6	2	2	17	9	6
5	2	15	8	11	6	4	15	14	16	0	2	16	19	17	4	4	16	18	19	3	2	17	24	24
6	2	15	8	8	0	5	15	12	12	1	2	16	11	9	1	5	16	14	14	4	2	17	11	10
7	2	15	13	13	3	5	15	14	13	3	2	16	30	29	2	5	16	14	12	0	3	17	13	11
0	3	15	25	22	4	5	15	10	12	4	2	16	13	13	2	0	17	17	15	1	3	17	14	17
1	3	15	21	20	1	6	15	22	21	5	2	16	14	15	4	0	17	15	13	2	3	17	7	6
2	3	15	13	11	3	6	15	16	17	6	2	16	8	4	0	1	17	21	20	1	4	17	11	11
4	3	15	11	13	2	0	16	10	7	1	3	16	18	18	1	1	17	23	23	0	0	18	37	33
5	3	15	6	10	4	0	16	14	13	2	3	16	34	31	2	1	17	12	10	2	1	18	9	7
6	3	15	8	8	6	0	16	8	9															

Table 3.12

Analyses of variance for β-parabutylchloral.

	GGG	UGG	GUG	UUG	GGU	UGU	GUU	UUU	ALL
N	228	162	165	179	174	149	192	168	1417
V	153	142	139	145	150	123	146	138	143

SIN THETA	0.00 -	.18 -	.23 -	.26 -	.29 -	.31 -	.33 -	.35 -	.36 -	.38 - .40
N	150	168	138	168	134	152	154	77	175	101
V	139	159	127	150	158	134	146	135	142	126

SURT(F/FMAX)	0.00 -	.21 -	.24 -	.27 -	.29 -	.32 -	.35 -	.39 -	.45 -	.54 - 1.00
N	147	139	169	129	144	130	139	141	144	135
V	155	149	154	142	154	145	157	147	113	97

ABS(H)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	79	146	163	145	152	125	140	108	110	77	76	47	39	10	0
V	147	148	156	126	133	146	145	135	155	143	151	121	145	97	0

ABS(K)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	96	183	187	171	163	153	133	113	92	68	42	16	0	0	0
V	149	135	132	151	163	146	141	135	128	134	142	178	0	0	0

ABS(L)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	104	110	113	117	110	107	99	98	93	83	80	69	64	53	117
V	174	135	137	142	129	150	149	138	149	134	142	149	127	121	147

Table 3.13

Hydrogen atom co-ordinates ($x10^4$) for β-parabutylchloral.

Atom	x/a	y/b	z/c
H(2)	1369(7)	-2362(8)	-1264(6)
H(22)	0147(7)	-0838(9)	-2646(6)
H(231)	-0294(8)	-1840(9)	-3808(7)
H(232)	-1353(8)	-1730(9)	-3227(7)
H(233)	-0766(8)	-3108(9)	-3359(7)
H(4)	2397(6)	-0654(7)	-0738(6)
H(42)	2153(7)	1770(8)	0381(6)
H(431)	3310(8)	3447(9)	0304(7)
H(432)	2207(8)	3682(9)	-0214(7)
H(433)	3347(8)	3424(9)	-0679(7)
H(6)	1734(7)	-2101(8)	0180(5)
H(62)	-0450(7)	-3386(8)	0696(6)
H(631)	-0697(9)	-4403(11)	1971(7)
H(632)	-1029(9)	-2904(11)	1875(7)
H(633)	0020(9)	-3302(11)	2414(7)

Table 3.14

Anisotropic temperature factors ($x10^3$ $Å^2$) for β-parabutylchloral.

Atom	U11	U22	U33	U23	U13	U12
CL(21)	045(1)	093(2)	073(2)	-016(2)	003(1)	-004(1)
CL(22)	119(2)	050(1)	059(2)	-005(1)	-001(2)	-039(2)
CL(23)	061(2)	145(3)	054(2)	-005(2)	003(1)	021(2)
CL(41)	056(1)	057(1)	044(1)	007(1)	014(1)	-007(1)
CL(42)	038(1)	058(1)	091(2)	007(1)	006(1)	009(1)
CL(43)	048(1)	055(1)	077(2)	004(1)	-013(1)	-005(1)
CL(61)	069(2)	062(2)	044(1)	002(1)	-018(1)	-011(1)
CL(62)	051(1)	054(1)	064(2)	004(1)	006(1)	015(1)
CL(63)	077(2)	044(1)	133(3)	019(2)	022(2)	015(1)

Table 3.15

Torsion angles (°) in β-parabutylchloral.

C(6) -- O(1) -- C(2) -- H(2)	64.0
C(6) -- O(1) -- C(2) -- O(3)	-56.6
C(6) -- O(1) -- C(2) -- C(21)	-173.7
C(2) -- O(1) -- C(6) -- O(5)	57.5
C(2) -- O(1) -- C(6) -- H(6)	-62.2
C(2) -- O(1) -- C(6) -- C(61)	176.1
O(1) -- C(2) -- O(3) -- C(4)	57.9
H(2) -- C(2) -- O(3) -- C(4)	-62.4
C(21) -- C(2) -- O(3) -- C(4)	175.9
O(1) -- C(2) -- C(21) -- C(22)	172.4
O(1) -- C(2) -- C(21) -- CL(21)	54.4
O(1) -- C(2) -- C(21) -- CL(22)	-63.4
H(2) -- C(2) -- C(21) -- C(22)	-67.0
H(2) -- C(2) -- C(21) -- CL(21)	175.0
H(2) -- C(2) -- C(21) -- CL(22)	57.2
O(3) -- C(2) -- C(21) -- C(22)	53.4
O(3) -- C(2) -- C(21) -- CL(21)	-64.6
O(3) -- C(2) -- C(21) -- CL(22)	177.6
C(2) -- O(3) -- C(4) -- H(4)	60.3
C(2) -- O(3) -- C(4) -- O(5)	-60.9
C(2) -- O(3) -- C(4) -- C(41)	-178.5
O(3) -- C(4) -- O(5) -- C(6)	62.4
H(4) -- C(4) -- O(5) -- C(6)	-59.2
C(41) -- C(4) -- O(5) -- C(6)	180.0
O(3) -- C(4) -- C(41) -- C(42)	171.1
O(3) -- C(4) -- C(41) -- CL(41)	-65.7
O(3) -- C(4) -- C(41) -- CL(42)	52.5
H(4) -- C(4) -- C(41) -- C(42)	-67.3
H(4) -- C(4) -- C(41) -- CL(41)	56.0
H(4) -- C(4) -- C(41) -- CL(42)	174.1
O(5) -- C(4) -- C(41) -- C(42)	53.5
O(5) -- C(4) -- C(41) -- CL(41)	176.7
O(5) -- C(4) -- C(41) -- CL(42)	-65.2
C(4) -- O(5) -- C(6) -- O(1)	-60.8
C(4) -- O(5) -- C(6) -- H(6)	62.7
C(4) -- O(5) -- C(6) -- C(61)	-176.0
O(1) -- C(6) -- C(61) -- C(62)	57.4
O(1) -- C(6) -- C(61) -- CL(61)	180.0
O(1) -- C(6) -- C(61) -- CL(62)	-62.2
O(5) -- C(6) -- C(61) -- C(62)	175.1
O(5) -- C(6) -- C(61) -- CL(61)	-62.7
O(5) -- C(6) -- C(61) -- CL(62)	55.6
H(6) -- C(6) -- C(61) -- C(62)	-65.8
H(6) -- C(6) -- C(61) -- CL(61)	56.4
H(6) -- C(6) -- C(61) -- CL(62)	174.6
C(2) -- C(21) -- C(22) -- H(22)	-68.2
C(2) -- C(21) -- C(22) -- C(23)	175.5
C(2) -- C(21) -- C(22) -- CL(23)	52.7
CL(21)-- C(21) -- C(22) -- H(22)	51.2
CL(21)-- C(21) -- C(22) -- C(23)	-65.1

continued/......

Table 3.15 (continued)

CL(21)-- C(21) -- C(22) -- CL(23)	172.1
CL(22)-- C(21) -- C(22) -- H(22)	170.3
CL(22)-- C(21) -- C(22) -- C(23)	54.0
CL(22)-- C(21) -- C(22) -- CL(23)	-68.8
C(21) -- C(22) -- C(23) -- H(231)	180.0
C(21) -- C(22) -- C(23) -- H(232)	62.9
C(21) -- C(22) -- C(23) -- H(233)	-61.2
H(22) -- C(22) -- C(23) -- H(231)	64.3
H(22) -- C(22) -- C(23) -- H(232)	-52.6
H(22) -- C(22) -- C(23) -- H(233)	-176.7
CL(23)-- C(22) -- C(23) -- H(231)	-56.6
CL(23)-- C(22) -- C(23) -- H(232)	-173.5
CL(23)-- C(22) -- C(23) -- H(233)	62.5
C(4) -- C(41) -- C(42) -- H(42)	-66.1
C(4) -- C(41) -- C(42) -- C(43)	178.0
C(4) -- C(41) -- C(42) -- CL(43)	54.3
CL(41)-- C(41) -- C(42) -- H(42)	173.2
CL(41)-- C(41) -- C(42) -- C(43)	57.4
CL(41)-- C(41) -- C(42) -- CL(43)	-66.3
CL(42)-- C(41) -- C(42) -- H(42)	54.2
CL(42)-- C(41) -- C(42) -- C(43)	-61.6
CL(42)-- C(41) -- C(42) -- CL(43)	174.7
C(41) -- C(42) -- C(43) -- H(431)	177.4
C(41) -- C(42) -- C(43) -- H(432)	60.6
C(41) -- C(42) -- C(43) -- H(433)	-60.8
H(42) -- C(42) -- C(43) -- H(431)	60.7
H(42) -- C(42) -- C(43) -- H(432)	-56.1
H(42) -- C(42) -- C(43) -- H(433)	-177.5
CL(43)-- C(42) -- C(43) -- H(431)	-59.1
CL(43)-- C(42) -- C(43) -- H(432)	-175.9
CL(43)-- C(42) -- C(43) -- H(433)	62.7
C(6) -- C(61) -- C(62) -- H(62)	-66.0
C(6) -- C(61) -- C(62) -- C(63)	176.7
C(6) -- C(61) -- C(62) -- CL(63)	54.5
CL(61)-- C(61) -- C(62) -- H(62)	174.2
CL(61)-- C(61) -- C(62) -- C(63)	56.8
CL(61)-- C(61) -- C(62) -- CL(63)	-65.4
CL(62)-- C(61) -- C(62) -- H(62)	55.0
CL(62)-- C(61) -- C(62) -- C(63)	-62.3
CL(62)-- C(61) -- C(62) -- CL(63)	175.4
C(61) -- C(62) -- C(63) -- H(631)	174.2
C(61) -- C(62) -- C(63) -- H(632)	59.1
C(61) -- C(62) -- C(63) -- H(633)	-57.0
H(62) -- C(62) -- C(63) -- H(631)	58.3
H(62) -- C(62) -- C(63) -- H(632)	-56.8
H(62) -- C(62) -- C(63) -- H(633)	-172.9
CL(63)-- C(62) -- C(63) -- H(631)	-62.5
CL(63)-- C(62) -- C(63) -- H(632)	-177.6
CL(63)-- C(62) -- C(63) -- H(633)	66.3

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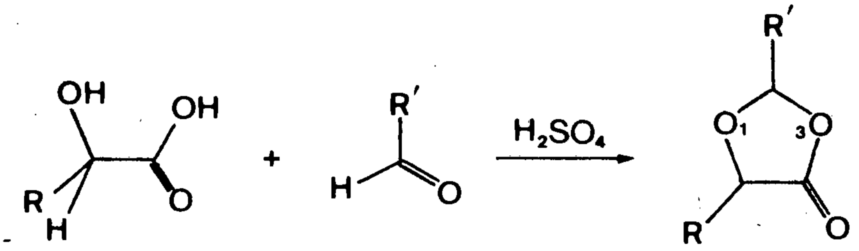
4.1 INTRODUCTION

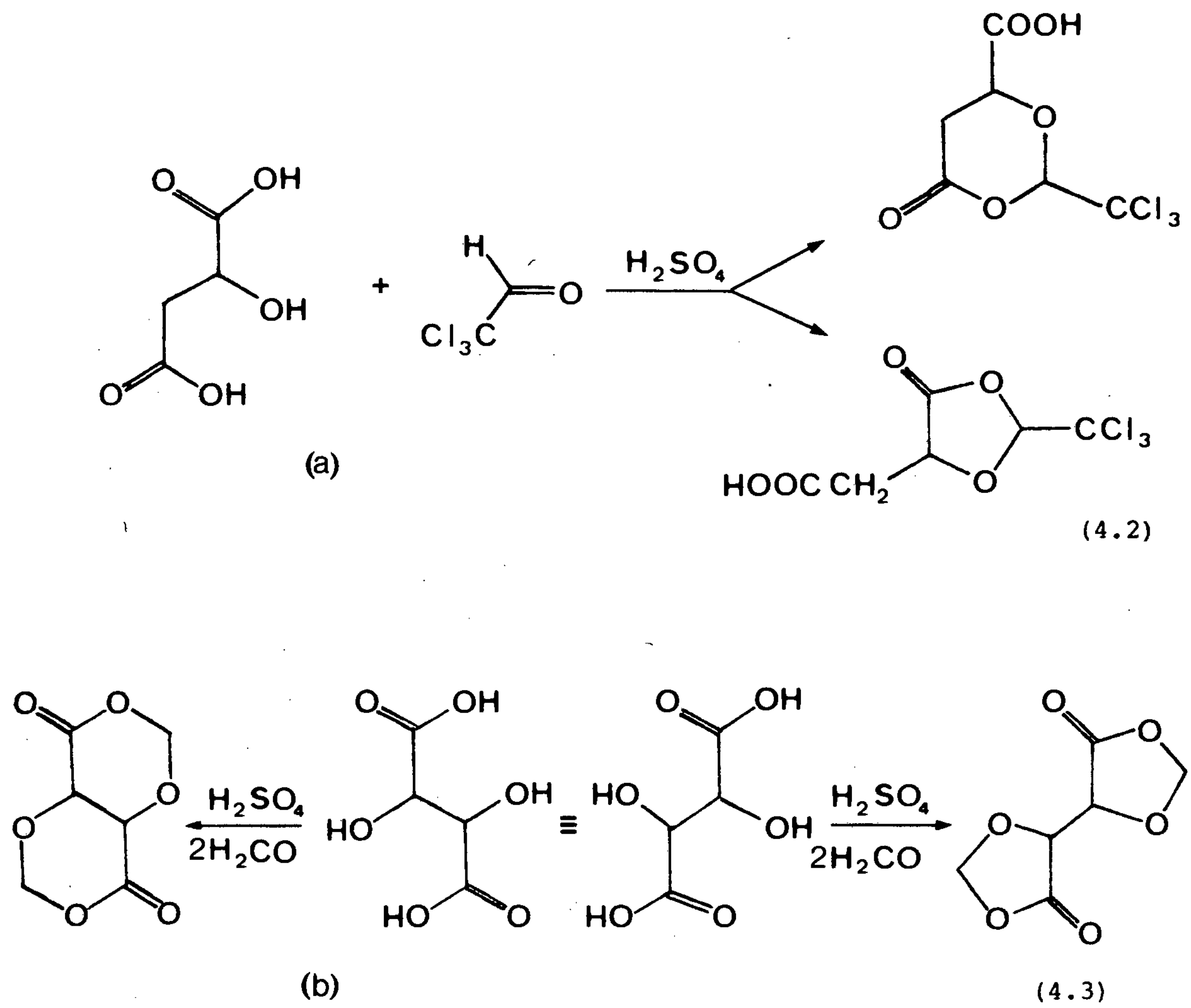
It was mentioned in Section 1.2 that chloralide (4.1), a five-membered heterocycle, is a co-product of the action of sulphuric acid on chloral hydrate. Chloralide was originally prepared by heating oleum and chloral hydrate (Städeler, 1847). Städeler's proposed cyclic structure was confirmed by Wallach (1878) who demonstrated its formation from chloral and trichlorolactic acid (Scheme 4.1). This remains a standard preparation for 1,3-dioxolan-4-ones and a great variety of these compounds have been so prepared, with lactic, malic, tartaric, citric, mandelic and benzilic acids (Shah and Alimchandani, 1934, 1936). Of course, any α-hydroxy acid and any aldehyde (or ketone) may be used. *p*-Toluenesulphonic acid, Girdler's catalyst and boron trifluoride have been used successfully in place of sulphuric acid, to catalyse the condensation of many 1,3-dioxolan-4-ones (Farines and Soulier, 1970). However, chloralide is unique in that it may be prepared from sulphuric acid and chloral alone, a reaction that involves the formation of a new carbon—carbon bond. The mechanism of this singular reaction is discussed in Section 4.5.

Malic acid is both an α- and a β-hydroxy acid and may therefore react with chloral in two possible ways (Scheme 4.2). However, it has been proved by an nmr study that the chloralide (4.2) is the sole product (Baron and Hollis, 1965). The condensation of tartaric acid with formaldehyde may also proceed by two possible pathways (Scheme 4.2). By an nmr and infrared study, the only product has been identified as the bisdioxolan-4-one (4.3) (Cort and Stewart, 1971). These examples point to the inherent stability in the 1,3-dioxolan-4-one ring system.



(4.1) R=R'=CCl$_3$

Scheme 4.1. Standard 2,5-disubstituted-1,3-dioxolan-4-one preparation.



Scheme 4.2. Alternative pathways for condensation reaction between (a) malic acid and (b) tartaric acid and an aldehyde.

Although the cyclic structure of chloralide was determined in the latter half of last century, modern physical techniques were required to establish its structural subtleties. A noteworthy investigation has been made, in which such problems as deviation of the ring from planarity, configuration, conformation and stereoisomerism have been discussed, in the light of infrared, nmr and dipole moment measurements (Chia and Huang, 1968). These subjects form the basis of the current discussion.

Two geometric isomers are expected in a 2,5-disubstituted-1,3-dioxolan-4-one; the *cis*-isomer with the 2,5-hydrogen atoms on the same side of the ring, and the *trans*-isomer. Since the ring has two chiral centres, each isomer is a racemic mixture of two enantiomers. In most cases, both isomers have been isolated, but in previous studies on chloralide, the *cis*-isomer has not been reported (Wallach, 1878; Otto, 1887; Baron and Hollis, 1965; Chia and Huang, 1968). Possible reasons for its illusive nature are discussed in Section 4.2.

4.2 PREPARATION OF CHLORALIDES

There are two important methods for preparing chloralide:

(i) by heating chloral hydrate in oleum, and

(ii) by condensing chloral and trichlorolactic acid.

Both methods have been investigated here in some depth.

In method (ii), the yield of *cis*- and *trans*-isomers, determined by ^{1}Hnmr, was found to depend on reaction temperature, as Figure 4.1 shows. At room temperature the yield of chloralide is very low but the *cis/trans* isomer ratio is almost unity. As the reaction temperature is raised,

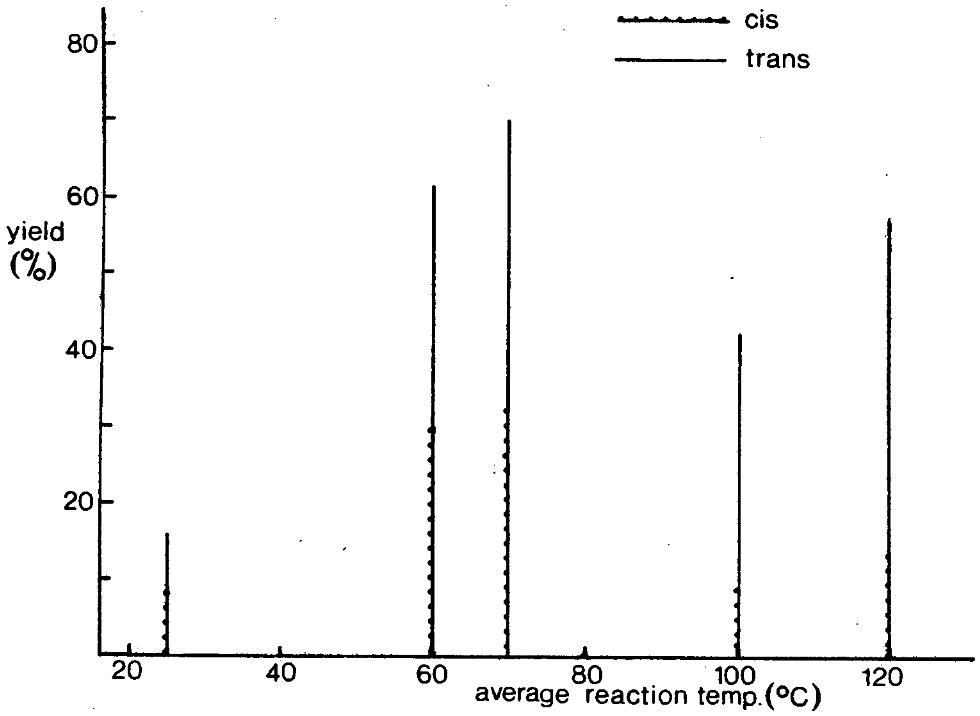
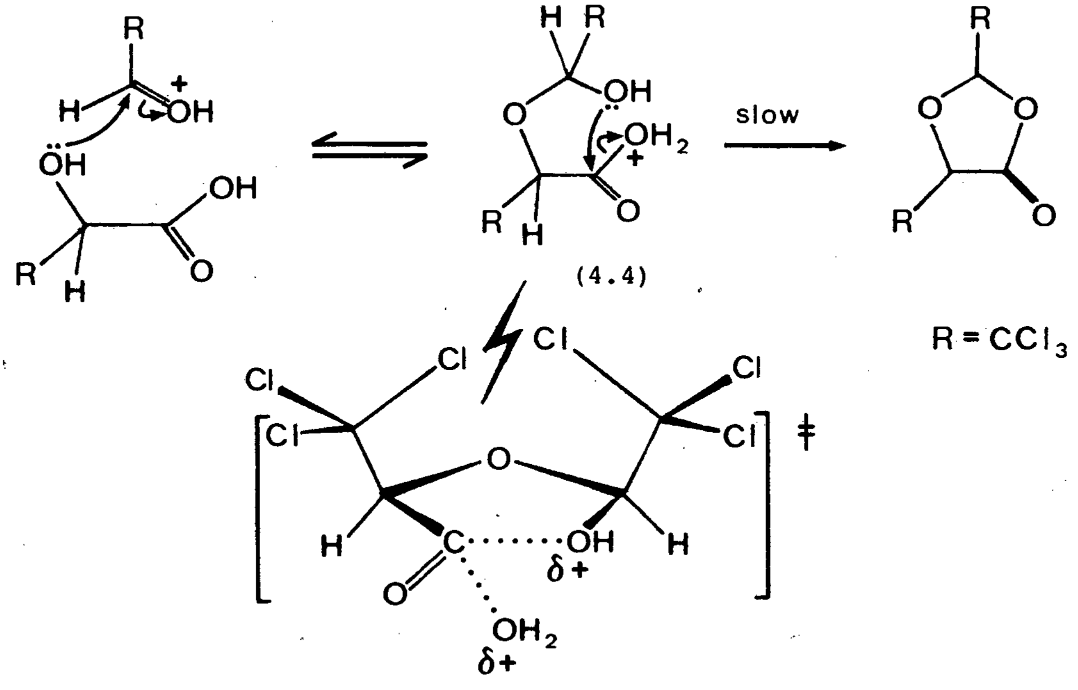


Figure 4.1. Dependence of chloralide yield on temperature.



Scheme 4.3. Formation of chloralide from chloral and trichlorolactic acid.

better yields of chloralide are obtained, but the *cis/trans* isomer ratio decreases. The optimum temperature is about 70°C. When prepared by method (i), only *trans*-chloralide is obtained. There are three possible reasons for this temperature dependence:

(a) Isomerisation of *cis*-chloralide into *trans*-chloralide occurs in hot concentrated sulphuric acid. This has been demonstrated and is discussed in Section 4.7. It is more than likely that at higher temperatures and sulphuric acid concentrations, isomerisation is more pronounced.

(b) Consider the mechanism described in Scheme 4.3. The rate of formation of intermediate (4.4) should be independent of the configuration at C2 and C5. Once this intermediate has been formed, the configuration of the product is determined. Models suggest that ring closure is less favourable for the *cis*-isomer because of steric interactions of *cis*-CCl_3 groups (4.5). Thus, a greater degree of reversion of (4.4) to starting materials is envisaged in the case of *cis*-geometry, and the *trans*-isomer should predominate in the product.

(c) It was noticed that the *cis*-isomer is more volatile than the *trans*-isomer. For example, when solvent is removed from a mixture of isomers, using a rotary evaporator, much *cis*-isomer is lost, especially at higher temperatures. The *cis*-isomer is also lost more readily than the *trans*-isomer by volatilisation from silica gel chromatographic plates. This preferential loss served to complicate further the already difficult chromatographic separation of isomers and could be partly responsible for the decrease in *cis/trans* ratio with temperature.

Although the isomers could be separated by silica gel chromatography, both contained a common impurity from which they could not be freed by further chromatography. Consequently, the pure *trans*-isomer was prepared by method (i), and the impurity was removed from the *cis*-isomer by fractional recrystallisation. The impurity later proved to be interesting (Section 4.7). The pure isomers were characterised by melting point and microanalysis (Section 4.8.1), nmr (Section 4.4) and mass spectrometry (Section 4.3).

4.3 MASS SPECTROMETRY

As with the trioxanes (Section 3.3) the molecular ion of chloralide was not observed until the electron beam energy was lowered to 11 eV. Mass spectra of *trans*-chloralide are shown in Figure 4.2 and a fragmentation pattern is suggested in Scheme 4.4. The low energy spectrum is complicated by overlapping peaks.

4.4 NMR SPECTROSCOPY

A 2,5-disubstituted-1,3-dioxolan-4-one has eight possible stereoisomers, (4.6a)-(4.9b); Figure 4.3 shows the molecules drawn in twist conformations and viewed down the carbonyl bond. (4.6a) and (4.6b) are enantiomers, as are the other a, b pairs. Any one of these isomers may undergo conformational inversion into its alternative twist form as Figure 4.3 shows. At ordinary temperatures, it is likely that conformational interchange occurs very rapidly in solution, so that conformers will be indistinguishable. Thus, at room temperature, only two different forms of these compounds are observable by nmr; the *trans*-isomer consisting of (4.8a), (4.8b), (4.9a) and (4.9b), and the *cis*-isomer consisting of the remaining forms.

The ^{1}Hnmr spectrum of the ring protons of a 2,5-disubstituted-1,3-dioxolan-4-one is relatively simple. A single isomer (and its enantiomer)

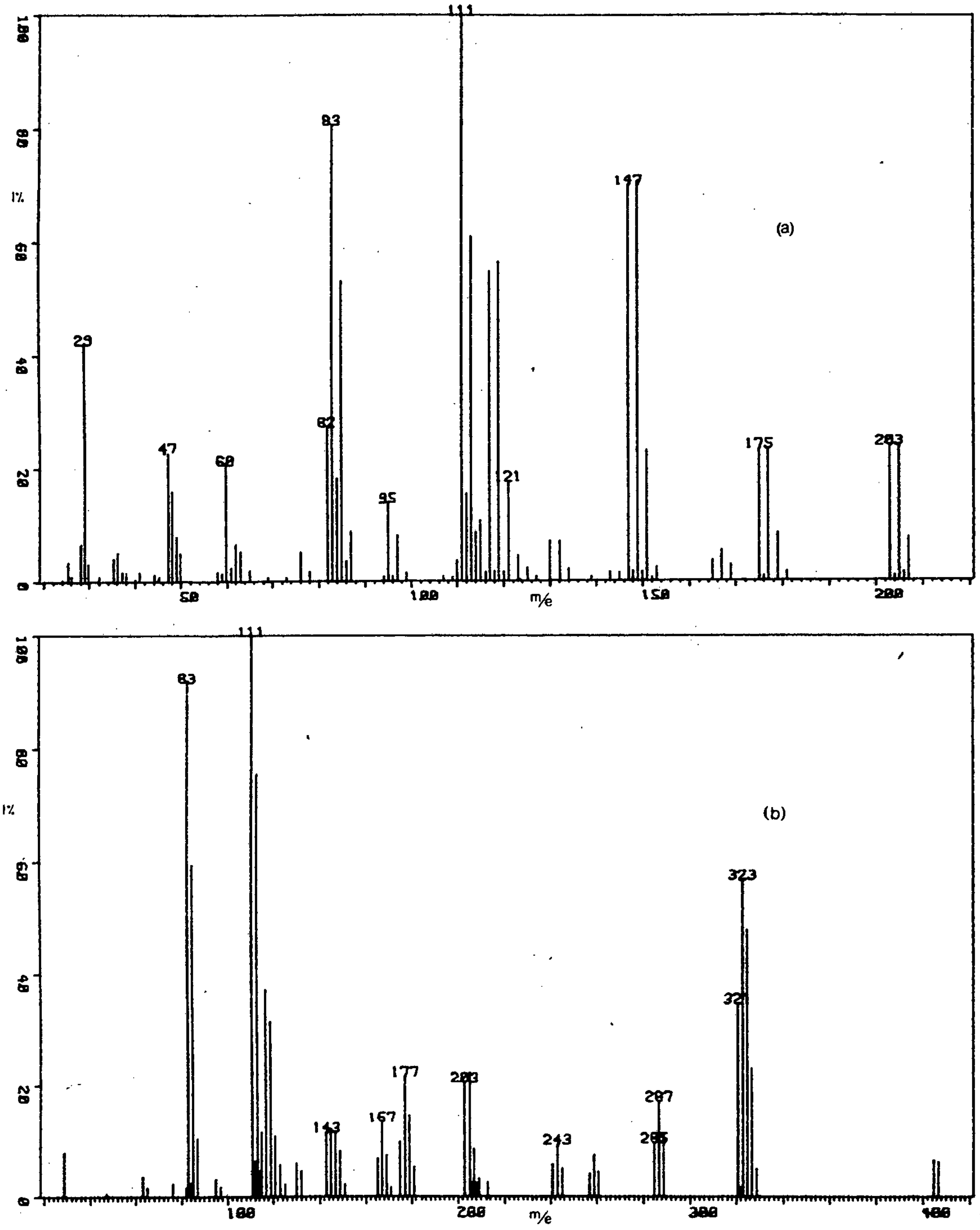
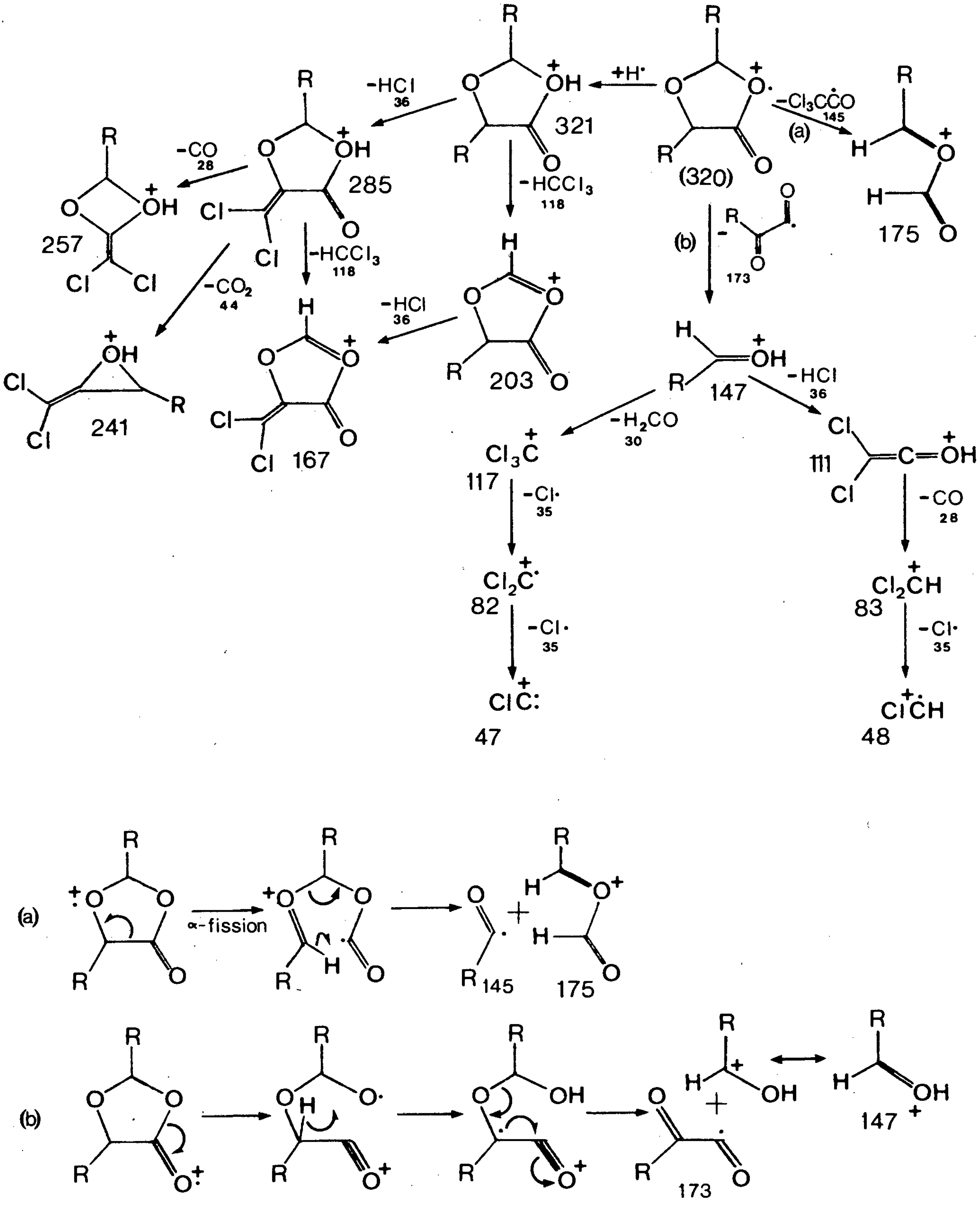


Figure 4.2. (a) 70 eV and (b) 11 eV mass spectra of trans-*chloralide.*



Scheme 4.4. Suggested mass spectral fragmentation pattern of trans-*chloralide.*

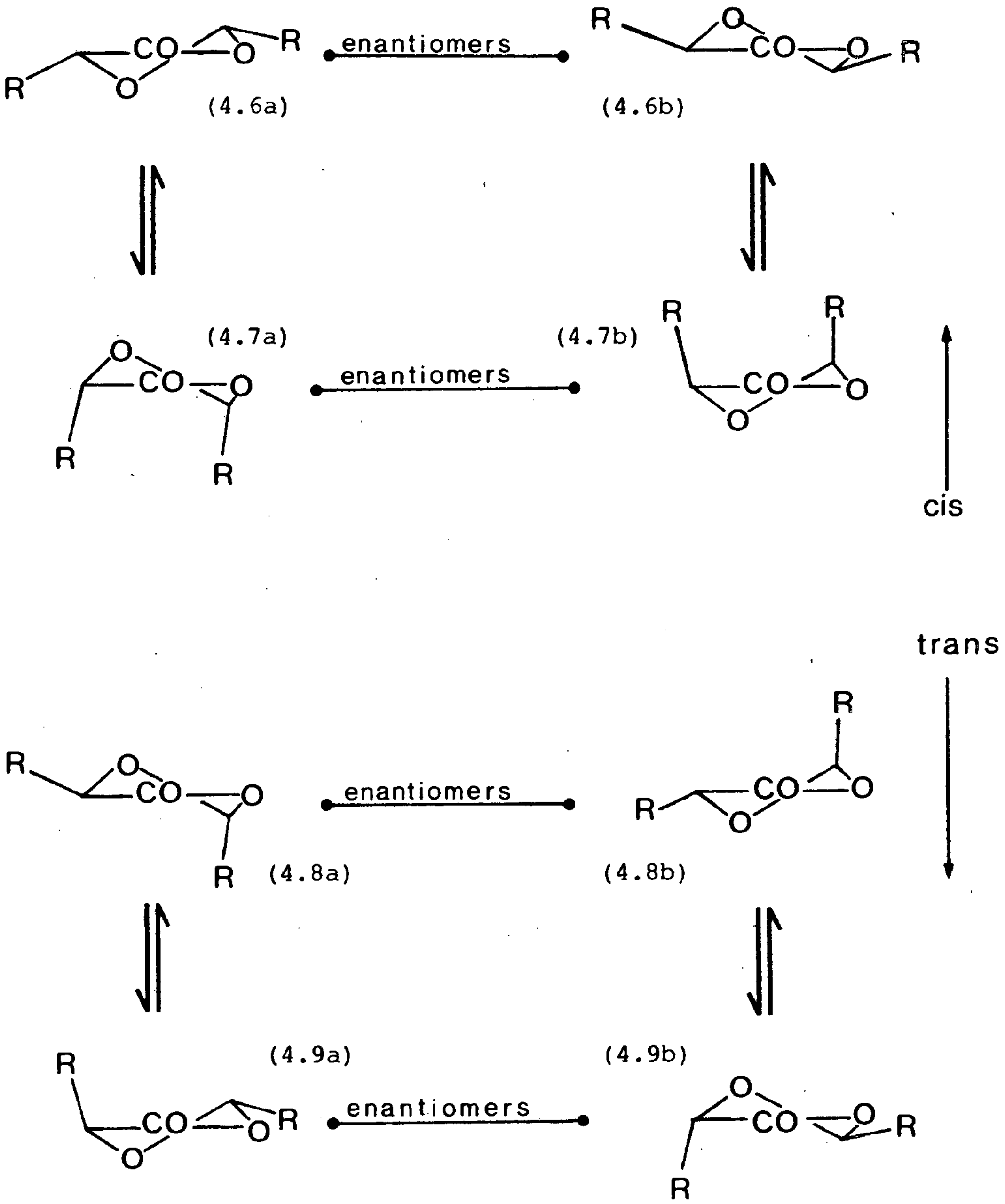


Figure 4.3. Possible stereoisomers of 2,5-disubstituted 1,3-dioxolan-4-ones.

gives a spectrum of two doublets, one from each proton. The splitting of the signals is due to long-range coupling between the protons. Of course, if a substituent carries a proton α to the ring, the spectrum is more complicated.

The ^{1}Hnmr spectra of a large number of these compounds have been reported in the literature, and three different empirical methods have emerged for distinguishing between their geometric isomers.

(i) The first method applies only to compounds whose substituents have far-reaching deshielding anisotropic effects, for example, phenyl rings and trihalomethyl groups. In such compounds, protons on the same side of the ring as the substituents tend to be deshielded. Thus, in the *trans*-isomers, the protons on both C2 and C5 are deshielded relative to the corresponding protons in the *cis*-isomers (Asabe *et al*., 1973, 1975; Brettle and Logan, 1973; Pilgram and Zupan, 1977).

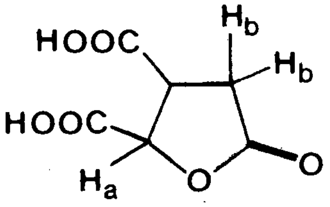
(ii) In compounds with one aryl substituent and one trihalomethyl substituent, steric interactions in *cis*-isomers force the aryl groups to orientate themselves so that the aromatic protons are in markedly different magnetic environments. In the *trans*-isomers however, chemical shifts of aromatic protons are closely grouped (Asabe *et al*., 1973, 1975; Cort and Stewart, 1971).

(iii) The third is the most generally applicable method. For all compounds observed so far, the magnitude of the long-range coupling constant J_{25} is greater in the *trans*- than in the *cis*-isomer (Asabe *et al*., 1973, 1975; Brettle and Logan, 1973).

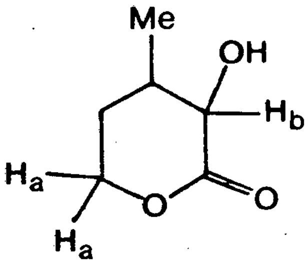
This method was used throughout the present work to distinguish between isomers of chloralide. The spectrum of *trans*-chloralide has been reported twice previously (Baron and Hollis, 1965; Chia and Huang, 1968) but, as mentioned, the *cis*-isomer has not been observed before. Figure 4.4 shows ^{1}Hnmr spectra of a mixture of *cis*- and *trans*-isomers. The spectra show the characteristic doublets of a 2,5-disubstituted-1,3-dioxolan-4-one. As with all such compounds, H2, lying between two oxygen atoms is more deshielded than H5, and $J_{25}(trans) > J_{25}(cis)$. Numerical chemical shift and coupling constant data is given in Table 4.1.

The spectrum of chloralide is strongly solvent-dependent (Figure 4.4), which is not surprising, remembering similar behaviour in parachloral (Section 2.6.3). The protons in chloralide are suitably "activated" to participate in hydrogen-bonding with a donor solvent. H5 is especially acidic being in an α-position to the carbonyl group. Thus, the proton chemical shifts depend upon solvent donor strength.

Although long-range coupling provides an unambiguous method for distinguishing between isomers of 2,5-disubstituted-1,3-dioxolan-4-ones, its appearance was at first a complete puzzle. In the first discussion of the matter, it was noted that such coupling is not observed in 1,3,5-trioxanes or 1,3,5,7-tetroxacanes (Baron and Hollis, 1965). Suspecting that the coupling may occur through the lactone function, the spectra of the lactones (4.10) and (4.11) were studied. However, no coupling is observed between protons H_a and H_b in these compounds. It



(4.10)



(4.11)

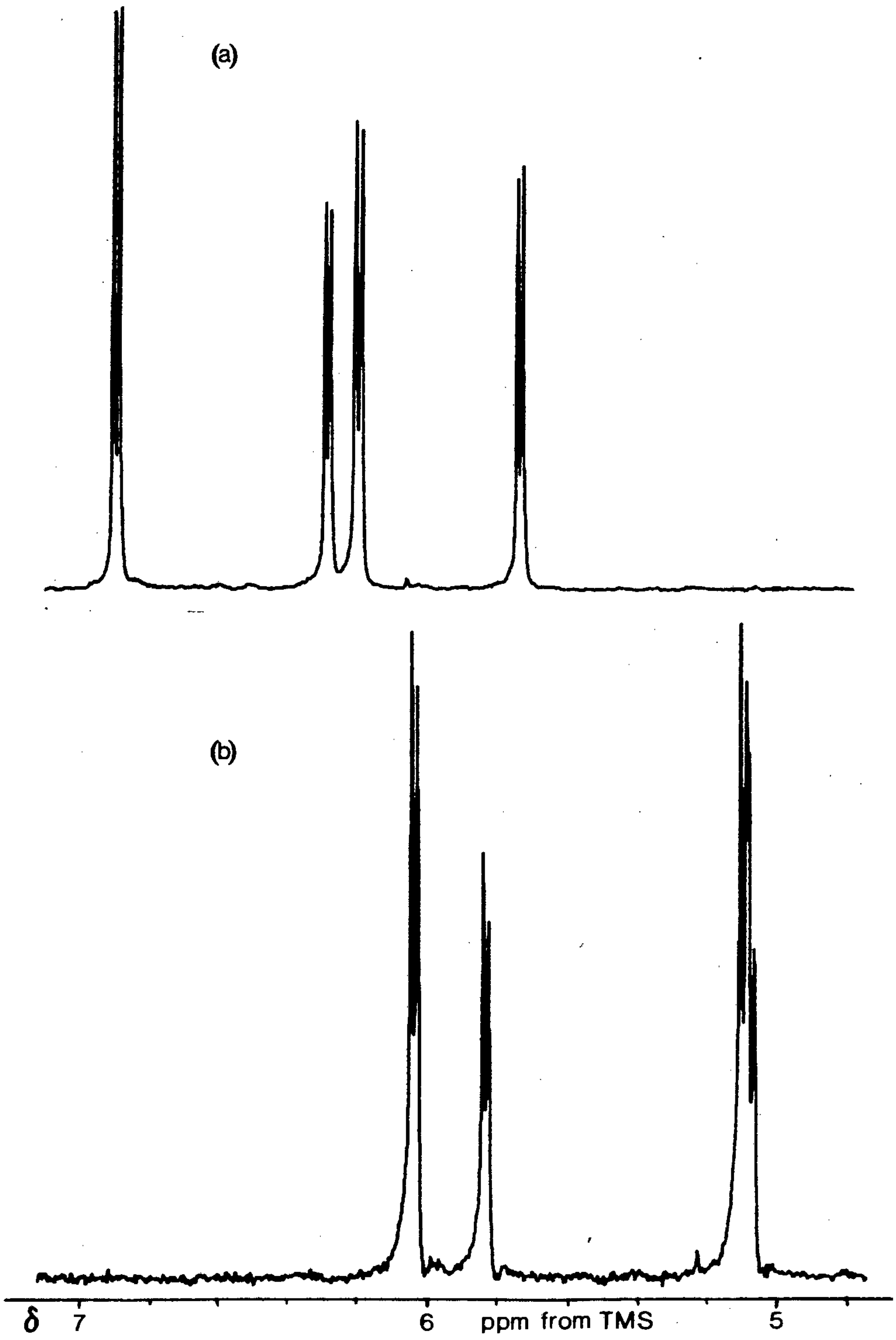


Figure 4.4. ^{1}*Hnmr spectrum of* cis- *and* trans-*chloralides in (a) DMSO-*d_6 *and (b)* $CDCl_3$.

Table 4.1

^1H *Chemical shifts (δ ppm) and coupling constants (Hz) for* cis- *and* trans-*chloralides in (a) DMSO*-d_6 *and (b)* $CDCl_3$.

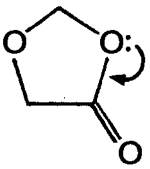
		H2	H5	J_{25}
(a)	*cis*	6.27	5.72	1.1
	trans	6.88	6.19	1.4
(b)	*cis*	5.86	5.10	1.1
	trans	6.07	5.13	1.4

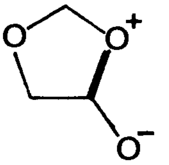
Table 4.2

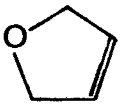
^{13}C *Chemical shifts (δ ppm from TMS) for* cis- *and* trans-*chloralides in* $CDCl_3$.

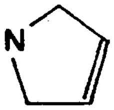
	C4	C2	C21	C51	C5
cis	161.3	102.3	94.4	92.3	83.9
trans	162.0	104.1	96.9	93.8	83.4

was concluded that the coupling must arise from the combination of structural features - ether and lactone - present in 1,3-dioxolan-4-ones. Asabe and co-workers (1975) consider 1,3-dioxolan-4-ones to be isoelectronic with 2,5-dihydrofurans (4.14) and 2,5-dihydropyrroles (4.15). In the 1,3-dioxolan-4-one ring, the lactone group contributes to ring planarity (4.13). In view of this proposed tendency, these authors


(4.12)


(4.13)


(4.14)


(4.15)

envisage a similar coupling mechanism in all three classes of compounds.

The ^{13}Cnmr spectrum of *trans*-chloralide is shown in Figure 4.5. The ring carbon atoms C2 and C5 are easily identifiable by their nuclear overhauser enhancement. C2, lying between the two ring oxygen atoms, probably resonates downfield from C5. Applying the same argument to the CCl$_3$ carbon atoms, C21 and C51, the assignments will be as given in Table 4.2. C4 is, of course, the most deshielded carbon atom. The ^{13}C spectrum of a mixture of the isomers is shown in Figure 4.5 and the assignments of signals from the *cis*-isomer are given in Table 4.2. This spectrum was measured in the presence of chromium acetylacetonate because of the slow relaxation times of C4, C21 and C51.

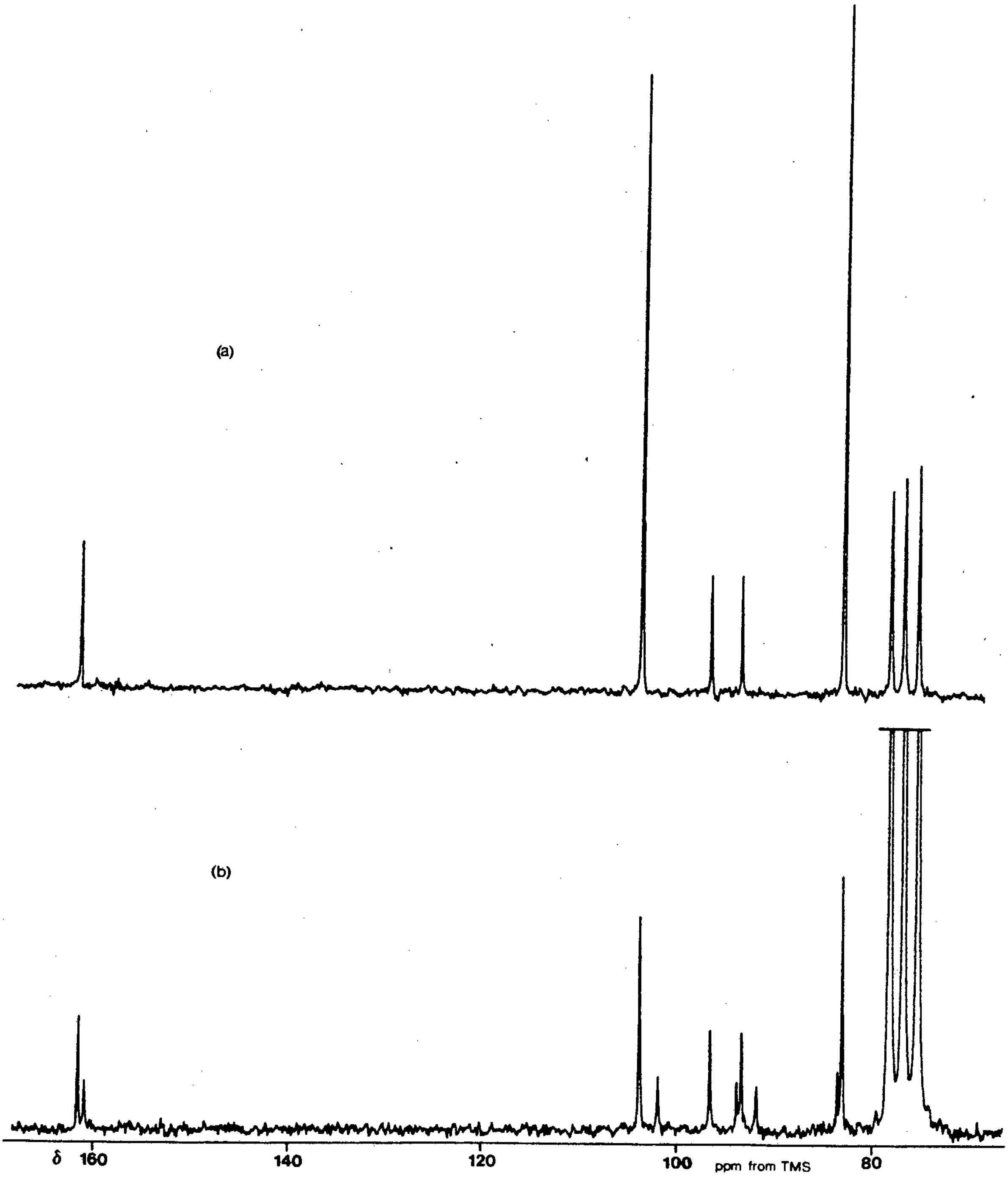


Figure 4.5. Broad band decoupled ^{13}*Cnmr spectra of (a) pure* trans-*chloralide and (b) a mixture of* cis- *and* trans-*chloralides in* $CDCl_3$.

4.5 MECHANISM OF CHLORALIDE FORMATION FROM CHLORAL HYDRATE AND OLEUM

It was mentioned in Section 4.1 that chloralide is the only 1,3-dioxolan-4-one which has been prepared from an aldehyde and sulphuric acid alone. The mysterious appearance of an endocyclic carbon—carbon bond during this reaction has now been investigated (Archer *et al*., 1984).

The possible occurrence of the sequence chloral → parachloral → chloralide has been ruled out. Samples of α-parachloral, β-parachloral and metachloral (Section 2.1) were heated with fuming sulphuric acid, and although carbon monoxide was freely evolved, no chloralide was detected on work-up in any case. Depolymerisation is known to occur when these substances are distilled (Chattaway and Kellett, 1928), but it appears that their decomposition in oleum to yield carbon monoxide and other products, must proceed faster than the necessary excess of free aldehyde can accumulate to permit the formation of chloralide.

The reaction between chloral hydrate and hot fuming sulphuric acid is accompanied by a copious evolution of gases among which hydrogen chloride, sulphur dioxide and trioxide, carbon monoxide and dioxide, phosgene and sulphuryl chloride have been identified (Böeseken, 1910). In order to determine their relative amounts, these exit gases were swept out from the reaction vessel by a stream of dry nitrogen, and after removing the acidic gases with aqueous alkali, carbon monoxide was determined by absorption in ammoniacal copper(I) chloride solution in an Orsat apparatus. Six successive experiments agreed that 0.54 mole of carbon monoxide was released per 1 mole of chloral hydrate.

This abundant evolution of carbon monoxide suggested that it might participate in the formation of chloralide. To investigate this possibility, carbon monoxide was passed continuously through the reaction mixture, or generated *in situ* by the dropwise introduction of formic acid. Although, in some experiments, there was an increase in the yield of chloralide relative to that in parallel condensations in which no additional carbon monoxide was made available, these experiments were found to be unsuitable. Firstly, the passage of gas through the non-homogeneous reaction mixture affects the reaction rate, and secondly, the dehydration of formic acid introduced during the course of a reaction diminishes the potency of the oleum. Thus, the yields cannot be compared with those of parallel experiments where no carbon monoxide was introduced.

However, when the reaction of chloral hydrate and oleum was carried out in two sealed containers, one containing also a known mass of sodium formate and the other an identical mass of a mixture of sodium formate and [^{13}C]-sodium formate, the chloralide isolated from the second container was found to have a very high ^{13}C content at C4. Figure 4.6 shows the ^{13}Cnmr spectra of the chloralide obtained in the two cases. Although the *trans*-isomer predominates in the product, some *cis*-chloralide is also formed. Intensity measurements show that the carbonyl groups in at least 40% of the product molecules were formed from [^{13}C]-carbon monoxide generated *in situ*.

During the formation of chloralide, carbon monoxide could be produced in two ways: (i) directly by disproportionation of chloral to give chloroform and carbon monoxide, or (ii) *via* the sequence chloral → chloroform → carbon monoxide, for the last stage is known to occur in fuming sulphuric acid (Mazurs, 1942).

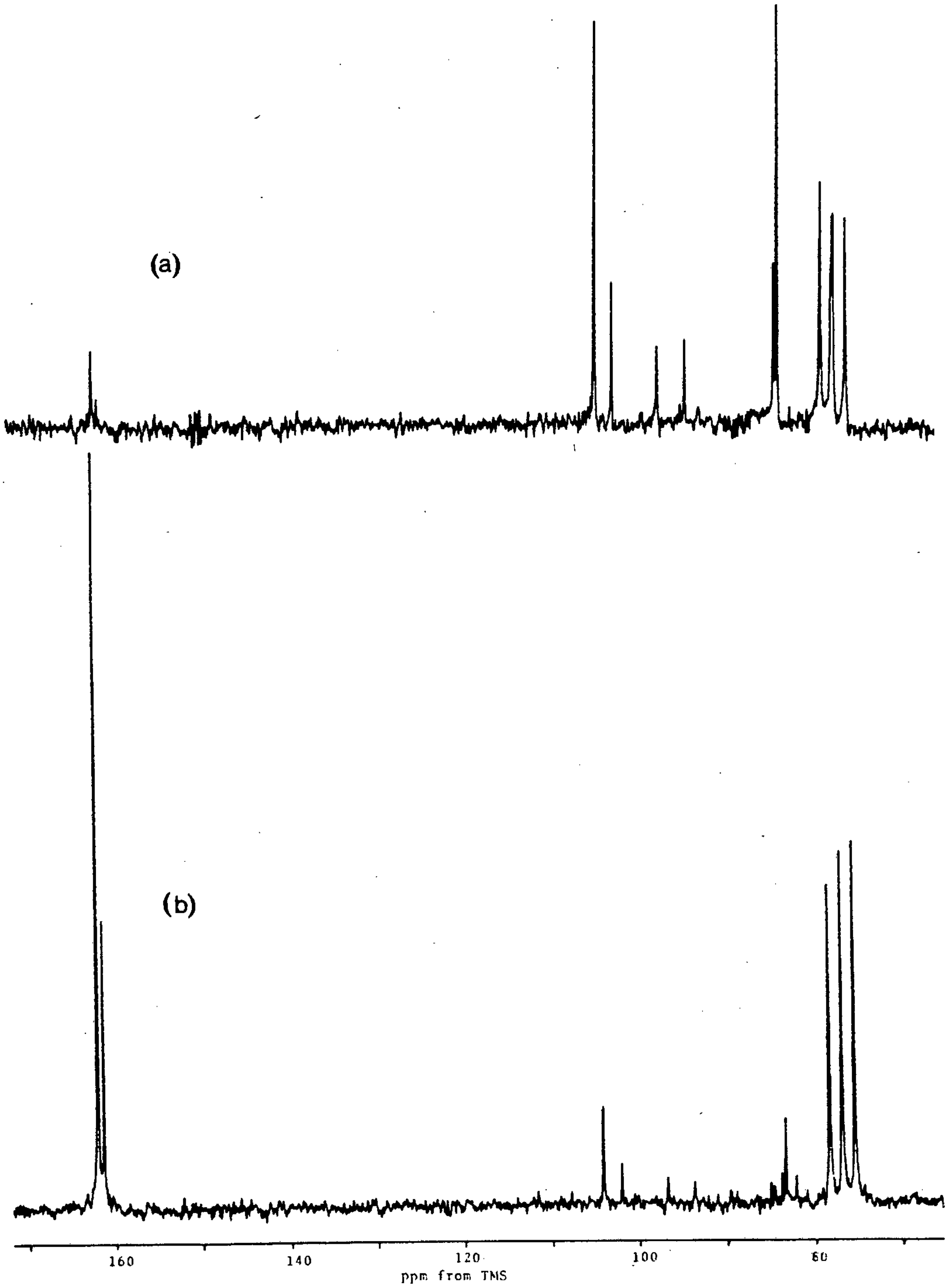


Figure 4.6. Broad band proton decoupled ^{13}Cnmr spectra of chloralides in $CDCl_3$: (a) product from reference reaction between chloral hydrate and sodium formate; (b) product from reaction between chloral hydrate and [^{13}C]-sodium formate.

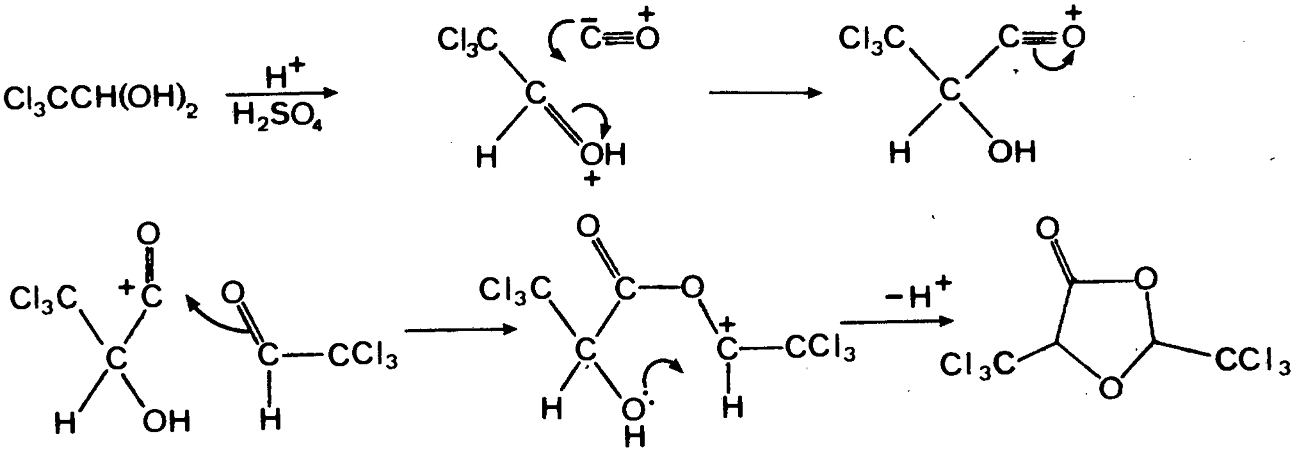
The proposed mechanism of formation of chloralide is shown in Scheme 4.5. The oleum used in the reaction contained about 40% free sulphur trioxide. It is possible that this powerful Lewis acid plays a significant catalytic part in chloralide formation as Scheme 4.6 suggests.

Although carbon monoxide is isoelectronic with the cyanide ion, its role as a nucleophile is less familiar. It is known to react with formaldehyde under conditions of high temperature and pressure, or in the presence of a catalyst, to give a product which yields glycolic acid on hydrolysis; here too a new carbon—carbon bond has been formed (Kuraishi, 1975; Suzuki, 1976, 1976; Hubbard *et al.*, 1971). Other examples of the nucleophilic behaviour of carbon monoxide are to be found in the Koch-Haaf reaction, Scheme 4.7 (Koch and Haaf, 1958, 1960). In a comparative study of the Koch-Haaf and Ritter reactions, Christol and Solladie (1966) showed that carbon monoxide is more reactive than its nitrile counterpart.

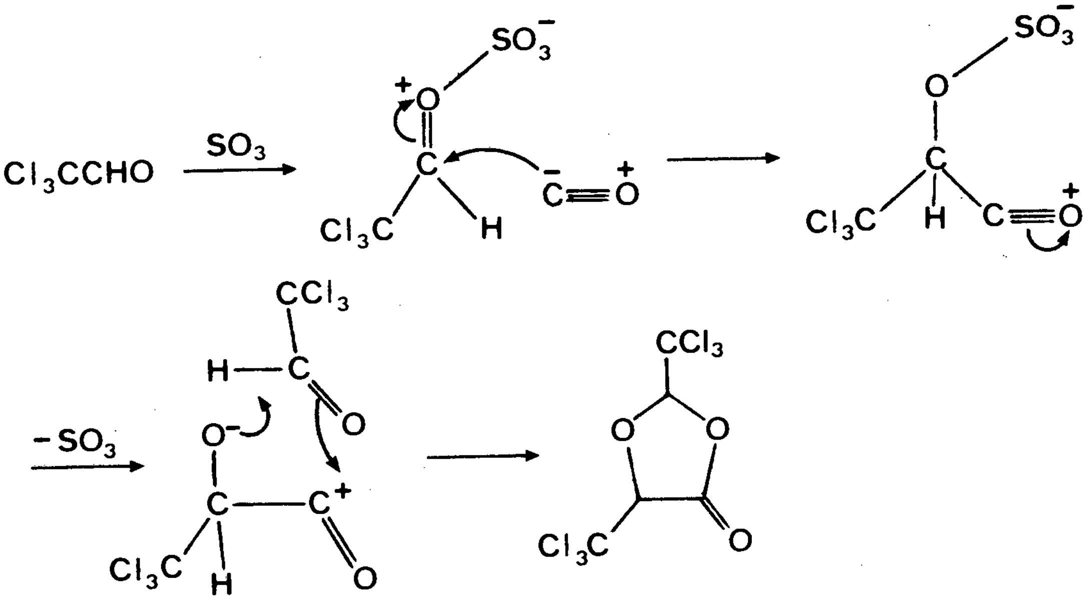
That carbon monoxide is so effective as a nucleophile in the present reactions must be largely due to the electron-withdrawing strength of the trichloromethyl group.

4.6 *CONFORMATION OF CHLORALIDES*

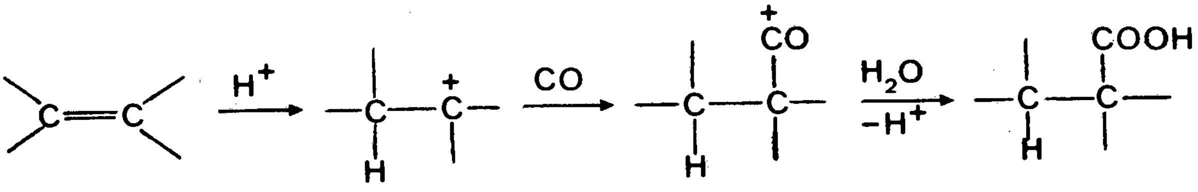
Cyclopentane could exist in planar form, effectively free from angle strain. However, this would give rise to five eclipsed ethane units, and it is well recognised that puckering of the ring occurs to reduce this torsional strain (Eliel *et al.*, 1967). The puckering is not fixed but rotates around the ring, so that the five methylene groups are in constant up-and-down motion. This phenomenon in five-membered rings is called pseudorotation. The nature of the puckering depends upon the



Scheme 4.5. Formation of chloralide with H^+ as catalyst.

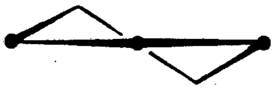


Scheme 4.6. Formation of chloralide with SO_3 as catalyst.



Scheme 4.7. The Koch-Haaf reaction.

substituents on the ring. There are various possible puckered forms, but two are particularly favoured as models because of their higher symmetry. These are the twist or half-chair (4.16) and the envelope forms (4.17), with C_2 and C_s symmetry respectively. Calculations on cyclopentane derivatives containing heteroatoms in the ring show some uncertainty about their conformations (Cremer and Pople, 1975), but both theory and experiment agree that cyclopentanone exists in the twist conformation, with maximum puckering occuring on the opposite side of the ring from the sp^2-hybridised carbon atom (Eliel *et al.*, 1967). This carbon atom is not seriously troubled by bond eclipsing, and it is therefore reasonable that puckering should occur mainly in other parts of the molecule.



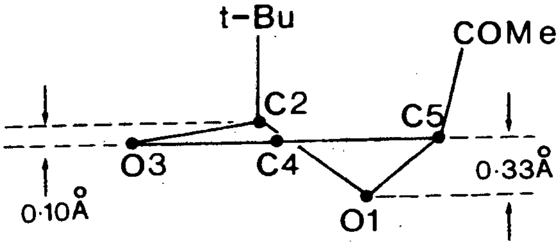
(4.16)

(4.17)

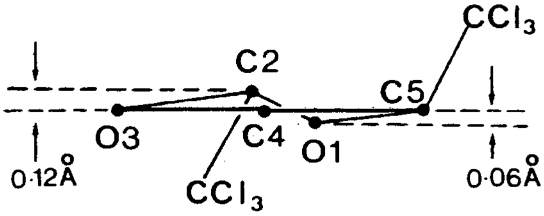
In the 1,3-dioxolan-4-one ring, some double bond character is expected in the C4—O3 bond (4.13). This would have the effect of forcing the atoms C2, O3, C4 and C5 into a more planar arrangement, leaving O1 with the greatest puckering. This corresponds, of course, to the O1-envelope conformation.

In most five-membered cyclic compounds, the more stable conformations are very close in energy, so their interconversion in solution is extremely rapid and cannot be observed even at very low temperatures (Lambert *et al.*, 1974). Dynamic nmr is therefore not a suitable technique for the conformational analysis of chloralide, so crystallographic evidence was sought.

It has been pointed out that *x*-ray crystallography is not as powerful an aid in the analysis of five-membered rings as it is in that of six-membered rings (Lambert *et al.*, 1974). Since the conformational possibilities in the former systems are varied and complex, the solid state structure is not necessarily a good reflection of the situation in solution. Nevertheless, the two 1,3-dioxolan-4-one structures which have been determined have proved enlightening. Gabrielsen (1975) has shown that the ring of (2S,5S)-2-t-butyl-5-carboxymethyl-1,3-dioxolan-4-one adopts a near perfect O1-envelope conformation as expected for compounds of this type. More precisely, C2 lies 0.1 Å "above" the plane defined by the carbonyl fragment, while O1 lies more than 0.3 Å "below" that plane (4.18). Thus, the conformation is not a pure envelope, but possesses some twist character. The conformation allows both bulky substituents to occupy pseudoequatorial positions.



(4.18)



(4.19)

The crystal structure of *trans*-chloralide was determined during the course of this research. After completion of the work, it was found that its crystal structure had been published by other workers a few months earlier (Hashimoto *et al.*, 1980). These earlier results compare favourably with those reported here. Figure 4.7 shows the molecular structure of *trans*-chloralide in the solid state. Bond lengths and angles and principal torsion angles are given in Figure 4.8, and Table 4.3 gives the deviations of ring atoms from two least-squares ring planes.

Although the related molecule (4.18) chooses an O1-envelope conformation in the solid state, the *trans*-chloralide ring is very nearly planar. In (4.18) O1 lies more than three times further from the carbonyl plane than does C2, but in chloralide the difference between these deviations, which are themselves small, is not so significant (4.19).

Two canonical forms (4.12) and (4.13) may be drawn for the 1,3-dioxolan-4-one ring. In both (4.18) and *trans*-chloralide, the bond C4—O3 is significantly shorter than the other endocyclic C—O bonds, indicating some contribution from (4.13). As mentioned earlier, appreciable double-bond character in C4—O3 is expected to bring C2 into the carbonyl plane and thereby restrict ring puckering to O1 giving rise to the O1-envelope conformation. Nonetheless, although a shorter lactone C—O bond *is* observed in chloralide the expected conformation is not.

The operation of two forces seems to determine the conformation of these rings. The first is this tendency towards coplanarity of the atoms C2—O3—C4—C5. The second is the trans-annular repulsion between substituents (including H) situated *cis* to each other on the ring. In the *cis* compound (4.18), both forces acting together, result in an envelope conformation, which allows the bulky substituents to be as far apart as possible (the H—H interaction on the other side of the ring offers little resistance) and the atoms C2—O3—C4—C5 to be coplanar. However, in *trans*-chloralide, these forces are in opposition and

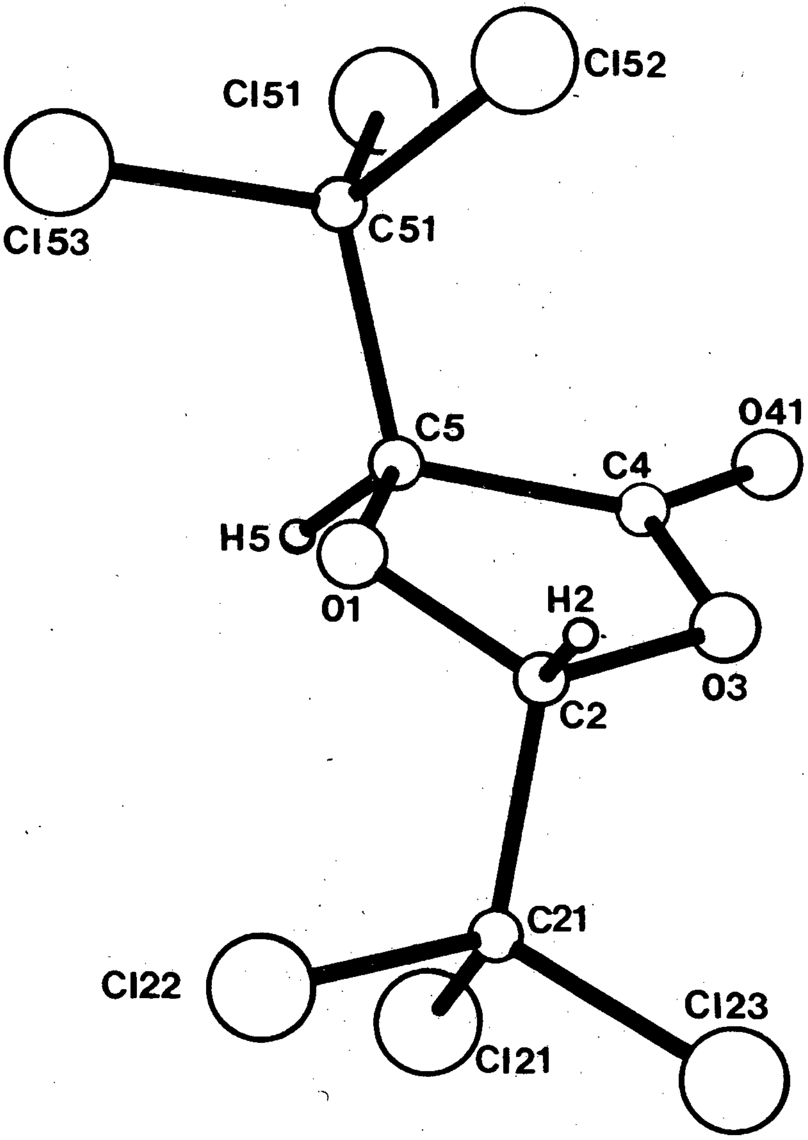


Figure 4.7. Molecular structure of trans*-chloralide.*

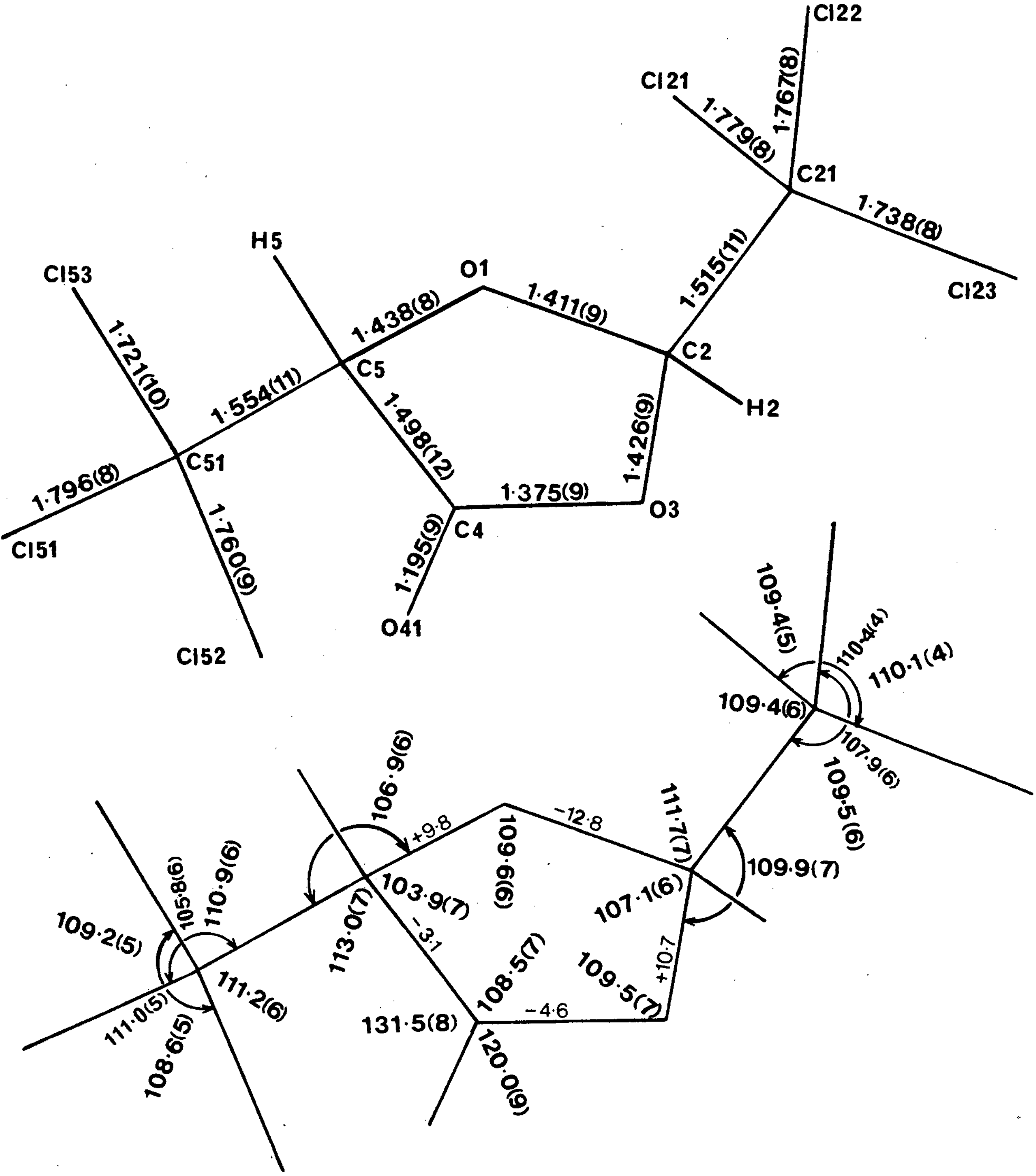


Figure 4.8. Bond lengths (Å), bond angles (°) and principal torsion angles (°) in trans*-chloralide.*

Table 4.3

Deviations (Å) of atoms from least-squares ring planes in trans-*chloralide.*

Plane 1; O3—C4—(O41)—C5		Plane 2; O1—C2—O3—C4—C5	
Atom	Deviation	Atom	Deviation
O1	0.058	O1	0.066
C2	-0.124	C2	-0.068
O3	-0.002	O3	0.043
C4	0.007	C4	-0.003
C5	-0.002	C5	-0.038
O41	-0.003	O41	-0.031

trans-annular interactions between H atoms and CCl_3 groups on the same side of the ring forbid the O1-envelope conformation.

It has long been known that carbonyl groups incorporated in five-membered rings show higher stretching frequencies (νCO) than their acyclic analogues. In fact, νCO depends upon ring size, and increases in the order acyclic < 7-ring < 6-ring < 5-ring. According to one interpretation, this phenomenon is caused by coupling effects and not by any change in the force constant of the carbonyl bond, while another holds that ring contraction does bring about a shortening of the bond (Bellamy, 1980).

The carbonyl bond in *trans*-chloralide is much shorter than a typical ester carbon—oxygen double bond. Only a few γ-lactones have been studied by *x*-ray crystallography (Cheng *et al.*, 1971; Glusker *et al.*, 1973) but they all display the same lactone geometry as chloralide; a short C=O bond, a short C—O bond, O=C—O angle ≈ 120°, O=C—C > 120° and O—C—C < 120°. The mean lactone geometry obtained from these structures is shown in Figure 4.9. This pattern of bond angles around the carbonyl carbon atoms is of interest. The endocyclic O—C—C angle is less than 120° due to ring constraints. Perhaps the O=C—O angle remains at 120° to preserve the stabilisation arising from delocalisation of π-electrons over both C—O bonds. The shortening of the endocyclic C—O bond supports this.

Figure 4.10 shows the crystal structure of *trans*-chloralide viewed down the x-axis. The molecular conformation is apparently determined by intramolecular forces only; there is no evidence of significant intermolecular interactions.

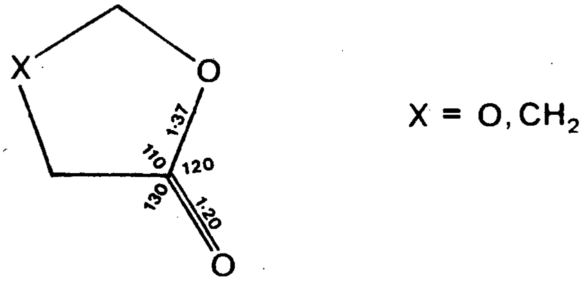
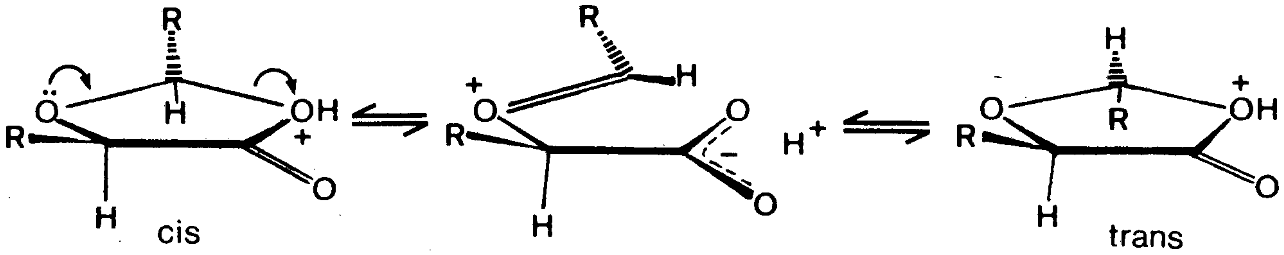


Figure 4.9. Average γ-lactone geometry (Å and °).



Scheme 4.8. Isomerisation of chloralide.

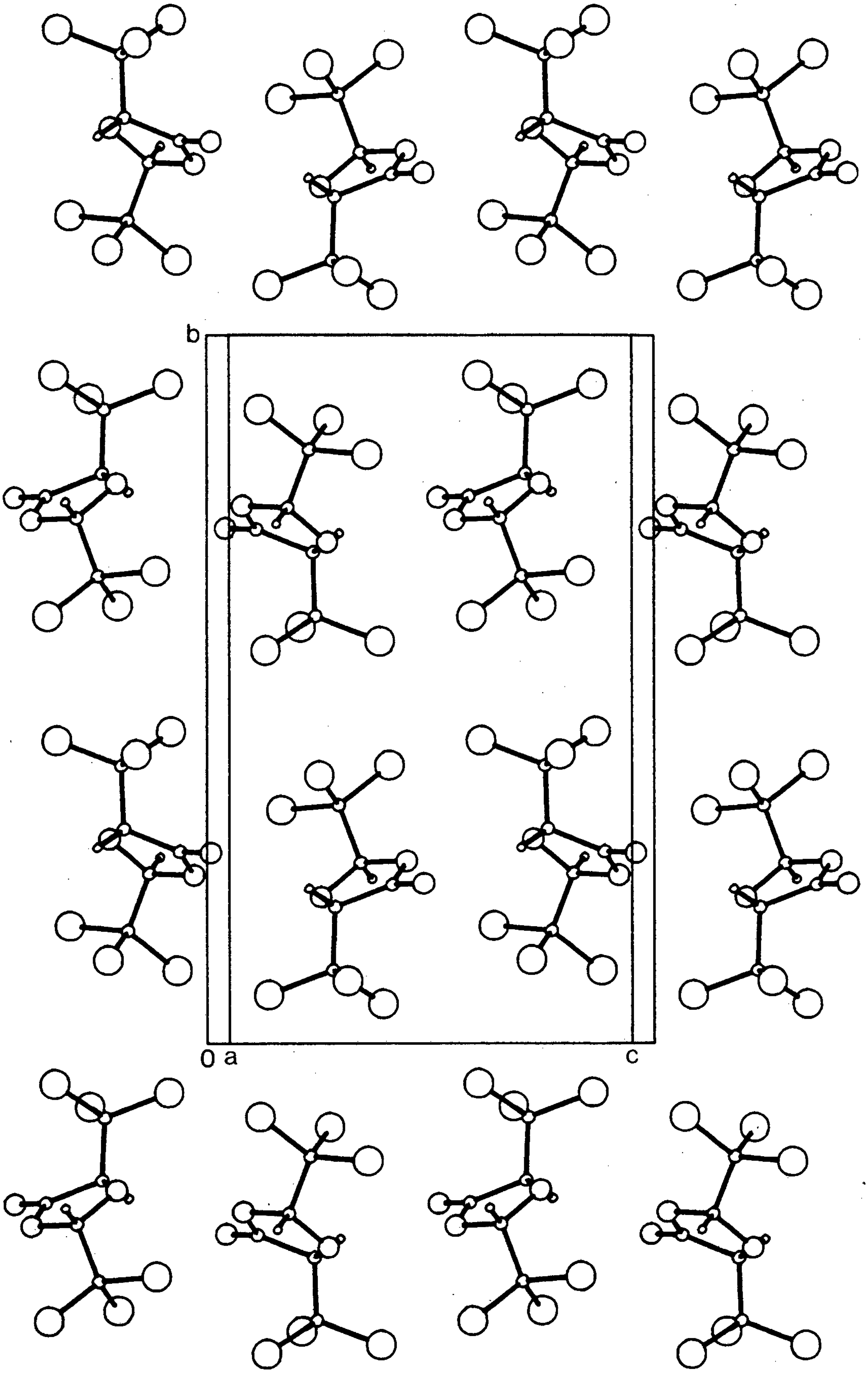


Figure 4.10. Crystal structure of trans-chloralide viewed down the x-axis.

4.7 *ISOMERISATION AND DEHYDROHALOGENATION OF CHLORALIDE*

One proposed reason for the observed decrease in *cis/trans* ratio with increasing temperature in the preparation of chloralide, is *cis-trans* isomerisation (Section 4.2). This process has now been shown to occur in hot sulphuric acid. A mixture of *cis-* and *trans*-chloralides were heated in an oven at 80°C with concentrated sulphuric acid in a sealed glass tube. After 5 hours the chloralide was isolated and its ^{1}Hnmr spectrum measured. As Figure 4.11 shows, under these conditions, considerable conversion of *cis*-chloralide into *trans*-chloralide occurs. Isomerisation is thought to proceed *via* the mechanism shown in Scheme 4.8. It is likely that transannular interactions between trichloromethyl groups destablise the *cis*-isomer relative to the *trans*-isomer.

The isomerism of some 2,5-dialkyl-1,3-dioxolan-4-ones has been discussed (Salomaa and Sallinen, 1965). It was found that isomers could not be separated by fractionation. Furthermore, the products behaved as single compounds in gas-liquid chromatography. However, subsequent kinetic measurements showed two isomers present in each case. Apparently, at temperatures near the boiling point, isomerisation occurs. The lower boiling isomer is preferentially removed from the equilibrium mixture whilst equilibrium is constantly re-established in the remaining liquid due to facile interconversion of isomers. Thus, the compounds behave as single isomers in glc and fractionating columns.

This same phenomenon was observed more recently when a study of the isomerisation of the chloralide derived from S-(+)-lactic acid was attempted (Baron, 1972). Although experimental details are very unclear, when a pure sample of one isomer was sealed in a glass tube and heated at

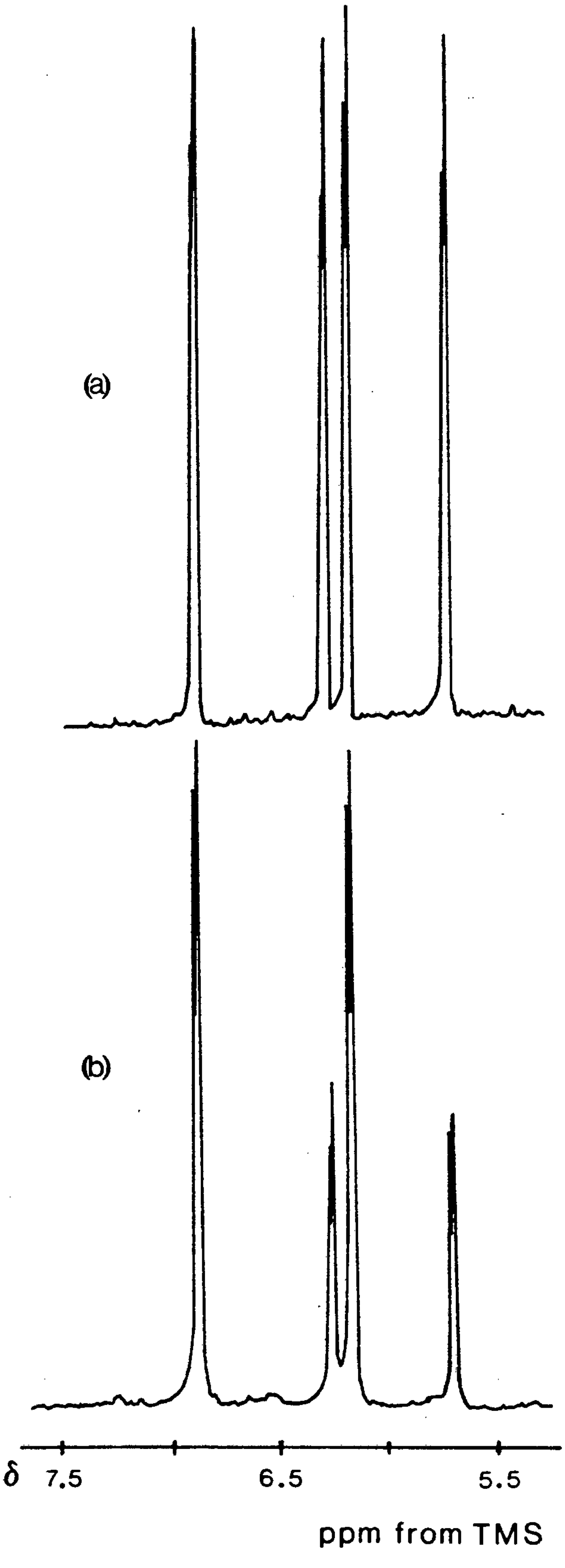
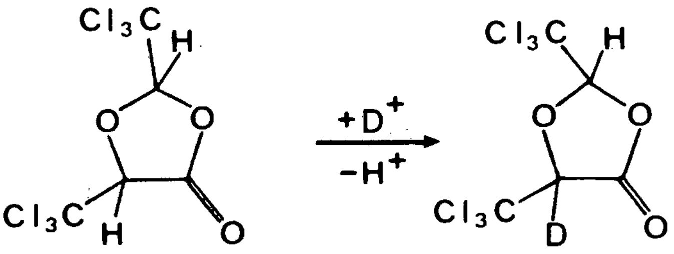


Figure 4.11. Isomerisation of chloralide. (a) A 1:1 mixture of cis- *and* trans-*chloralides. (b) Same mixture after 5 h at 80°C in concentrated H_2SO_4.*

200°C for 2 hours, isomerisation was seen to occur. In the present research however, no isomerisation was found to take place in molten chloralide up to 200°C.

An attempt was made to detect isomerisation under milder conditions. When a mixture of chloralides in dimethylsulphoxide-d_6 was kept at 80°C in the presence of a catalytic amount of sulphuric acid-d_2, isomerisation appeared to take place to some extent, together with the appearance of a signal at δ 6.74 ppm (from DSS). This signal increased with time at 80°C (Figure 4.12) and was found to be considerably temperature-dependent; when the reaction mixture was cooled to room temperature, it shifted to δ 6.66 ppm. On closer examination it was found that although the concentration of *cis*-isomer had decreased with time, that of the *trans*-isomer had hardly changed. When the same experiment was carried out with pure *cis*-chloralide at 100°C, no *trans*-chloralide appeared, but the signal at δ 6.68 ppm (from DSS) increased as the *cis*-isomer disappeared (Figure 4.13). Under the same conditions, pure *trans*-chloralide yields the same product, but at a much slower rate.

Deuterium exchange of the acidic proton H5, resulting in the product (4.20), was at first thought to be responsible for these observations.



(4.20)

Figure 4.12. Decomposition of chloralide as a function of time (min) in D_2SO_4*/DMSO-*d_6 *at 80°C.*

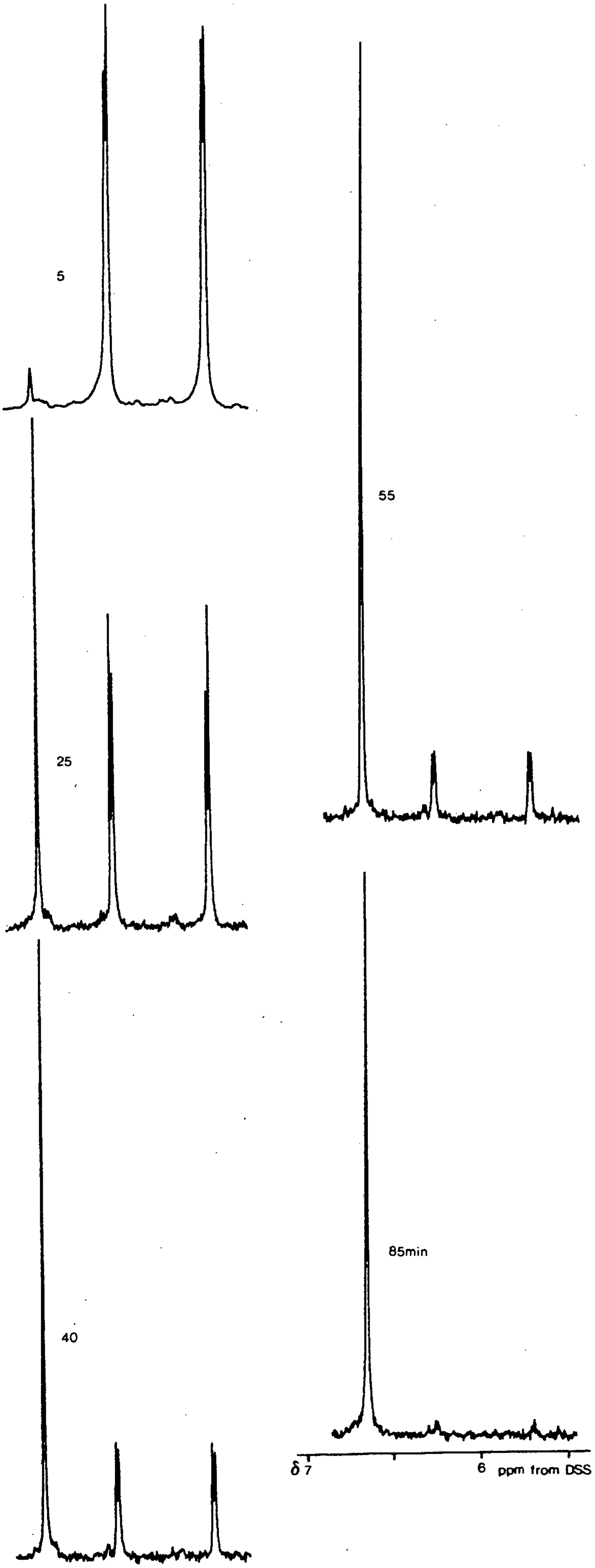
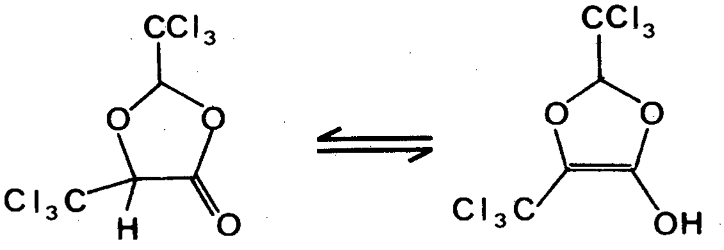


Figure 4.13. Decomposition of cis-chloralide as a function of time (min) in D_2SO_4/DMSO-d_6 at 100°C.

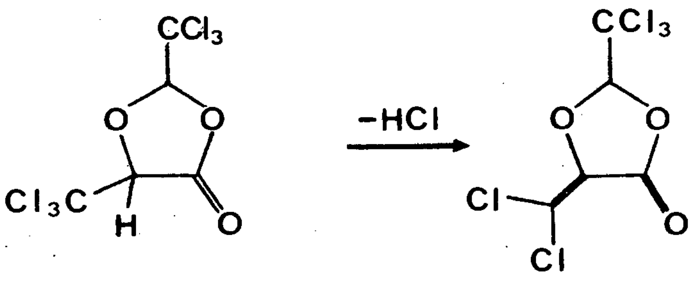
The signal of the decomposition product is very close to that of H2 in chloralide so the removal of H5 is a reasonable postulate. However, when the experiment was carried out with undeuterated sulphuric acid and undeuterated solvent, the result was still the same.

Acid catalysed keto-enol tautomerism was the second proposal for the decomposition of chloralide. The enol form of chloralide (4.21) would give rise to a ring proton signal in the region of that from H2 in chloralide. However, the necessary hydroxyl proton was not evident in the nmr spectrum and although a C=C bond was detected by infrared spectroscopy, an O–H bond was not.



(4.21)

A pure sample of the unidentified product was obtained, and its mass spectrum was the key to its identity. Its molecular ion has a mass of 284 and contains five chlorine atoms. The compound (4.22) fits this description perfectly, and is the product of loss of HCl across an



(4.22)

exocyclic carbon–carbon bond in chloralide. By repeating the experiment without acid present, the process was shown to result from the base action of dimethylsulphoxide. The identity of the product was verified by microanalysis. It is understandable that both isomers of chloralide give rise to the same dehydrochlorination product.

This interesting diversion unexpectedly connects with the problem of separating *cis*- and *trans*-isomers by chromatography. It was mentioned in Section 4.2 that the preparation of chloralide by the condensation of chloral and trichlorolactic acid, seems to produce an impurity from which the isomers are not readily separable by silica gel chromatography. Thin-layer chromatography of the crude condensation product *A* indicated a three-component mixture as depicted in Figure 4.14. Subsequent column chromatography yielded three distinct fractions, *B*, *C* and *D*, with the component *b* contained in all. Their ^{1}Hnmr spectra in chloroform-*d* and dimethylsulphoxide-d_6 (Figure 4.14) show that fractions *B* and *D* consist mainly of *trans*- and *cis*-chloralide (*a* and *c*) respectively, each also containing a small amount of impurity. Further chromatography of fraction *D* allowed the isolation of a small amount of *b*, and its ^{1}Hnmr spectrum (Figure 4.14) was shown to consist of but one signal (δ 6.04 ppm in $CDCl_3$ and δ 6.78 ppm from TMS in DMSO-d_6). In chloroform-*d*, this single signal is fortuitously coincident with the low-field doublet of *trans*-chloralide. Further chromatography failed to isolate pure *c* or to separate *a* from *b*.

A series of experiments revealed that both *cis*- and *trans*-chloralides decompose on silica gel to give the compound *b*, which is not a by-product of the condensation reaction as was originally thought. Firstly, a sample of pure *trans*-chloralide (Section 4.2) was chromatographed as a

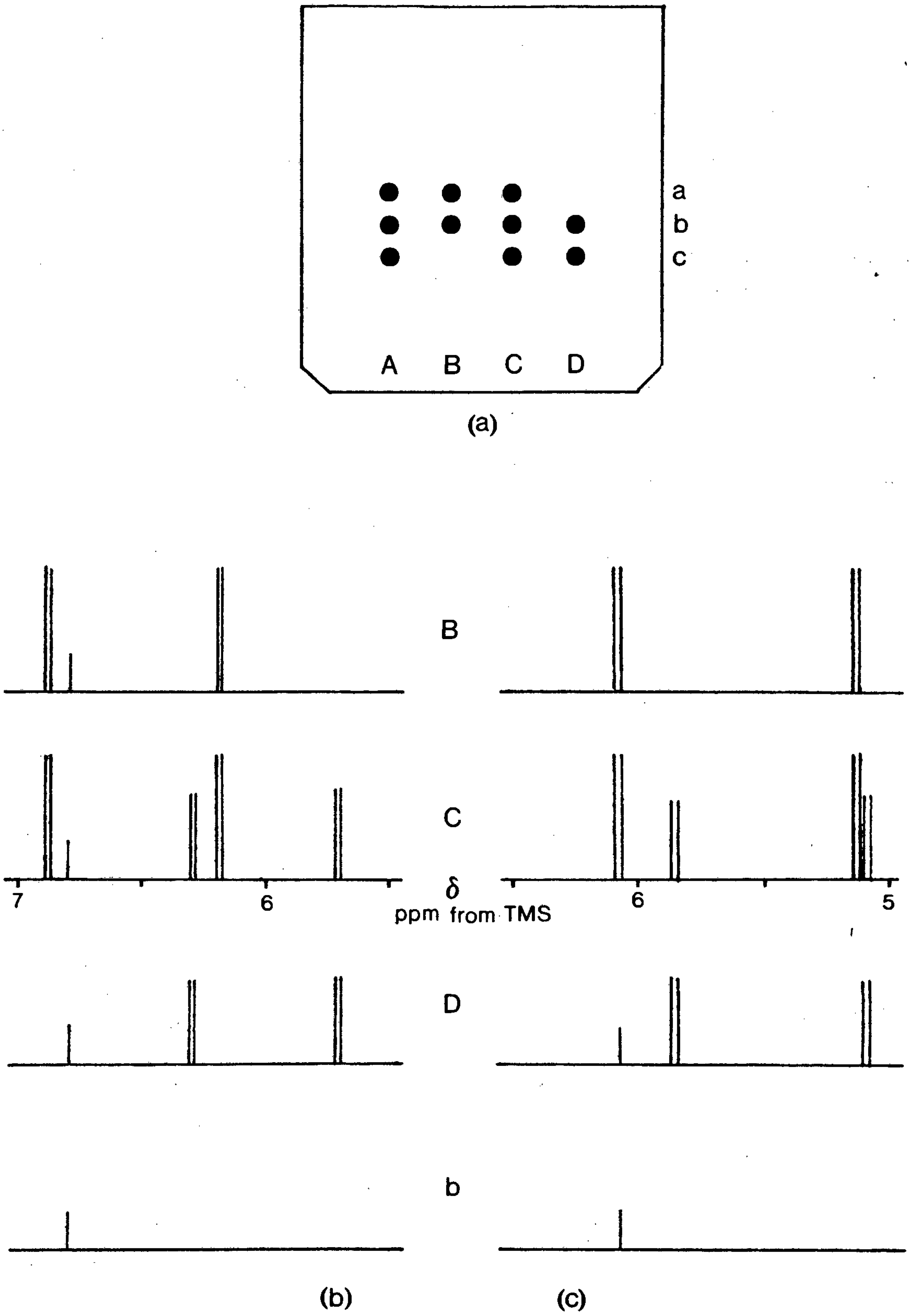


Figure 4.14. The problem of separating cis- *and* trans-*chloralides. (a) Results of tlc of crude condensation product, A, and subsequent chromatographic fractions, B, C and D. Diagrammatic* ^{1}*Hnmr spectra of fractions in (b) DMSO-*d_6 *and (c)* $CDCl_3$.

band on a thin-layer plate. The two resulting component bands, *a* and *b*, were scraped from the plate and rechromatographed separately. Component *a* again separated into two spots *a* and *b*, while *b* remained as one spot. The same experiment with fraction *D* gave parallel results, implying that both *cis*- and *trans*-chloralide decompose on silica gel to give the same product *b*. The nmr spectrum of *b* is identical to that of (4.22), the product of the action of dimethylsulphoxide on chloralide. Apparently, the basic sites on silica gel are strong enough to bring about dehydrochlorination of chloralide.

This phenomenon was not observed in the case of the parachlorals or the parabutylchlorals, and therefore offers evidence of the stronger acidity of H5 in chloralide.

4.8 *EXPERIMENTAL DETAILS*

4.8.1 *Preparation of chloralides*

Method (i). Chloral hydrate (24.2 mmoles) was heated under reflux at 85-95°C for 1½ h with fuming sulphuric acid (s.g. 1.85; 10 mℓ), as described by Otto (1887). Pouring the cooled reaction mixture over crushed ice gave *trans*-chloralide, which melted at 115-116°C (115°C, Chattaway and Kellett, 1928) after three recrystallisations from ethanol (Found: C 18.5, H 0.6%. Calc. for $C_5H_2Cl_6O_3$: C 18.61, H 0.62%). A 60% yield was obtained. The ^{1}Hnmr spectrum of *trans*-chloralide is identical to that reported by Chia and Huang (1968).

Method (ii). A solution of trichlorolactic acid (30 mmoles; Kölln, 1918) in water (10 mℓ) was added dropwise to a solution of chloral hydrate (45 mmoles) in concentrated sulphuric acid (30 mℓ) in an ice bath. The mixture was then stirred at 70°C and after 4½ h, poured onto ice (100 g). The crude solid product, when washed with water and dried on a water bath, represented a total yield of 70% and was found by ^{1}Hnmr to contain both isomers of chloralide in the ratio *cis*:*trans* = 1:1.

All column chromatography was performed on dry-packed, deactivated Merck silica gel 60 (Section 2.8.1). A solute:stationary-phase ratio of about 1:200 was used. Prior to elution, the solute was crushed with silica gel and chloroform was added. The solvent was removed on a rotary evaporator and the solute, now adsorbed onto silica gel, was placed at the top of the column and covered with a layer of sand. Elution was with 7% ethyl acetate in petroleum ether (60-80°C) and 5 mℓ fractions were collected and analysed by tlc on Merck 60 F_{254} thin-layer plates. Pure *cis*-chloralide (m.p. 77-80°C) was obtained by recrystallisation (from ethanol) of the slower-moving fraction (Section 4.7) (Found: C 18.7, H 0.7%).

4.8.2 *Instrumental details*

Mass spectra were measured on a V.G. Micromass 16F Spectrometer. ^{1}Hnmr and ^{13}Cnmr spectra were measured on a Varian XL100 and a Bruker WH90 FT instrument. The infrared spectrum of (4.22) was recorded on a Perkin Elmer 983 spectrophotometer.

4.8.3 *Formation of chloralide from chloral hydrate and oleum*

In order to test the possible reaction sequence chloral → parachloral → chloralide, samples (1 g) of α-parachloral, β-parachloral and metachloral were heated in oleum under the conditions described in Section 4.8.1. During the respective reactions, evolution of carbon monoxide was proved by the blackening of a palladium(II) solution through which the effluent gases were passed. On cooling, reaction mixtures were poured over ice but in no case was a solid product isolated.

Fuming sulphuric acid (s.g. 1.84; 4 mℓ) was placed in the teflon linings of two identical stainless steel bombs (Parr Instrument Company, USA) and then frozen by immersing the bombs in liquid nitrogen. In one bomb was placed an intimate mixture of chloral hydrate (3.0 mmoles) and sodium formate (3.0 mmoles), and in the other an intimate mixture of chloral hydrate (3.0 mmoles), sodium formate (1.5 mmoles) and [^{13}C]-sodium formate (1.5 mmoles; 91.7 atom % ^{13}C, B.O.C. Ltd., UK). The bombs were closed without delay and both were kept in an oven at 85°C for 2 h. After cooling, the bombs were opened and the contents poured separately over ice (10 g). Solid chloralide (0.3 mmoles) was collected, washed with distilled water and dried.

4.8.4 Isomerisation and dehydrohalogenation of chloralide

Isomerisation in molten chloralide was investigated by sealing a known mixture of isomers in a pyrex tube and heating in an oven at 200°C for 5 hours. The ^{1}Hnmr spectrum of the sample was unchanged after the experiment.

To test the postulated deuterium exchange of proton H5 in chloralide in dimethylsulphoxide-d_6 and D_2SO_4, a sample (2 g) of pure *trans*-chloralide was heated with concentrated H_2SO_4 (0.5 mℓ) in dimethylsulphoxide (20 mℓ) on a boiling water-bath for 6 h. The reaction mixture was then poured over ice and the solid product washed with distilled water and dried. ^{1}Hnmr showed that this product consisted of a 1:1 mixture of *trans*-chloralide and the compound giving rise to the signal at δ 6.04 ppm ($CDCl_3$). A pure sample of the compound was obtained by fractional recrystallisation of this mixture from n-hexane (Found: C 20.3, H 0.4%. Calc. for $C_5HCl_5O_3$: C 20.98, H 0.35%).

4.8.5 X-ray crystallography of trans-*chloralide*

Single flat prisms of *trans*-chloralide were grown from ethanol. Preliminary photography revealed space group symmetry and initial cell dimensions (Table 4.4). Accurate lattice constants were obtained from a least-squares analysis of the settings of 25 high order reflections measured on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo *Kα* radiation ($\lambda = 0.7107$ Å). Crystal stability was checked by periodically monitoring three reference reflections during data collection. The large stability constants (Table 4.4) indicate marked deterioration of the crystals. This resulted in a high R value, although R_w is satisfactory. Intensities were collected by the ω-2θ scan technique. Corrections were made for Lorentz and polarisation effects, but not for absorption. Table 4.4 gives details of crystal and data collection parameters.

The structure was solved using the automatic centrosymmetric direct-methods routine of SHELX (Sheldrick, 1978). All the heavy atoms were located in the *E* map despite the instability of the crystal during the data collection. The position of only one H atom was found in subsequent least-squares refinements. In the final refinements the heavy atoms were treated anisotropically with the H atoms in calculated positions (C—H = 1.08 Å). The isotropic temperature factors of the H atoms were treated as a single parameter. Table 4.4 gives details of the final refinement, and the final atomic parameters are listed in Table 4.5.

Table 4.4

Crystal data and experimental and refinement parameters for trans-*chloralide.*

Space group	$P2_1/c$
$\underline{a}$ (Å)	6.200(3)
$\underline{b}$ (Å)	17.170(9)
$\underline{c}$ (Å)	10.382(5)
β (°)	95.05(2)
Z	4
M_r	322.8
V (Å^3)	1101(1)
D_c (Mg m^{-3})	1.95
μ(Mo *K*α) (mm^{-1})	1.42
F(000)	632

Data collection	
Crystal dimensions (mm)	0.45 x 0.35 x 0.15
Scan mode	ω-2θ
Scan width (°θ)	1.3
Scan speed (°θ s^{-1})	0.043
Range scanned (2θ) (°)	6-52
Stability of 3 standard reflections (%)	14, 11, 11
Number of reflections collected	1808
Number of observed reflections	1655 with $I_{(rel)} > 2\sigma I_{(rel)}$
Number of variables	128
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.116
$R_w = \sum w^{\frac{1}{2}}\|\|F_o\| - \|F_c\|\|/\sum w^{\frac{1}{2}}\|F_o\|$	0.077
Weighting scheme	$(\sigma^2 F)^{-1}$
U_{iso} of H atoms (Å^2)	0.10(2)

Table 4.5

Fractional atomic co-ordinates ($x10^4$) *and thermal parameters* ($Å^2$ x 10^3) *for non-H atoms in* trans-*chloralide.*

U(equiv) = $\frac{1}{3}$ (trace of the orthogonalised U_{ij} matrix)

Atom	x/a	y/b	z/c	U(equiv)
C2	1272(12)	2427(5)	1445(9)	50(6)
C4	4655(15)	2734(5)	885(9)	48(5)
C5	4457(12)	3056(5)	2210(9)	47(5)
C21	897(12)	1612(5)	1937(8)	47(5)
C51	4802(13)	3952(5)	2287(9)	56(6)
O1	2233(8)	2913(3)	2430(6)	52(4)
O3	2711(9)	2401(3)	447(6)	57(4)
O41	6146(8)	2716(4)	230(6)	65(4)
Cl21	3417(4)	1195(1)	2533(3)	35(2)
Cl22	-807(3)	1683(2)	3209(3)	70(2)
Cl23	-332(4)	1048(2)	690(3)	84(2)
Cl51	7617(4)	4107(2)	2086(3)	80(2)
Cl52	3246(4)	4433(1)	1028(3)	78(2)
Cl53	4234(4)	4305(1)	3771(3)	76(2)

Observed and calculated structure factors, analyses of variance, hydrogen atom co-ordinates, anisotropic temperature factors, equations of some least-squares planes and torsion angles are presented in Tables 4.6-4.11. All computations were performed at the University of Cape Town Computer Centre on a Univac 1100/81 computer with SHELX (data reduction, structure solution and refinement), XANADU (molecular geometry) and PLUTO (illustrations) (Roberts and Sheldrick, 1975; Motherwell, 1975).

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Table 4.6

Observed and calculated structure factors for trans-*chloralide.*

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	0	0	54	-47	1	5	0	69	-61	6	9	0	2	-4	2	15	0	25	-25	4	1	1	8	6
2	0	0	9	8	2	5	0	11	-8	0	10	0	8	8	3	15	0	15	-14	5	1	1	28	31
3	0	0	65	61	3	5	0	29	-29	1	10	0	11	10	4	15	0	10	10	6	1	1	10	-12
4	0	0	9	7	4	5	0	15	-15	2	10	0	8	5	5	15	0	6	-10	7	1	1	13	15
5	0	0	11	-11	5	5	0	17	-18	3	10	0	13	-15	0	16	0	11	9	-7	2	1	5	-5
6	0	0	20	-20	6	5	0	11	12	4	10	0	34	35	1	16	0	26	-24	-6	2	1	15	-17
7	0	0	17	-18	7	5	0	8	-6	5	10	0	17	20	2	16	0	5	-6	-5	2	1	31	31
3	1	0	24	23	0	6	0	157	-149	6	10	0	2	2	3	16	0	14	13	-4	2	1	30	26
4	1	0	23	22	1	6	0	83	76	1	11	0	1	3	4	16	0	21	-20	-3	2	1	56	-49
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5	2	0	9	10	2	7	0	7	6	2	12	0	11	9	3	18	0	11	13	5	2	1	18	18
6	2	0	14	16	3	7	0	14	14	3	12	0	18	-18	4	18	0	8	-9	6	2	1	9	-7
7	2	0	5	3	4	7	0	15	16	4	12	0	14	14	1	19	0	15	-13	-7	3	1	5	-5
1	3	0	3	3	5	7	0	19	-18	5	12	0	5	-4	2	19	0	17	15	-6	3	1	8	-12
2	3	0	152	139	6	7	0	18	-20	6	12	0	19	-23	3	19	0	1	6	-5	3	1	38	36
3	3	0	73	-71	0	8	0	21	-21	1	13	0	47	44	0	20	0	6	-2	-4	3	1	17	-14
4	3	0	12	-11	1	8	0	21	21	2	13	0	13	-11	1	20	0	7	7	-3	3	1	4	-1
5	3	0	53	56	2	8	0	2	-2	3	13	0	4	3	2	20	0	5	-3	-1	3	1	34	-35
6	3	0	5	6	3	8	0	12	13	4	13	0	9	9	-7	1	1	4	-3	0	3	1	3	5
7	3	0	9	-11	4	8	0	3	1	5	13	0	6	8	-6	1	1	5	5	1	3	1	2	-2
0	4	0	94	-90	5	8	0	4	0	6	13	0	5	13	-5	1	1	9	9	2	3	1	42	-43
1	4	0	57	-50	6	8	0	16	19	0	14	0	10	-10	-4	1	1	10	10	3	3	1	37	-35
2	4	0	36	-35	7	8	0	6	-8	1	14	0	29	-28	-3	1	1	74	-68	4	3	1	2	-1
3	4	0	38	-37	1	9	0	33	-32	2	14	0	8	-6	-2	1	1	84	74	5	3	1	25	-27
4	4	0	7	-9	2	9	0	19	-19	3	14	0	6	-5	-1	1	1	49	44	7	3	1	6	0
5	4	0	5	3	3	9	0	28	30	4	14	0	4	2	1	1	1	12	11	-7	4	1	12	-12
6	4	0	5	-4	4	9	0	21	-22	5	14	0	8	9	2	1	1	65	60	-6	4	1	25	-27
7	4	0	18	19	5	9	0	2	5	1	15	0	31	28	3	1	1	53	51	-5	4	1	9	-8
-4	4	1	64	-59	1	6	1	44	-44	5	8	1	5	-9	3	11	1	49	47	3	14	1	3	0
-3	4	1	4	4	2	6	1	23	-21	6	8	1	17	22	4	11	1	5	5	4	14	1	8	-7
-2	4	1	22	-20	3	6	1	19	21	-6	9	1	10	9	5	11	1	3	0	-4	15	1	7	6
-1	4	1	26	-26	4	6	1	12	-13	-5	9	1	30	-29	6	11	1	6	6	-3	15	1	5	-3
0	4	1	102	109	5	6	1	6	-8	-4	9	1	31	29	-6	12	1	12	-12	-2	15	1	17	15
1	4	1	41	40	6	6	1	1	0	-3	9	1	49	47	-5	12	1	6	-6	-1	15	1	27	-27
2	4	1	3	3	7	6	1	6	0	-2	9	1	40	-39	-4	12	1	15	15	0	15	1	5	-1
3	4	1	9	11	-7	7	1	5	6	-1	9	1	98	98	-3	12	1	43	-41	1	15	1	4	1
4	4	1	32	32	-6	7	1	6	1	1	9	1	8	-8	-2	12	1	5	-3	2	15	1	3	2
5	4	1	28	-30	-5	7	1	23	-20	2	9	1	25	24	-1	12	1	5	8	3	15	1	21	-21
6	4	1	11	-15	-4	7	1	13	-14	3	9	1	14	15	0	12	1	19	-21	4	15	1	22	-19
7	4	1	5	-4	-3	7	1	35	34	4	9	1	10	-14	1	12	1	13	13	5	15	1	4	5
-7	5	1	10	7	-2	7	1	76	-74	6	9	1	5	2	2	12	1	4	0	-4	16	1	3	-2
-6	5	1	9	-8	-1	7	1	20	20	-6	10	1	6	-5	3	12	1	9	-7	-3	16	1	6	7
-5	5	1	20	-19	0	7	1	11	12	-5	10	1	27	-25	4	12	1	9	9	-2	16	1	12	-10
-4	5	1	5	0	1	7	1	44	-42	-4	10	1	10	6	5	12	1	13	14	0	16	1	28	26
-3	5	1	23	22	2	7	1	27	27	-3	10	1	49	-49	-6	13	1	6	-4	1	16	1	9	6
-2	5	1	71	-68	3	7	1	12	-13	-2	10	1	14	14	-5	13	1	6	11	2	16	1	7	3
-1	5	1	99	-98	4	7	1	8	6	-1	10	1	42	42	-4	13	1	11	-8	3	16	1	4	-1
0	5	1	64	-67	5	7	1	8	3	0	10	1	31	-33	-3	13	1	17	-16	4	16	1	4	0
1	5	1	73	69	6	7	1	9	7	1	10	1	45	44	-2	13	1	13	14	-4	17	1	7	3
2	5	1	70	-67	7	7	1	12	-16	2	10	1	40	38	-1	13	1	13	-14	-3	17	1	5	-4
3	5	1	43	-45	-7	8	1	22	22	3	10	1	2	-2	1	13	1	12	-10	-2	17	1	7	-8
4	5	1	5	4	-6	8	1	28	29	4	10	1	4	-3	2	13	1	25	-24	-1	17	1	2	0
5	5	1	5	-8	-5	8	1	14	11	5	10	1	9	9	3	13	1	4	5	1	17	1	10	8
6	5	1	11	9	-4	8	1	9	-8	6	10	1	4	-5	4	13	1	7	0	2	17	1	5	5
7	5	1	9	-7	-3	8	1	56	52	-6	11	1	18	17	5	13	1	6	-11	3	17	1	7	-5
-7	6	1	10	-10	-2	8	1	40	39	-5	11	1	16	14	-5	14	1	6	7	4	17	1	4	2
-6	6	1	21	17	-1	8	1	22	-24	-4	11	1	8	-8	-4	14	1	21	20	-3	18	1	7	6
-5	6	1	14	14	0	8	1	74	-73	-3	11	1	15	-19	-2	14	1	22	-22	-2	18	1	10	10
-4	6	1	15	-14	1	8	1	18	16	-2	11	1	14	14	-1	14	1	5	8	0	18	1	7	-9
-3	6	1	77	70	2	8	1	28	-27	0	11	1	15	20	0	14	1	5	-4	2	18	1	20	17
-1	6	1	38	-40	3	8	1	19	18	1	11	1	26	-26	1	14	1	40	-38	3	18	1	4	-4
0	6	1	110	110	4	8	1	26	-30	2	11	1	20	19	2	14	1	14	-15	-3	19	1	5	3

continued/......

Table 4.6 (continued)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-2	19	1	5	7	4	1	2	22	-22	-7	4	2	13	-11	-3	6	2	22	20	4	8	2	41	48
-1	19	1	4	-2	5	1	2	15	-15	-6	4	2	5	-4	-2	6	2	27	-27	5	8	2	1	-4
0	19	1	6	-4	6	1	2	7	2	-5	4	2	5	-2	0	6	2	41	-41	6	8	2	13	-16
1	19	1	15	15	7	1	2	5	3	-4	4	2	17	-16	1	6	2	44	-45	-6	9	2	3	-4
2	19	1	6	2	-7	2	2	7	6	-3	4	2	12	13	2	6	2	55	-54	-5	9	2	16	13
3	19	1	10	-4	-6	2	2	5	9	-2	4	2	45	-43	3	6	2	51	-56	-4	9	2	14	11
-2	20	1	3	2	-5	2	2	35	-34	-1	4	2	20	-21	4	6	2	14	16	-3	9	2	11	15
-1	20	1	10	-10	-4	2	2	12	12	0	4	2	93	101	5	6	2	16	-19	-2	9	2	7	-8
0	20	1	9	-6	-3	2	2	52	-47	1	4	2	92	-96	6	6	2	5	-8	-1	9	2	4	-2
1	20	1	6	1	-2	2	2	9	-8	2	4	2	31	-31	7	6	2	5	4	0	9	2	11	-10
-7	0	2	24	27	-1	2	2	10	11	3	4	2	21	24	-7	7	2	6	7	1	9	2	37	37
-6	0	2	7	-9	0	2	2	3	3	4	4	2	5	-9	-6	7	2	10	-8	2	9	2	16	-14
-5	0	2	6	-6	1	2	2	72	76	5	4	2	17	-20	-5	7	2	22	-20	3	9	2	9	10
-4	0	2	43	41	2	2	2	55	52	6	4	2	5	3	-4	7	2	50	47	4	9	2	24	28
-3	0	2	43	38	3	2	2	20	20	7	4	2	12	-15	-3	7	2	40	41	5	9	2	3	-2
-2	0	2	88	77	4	2	2	22	-22	-7	5	2	9	10	-2	7	2	15	13	6	9	2	5	9
-1	0	2	47	49	5	2	2	19	21	-6	5	2	11	-11	-1	7	2	49	52	-6	10	2	1	-3
1	0	2	31	-31	6	2	2	8	-5	-5	5	2	28	25	0	7	2	58	60	-5	10	2	4	-6
2	0	2	13	11	7	2	2	3	-8	-4	5	2	11	13	1	7	2	39	38	-4	10	2	42	-41
3	0	2	24	24	-7	3	2	5	-9	-3	5	2	53	-48	2	7	2	37	36	-3	10	2	12	13
4	0	2	33	-35	-6	3	2	5	-2	-2	5	2	6	5	3	7	2	43	-45	-2	10	2	26	28
5	0	2	26	29	-5	3	2	20	20	-1	5	2	13	13	4	7	2	19	-22	0	10	2	35	-36
6	0	2	26	28	-4	3	2	64	-60	0	5	2	63	-68	5	7	2	13	18	1	10	2	71	68
7	0	2	15	15	-3	3	2	80	-74	1	5	2	58	-59	6	7	2	11	-16	2	10	2	47	48
-7	1	2	13	-15	-2	3	2	47	45	2	5	2	60	58	-6	8	2	32	-31	3	10	2	7	8
-6	1	2	20	-21	-1	3	2	34	-38	3	5	2	7	-4	-5	8	2	12	11	4	10	2	6	13
-5	1	2	18	18	0	3	2	2	-3	4	5	2	11	-13	-4	8	2	19	-18	5	10	2	4	4
-4	1	2	16	-12	1	3	2	78	-83	5	5	2	17	22	-3	8	2	19	-18	6	10	2	3	4
-3	1	2	43	-40	2	3	2	19	19	6	5	2	4	-2	-2	8	2	4	0	-6	11	2	5	7
-2	1	2	71	63	3	3	2	14	-16	7	5	2	6	-1	-1	8	2	20	21	-5	11	2	17	-19
-1	1	2	21	-22	4	3	2	10	10	-7	6	2	7	-10	0	8	2	16	16	-4	11	2	18	-19
1	1	2	23	23	5	3	2	8	-6	-6	6	2	19	18	1	8	2	38	39	-3	11	2	2	4
2	1	2	23	-22	6	3	2	14	-16	-5	6	2	39	39	2	8	2	20	20	-2	11	2	20	-22
3	1	2	24	23	7	3	2	18	22	-4	6	2	20	17	3	8	2	17	-17	-1	11	2	41	-41
0	11	2	16	-18	-2	14	2	9	7	-2	18	2	5	-5	-4	2	3	75	-73	2	4	3	68	-70
1	11	2	41	41	-1	14	2	23	-22	-1	18	2	5	9	-3	2	3	9	9	3	4	3	7	-6
2	11	2	50	-51	0	14	2	8	8	0	18	2	4	0	-2	2	3	60	-60	4	4	3	45	-48
3	11	2	10	8	2	14	2	7	-4	1	18	2	11	-10	-1	2	3	103	-114	5	4	3	8	6
4	11	2	13	17	3	14	2	8	7	2	18	2	5	3	0	2	3	14	16	6	4	3	4	8
5	11	2	6	-5	4	14	2	17	-18	3	18	2	5	0	1	2	3	26	-28	7	4	3	5	1
6	11	2	10	10	5	14	2	6	-7	-3	19	2	3	5	2	2	3	20	20	-7	5	3	4	3
-6	12	2	14	16	-5	15	2	4	-1	-2	19	2	7	7	3	2	3	56	55	-6	5	3	10	14
-5	12	2	5	4	-4	15	2	4	0	-1	19	2	3	-7	4	2	3	38	-39	-5	5	3	6	6
-4	12	2	10	12	-3	15	2	9	7	0	19	2	12	9	5	2	3	8	3	-4	5	3	4	-4
-3	12	2	27	25	-2	15	2	5	-9	1	19	2	9	10	6	2	3	13	16	-3	5	3	7	-7
-2	12	2	19	20	0	15	2	11	9	2	19	2	6	-2	7	2	3	6	-10	-1	5	3	84	89
-1	12	2	32	-31	1	15	2	17	-17	3	19	2	2	-6	-7	3	3	7	11	0	5	3	9	-9
0	12	2	2	4	2	15	2	14	11	-2	20	2	9	-10	-6	3	3	20	20	1	5	3	84	-89
1	12	2	21	-22	3	15	2	3	5	-1	20	2	7	8	-5	3	3	3	-1	2	5	3	36	36
2	12	2	34	-35	4	15	2	9	-10	1	20	2	4	-2	-4	3	3	15	12	3	5	3	2	-6
3	12	2	3	-1	5	15	2	5	-3	2	20	2	6	5	-3	3	3	10	10	4	5	3	22	-25
4	12	2	15	-16	-4	16	2	16	16	-7	1	3	13	-15	-2	3	3	21	-21	5	5	3	16	-17
5	12	2	5	6	-3	16	2	22	-23	-6	1	3	13	-15	-1	3	3	35	-38	6	5	3	13	-15
6	12	2	12	14	-2	16	2	6	-9	-5	1	3	13	-13	0	3	3	41	-44	7	5	3	5	0
-5	13	2	7	-8	-1	16	2	18	18	-4	1	3	4	-5	1	3	3	11	-11	-7	6	3	7	6
-4	13	2	13	-11	1	16	2	3	3	-3	1	3	2	1	2	3	3	27	-25	-6	6	3	5	7
-3	13	2	5	-3	2	16	2	12	-10	-2	1	3	29	28	3	3	3	4	-2	-5	6	3	4	4
-2	13	2	3	-1	3	16	2	4	5	-1	1	3	55	-59	4	3	3	12	-14	-4	6	3	15	15
-1	13	2	20	21	4	16	2	3	5	0	1	3	39	44	5	3	3	10	10	-3	6	3	4	-4
0	13	2	1	-5	-4	17	2	5	4	1	1	3	113	120	6	3	3	5	2	-2	6	3	31	30
1	13	2	26	-26	-3	17	2	5	-1	2	1	3	67	-67	-7	4	3	11	9	-1	6	3	22	23
2	13	2	11	-12	-2	17	2	10	9	3	1	3	19	18	-5	4	3	12	-12	0	6	3	19	21
3	13	2	15	15	-1	17	2	2	-9	4	1	3	36	39	-4	4	3	25	24	1	6	3	12	-11
4	13	2	4	-5	0	17	2	14	13	5	1	3	4	-10	-3	4	3	34	33	2	6	3	38	38
5	13	2	15	-19	1	17	2	9	-10	6	1	3	3	7	-2	4	3	25	26	3	6	3	1	4
-5	14	2	7	-8	2	17	2	9	8	-7	2	3	12	10	-1	4	3	74	-79	4	6	3	5	1
-4	14	2	2	-3	3	17	2	6	4	-6	2	3	6	6	0	4	3	32	34	5	6	3	5	-4
-3	14	2	13	-14	-3	18	2	5	-1	-5	2	3	48	-49	1	4	3	47	-51	6	6	3	5	-6

continued/......

Table 4.6 (continued)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-7	7	3	2	-1	2	9	3	17	17	-1	12	3	3	3	3	15	3	3	5	-6	0	4	5	-6
-6	7	3	9	-10	3	9	3	5	2	0	12	3	48	-47	4	15	3	3	1	-5	0	4	6	2
-5	7	3	18	17	4	9	3	20	21	1	12	3	16	16	-4	16	3	5	8	-4	0	4	4	-3
-4	7	3	28	-26	5	9	3	11	12	2	12	3	15	-17	-3	16	3	6	6	-3	0	4	92	-90
-3	7	3	9	9	6	9	3	5	10	3	12	3	12	-13	-2	16	3	28	28	-2	0	4	101	-105
-2	7	3	17	18	-6	10	3	10	10	5	12	3	6	-8	-1	16	3	4	1	-1	0	4	3	3
-1	7	3	2	-1	-5	10	3	15	16	-5	13	3	15	-18	0	16	3	2	-6	0	0	4	14	13
0	7	3	13	14	-4	10	3	4	1	-4	13	3	35	34	1	16	3	6	8	1	0	4	25	-25
1	7	3	15	-15	-3	10	3	27	26	-3	13	3	4	0	2	16	3	4	-2	2	0	4	6	10
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continued/......

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continued/......

Table 4.6 (continued)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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-4	6	7	9	-10	2	9	7	24	-19	-2	0	8	8	9	3	3	8	3	1	2	7	8	3	-2
-3	6	7	5	-3	3	9	7	11	-11	-1	0	8	36	-34	4	3	8	3	-3	3	7	8	6	5
-2	6	7	5	6	-4	10	7	12	-14	0	0	8	4	4	-5	4	8	6	-3	-4	8	8	6	-6
-1	6	7	21	20	-3	10	7	8	6	1	0	8	37	-31	-4	4	8	6	4	-3	8	8	4	-2
0	6	7	27	-26	-2	10	7	13	13	2	0	8	26	-23	-3	4	8	5	-5	-2	8	8	6	-9
1	6	7	8	7	-1	10	7	7	-4	3	0	8	8	5	-2	4	8	16	14	-1	8	8	18	16
2	6	7	22	19	0	10	7	19	17	4	0	8	9	-10	-1	4	8	17	16	0	8	8	4	-4
3	6	7	10	-9	1	10	7	11	-9	-5	1	8	2	3	0	4	8	8	8	1	8	8	5	-4
4	6	7	16	13	2	10	7	5	-3	-4	1	8	15	15	1	4	8	25	22	2	8	8	2	1
-5	7	7	5	-7	3	10	7	5	5	-3	1	8	5	5	2	4	8	6	2	3	8	8	4	2
-4	7	7	6	-4	-3	11	7	6	-4	-2	1	8	12	12	4	4	8	5	0	-4	9	8	4	3
-3	7	7	4	-2	-2	11	7	10	-10	-1	1	8	18	16	-4	5	8	9	-7	-3	9	8	3	-1
-2	7	7	18	16	-1	11	7	13	-11	0	1	8	11	9	-3	5	8	7	4	-2	9	8	9	6
-1	7	7	22	-21	0	11	7	4	1	1	1	8	13	-13	-2	5	8	9	-10	-1	9	8	9	-7
0	7	7	19	-18	1	11	7	4	3	2	1	8	3	4	-1	5	8	4	-5	0	9	8	15	-14
1	7	7	35	32	2	11	7	6	-8	3	1	8	10	-9	0	5	8	3	0	1	9	8	4	2
2	7	7	14	-14	3	11	7	4	-3	-5	2	8	6	-1	1	5	8	8	-8	2	9	8	3	3
3	7	7	13	10	-3	12	7	6	6	-4	2	8	20	-17	2	5	8	5	2	3	9	8	3	-2
4	7	7	5	1	-1	12	7	12	-12	-3	2	8	6	7	3	5	8	8	5	-3	10	8	6	-6
-4	8	7	5	9	0	12	7	12	12	-2	2	8	3	2	4	5	8	8	7	-2	10	8	8	-7
-3	8	7	27	-29	1	12	7	3	-1	-1	2	8	9	-10	-4	6	8	23	20	-1	10	8	4	3
-2	8	7	3	-2	2	12	7	10	-9	0	2	8	12	10	-3	6	8	11	11	0	10	8	4	-2
-1	8	7	11	-13	-2	13	7	11	-9	1	2	8	1	-2	-2	6	8	16	-16	1	10	8	6	-4
0	8	7	12	-6	-1	13	7	15	12	2	2	8	8	7	-1	6	8	3	-2	2	10	8	4	0
1	8	7	10	-11	0	13	7	9	5	3	2	8	3	-1	0	6	8	12	-14	-3	11	8	16	-15
2	8	7	5	-1	1	13	7	5	-8	4	2	8	4	4	1	6	8	5	4	-2	11	8	3	3
3	8	7	5	2	2	13	7	10	7	-5	3	8	6	6	2	6	8	4	-1	-1	11	8	2	-1
4	8	7	9	9	-2	14	7	5	-2	-4	3	8	5	3	3	6	8	4	0	0	11	8	1	0
-4	9	7	5	0	-1	14	7	10	-9	-3	3	8	20	18	-4	7	8	12	-10	1	11	8	5	-5
-3	9	7	5	-9	0	14	7	3	-3	-2	3	8	33	-30	-3	7	8	8	5	2	11	8	5	0
-2	9	7	13	12	1	14	7	4	6	-1	3	8	20	19	-2	7	8	5	-1	-2	12	8	8	8
-1	9	7	8	-7	-5	0	8	17	16	0	3	8	23	19	-1	7	8	4	-1	-1	12	8	4	4
0	9	7	7	-7	-4	0	8	5	-3	1	3	8	14	-11	0	7	8	9	9	0	12	8	14	-12
1	12	8	6	-9	-4	4	9	6	-3	0	7	9	7	5	0	1	10	6	-5	-1	6	10	6	5
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-3	1	9	3	-2	0	4	9	5	-5	-1	8	9	5	-4	-2	2	10	5	-6	-1	7	10	4	1
-2	1	9	9	6	1	4	9	8	-9	1	8	9	4	4	-1	2	10	4	1	0	7	10	8	-4
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1	1	9	4	-2	-3	5	9	9	8	-2	9	9	17	-15	-3	3	10	9	4	-1	8	10	6	1
2	1	9	4	5	-2	5	9	4	0	-1	9	9	3	-1	-2	3	10	10	7	0	8	10	15	-10
3	1	9	6	-5	-1	5	9	11	8	0	9	9	13	-11	-1	3	10	4	4	1	8	10	4	-2
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2	3	9	4	-2	-2	7	9	4	-6	-2	1	10	4	0	2	5	10	15	10	-1	4	11	8	-6
3	3	9	8	2	-1	7	9	8	6	-1	1	10	10	-8	-2	6	10	15	-10	0	4	11	12	6

Table 4.7

Analyses of variance for trans-chloralide.

	GGG	UGG	GUG	UUG	GGU	UGU	GUU	UUU	ALL
N	228	223	204	214	187	194	199	206	1655
V	213	247	229	206	225	217	215	213	221

SIN THETA	0.00 -	.20 -	.24 -	.28 -	.30 -	.33 -	.35 -	.37 -	.38 -	.40 - .44
N	194	146	200	133	217	171	179	115	139	161
V	446	230	180	227	176	149	136	136	154	110

SQRT(F/FMAX)	0.00 -	.16 -	.18 -	.20 -	.23 -	.26 -	.29 -	.33 -	.38 -	.48 - 1.00
N	206	183	177	123	175	145	178	144	166	158
V	61	77	88	144	139	187	204	206	254	518

ABS(H)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	162	323	314	287	233	173	109	54	0	0	0	0	0	0	0
V	266	267	235	216	193	151	142	123	0	0	0	0	0	0	0

ABS(K)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	61	120	125	120	122	115	114	109	105	97	88	85	75	70	249
V	330	301	299	260	267	245	221	196	216	180	150	152	135	158	122

ABS(L)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	126	224	245	220	198	151	148	114	107	65	45	12	0	0	0
V	284	273	262	226	210	154	139	170	174	157	202	246	0	0	0

Table 4.8

Hydrogen atom co-ordinates (x10^4) for chloralide.

Atom	x/a	y/b	z/c	U_{iso}(Å^2 x 10^2)
H2	-292(12)	2657(5)	1093(9)	10(2)
H5	5646(12)	2796(5)	2901(9)	10(2)

Table 4.9

Anisotropic temperature factors (x10^3 Å^2) for chloralide.

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
C2	28(5)	61(6)	62(7)	-13(5)	13(5)	9(5)
C4	37(5)	38(6)	70(7)	3(5)	5(5)	3(4)
C5	23(5)	47(6)	73(7)	3(5)	14(5)	-6(4)
C21	36(5)	40(5)	67(7)	-7(5)	2(5)	8(4)
C51	34(5)	46(6)	87(7)	8(6)	11(5)	-17(4)
O1	30(3)	50(4)	78(5)	-7(4)	19(3)	-5(3)
O3	36(3)	53(4)	82(5)	-4(4)	9(3)	-7(3)
O41	29(3)	81(5)	89(5)	-6(4)	22(3)	-3(3)
C121	42(1)	51(2)	123(2)	9(2)	5(1)	8(1)
C122	42(1)	73(2)	97(2)	3(2)	21(1)	-15(1)
C123	58(2)	82(2)	114(2)	-31(2)	9(2)	-26(2)
C151	38(1)	62(2)	145(3)	-15(2)	27(2)	-16(1)
C152	62(2)	57(2)	115(2)	20(2)	5(2)	9(1)
C153	73(2)	58(2)	99(2)	-20(2)	25(2)	-11(1)

Table 4.10

Equations of some least-squares planes in chloralide.

Plane through atoms	
O1—C2—O3—C4—C5	$-1.82x + 14.71y - 4.12z = 2.81$
O3—C4—(O41)—C5	$-1.63x + 15.02y - 3.97z = 2.99$
O3—C4—C5—O1	$-1.50x + 15.02y - 4.13z = 3.03$
C2—O3—C4	$-1.91x + 15.31y - 3.15z = 3.02$
C2—O3—C4—C5	$-1.98x + 14.91y - 3.64z = 2.85$
C5—O1—C2	$-1.43x + 13.83y - 5.43z = 2.39$

Table 4.11

Torsion angles (°) in chloralide.

H2—C2—C21—C121	180.0
H2—C2—C21—C122	-61.0
H2—C2—C21—C123	58.9
O1—C2—C21—C121	-59.9
O1—C2—C21—C122	59.1
O1—C2—C21—C123	178.9
O3—C2—C21—C121	58.8
O3—C2—C21—C122	177.8
O3—C2—C21—C123	-62.4
H2—C2—O1—C5	-134.0
C21—C2—O1—C5	107.6
O3—C2—O1—C5	-12.8
H2—C2—O3—C4	130.7
C21—C2—O3—C4	-110.9
O1—C2—O3—C4	10.7
O3—C4—C5—H5	121.6
O3—C4—C5—C51	-118.6
O3—C4—C5—O1	-3.1
O41—C4—C5—H5	-56.9
O41—C4—C5—C51	63.0
O41—C4—C5—O1	178.4
C5—C4—O3—C2	-4.6
O41—C4—O3—C2	174.1
C4—C5—C51—C151	-69.0
C4—C5—C51—C152	48.7

continued/......

Table 4.11 (continued)

C4—C5—C51—C153	172.7
H5—C5—C51—C151	52.4
H5—C5—C51—C152	170.1
H5—C5—C51—C153	-65.9
O1—C5—C51—C151	177.3
O1—C5—C51—C152	-65.0
O1—C5—C51—C153	59.0
C4—C5—O1—C2	9.8
H5—C5—O1—C2	-111.1
C51—C5—O1—C2	129.5

5

STEREOCHEMISTRY OF DITHIOPARACHLORAL (2,4,6-TRIS(TRICHLOROMETHYL)-1-OXA-3,5-DITHIANE), TRITHIOPARACHLORAL (2,4,6-TRIS(TRICHLOROMETHYL)-1,3,5-TRITHIANE) AND THEIR DEHYDROCHLORINATION PRODUCTS

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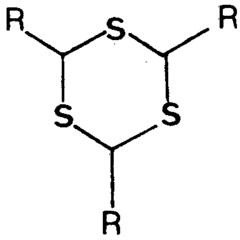
5.1 INTRODUCTION

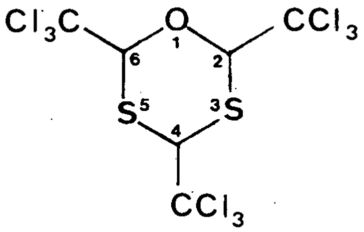
The successful trimerisation of aldehydes prompted early workers to explore the formation and isomerism of analagous sulphur-containing heterocycles. Hofmann (1868) opened the field to the braver and more determined researchers by preparing the parent compound 1,3,5-trithiane (5.1). The faint-hearted were repelled by the foul stench of these compounds and their precursors, or turned to other work for fear of social censure on account of the offensive odours which clung to their persons.



(5.1) $R = H$

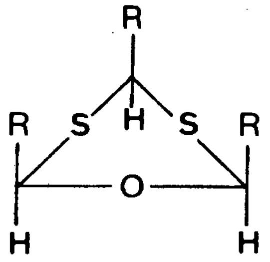
(5.2) $R = CH_3$

(5.3) $R = CCl_3$

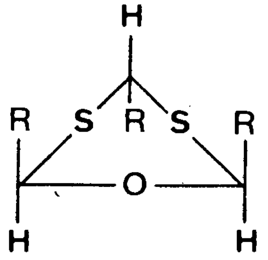


(5.4)

The stereoisomerism of 2,4,6-trisubstituted-1,3,5-trithianes was found to be analagous to that of parachloral. In an elegant and difficult proof (discussed in Section 1.2) Chattaway and Kellett(1930) assigned the correct configurations to the two different forms of trithioparaldehyde (5.2). Continuing their work on chloral derivatives, they prepared one of the two possible isomers of trithioparachloral (5.3) as well as two forms of the mixed heterocycle dithioparachloral (5.4) (Chattaway and Kellett,1929). There are four possible stereoisomers of this compound (5.5)-(5.8). The 2-*trans*- and 6-*trans*-isomers are enantiomers so that three separable forms of dithioparachloral are

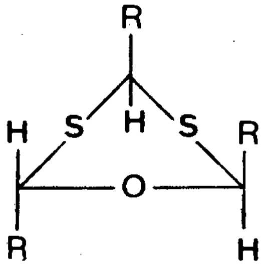


(5.5) cis

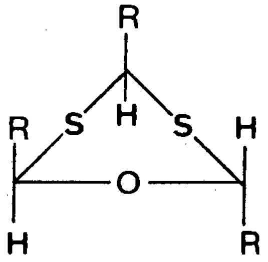


(5.6) 4- trans

$R = CCl_3$



(5.7) 2-trans



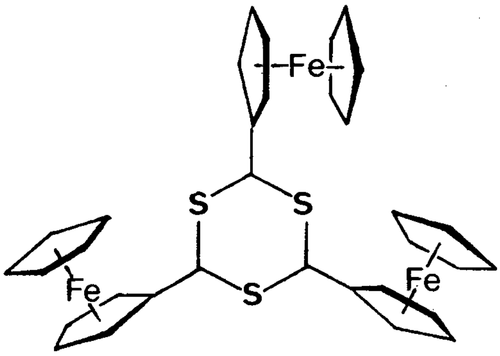
(5.8) 6- trans

expected. The structures of these isomers and their dehydrochlorination products are the subject of this chapter.

^{1}Hnmr offered a rapid, convenient tool to differentiate between *cis*- and *trans*-isomers of trithiopara-aldehydes, a welcomed alternative to laborious wet-chemical techniques which seldom provided unambiguous results. Thus, configurations were assigned to the two forms of trithioparaldehyde and many other 2,4,6-trisubstituted-1,3,5-trithianes (Matlack *et al.*, 1961; Campaigne *et al.*, 1962).

Three-dimensional crystal structure determinations have been carried out on the parent trithiane (Fleming and Lynton, 1967) and on the two isomers of trithioparaldehyde (Valle *et al.*, 1969; Sekido *et al.*, 1977). All three compounds choose the chair conformation in the solid state, *cis*, *trans*-trithioparaldehyde supporting an axial methyl substituent. The crystal structures of 1,3,5-triselenane (Mammi *et al.*, 1968), 1-oxa-3,5-diselenane (Valle *et al.*, 1975), *cis*-2,4,6-trimethyl-1,3,5-triselenane (Credali *et al.*, 1967) and *cis*-2,4,6-trimethyl-1,3-dioxa-5-selenane (Valle *et al.*, 1973) all reveal the expected chair conformations in the solid state. 1,3,5-tritellurane has also been prepared (Williams and Dunbar, 1968).

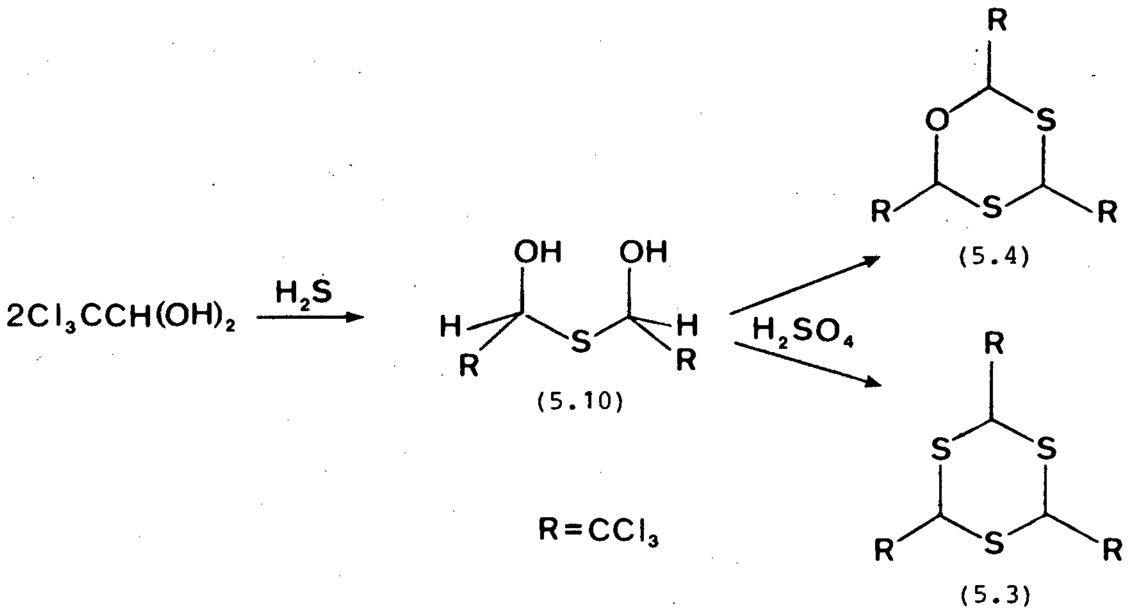
A structurally unusual trithiopara-aldehyde is found in 2,4,6-triferrocenyl-1,3,5-trithiane (5.9). *Cis*- and *trans*-isomers were isolated and shown to be characteristic of other compounds in this class (Ratajczak and Piórko, 1977).



(5.9)

5.2 *PREPARATION OF DITHIO- AND TRITHIOPARACHLORAL*

The preparation described by Chattaway and Kellett (1929) was repeated in this laboratory by Professor H. Irving. The steps in the preparation are outlined in Scheme 5.1. No monothioparachloral is formed under these conditions. The reaction mixture was subjected to a series of fractional crystallisations until three fractions remained, whose melting points matched those reported by Chattaway and Kellett. ^{1}Hnmr revealed however, that each fraction contained a small amount of impurity



Scheme 5.1. *Preparation of dithio- and trithioparachloral.*

(Section 5.4). Furthermore, ^{1}Hnmr evidence was found of the form of trithioparachloral not observed by Chattaway and Kellett. Thus, the three fractions contained:

(a) α-dithioparachloral (+ *cis*-trithioparachloral impurity);

(b) β-dithioparachloral (+ *trans*-trithioparachloral impurity);

(c) *trans*-trithioparachloral (+ β-dithioparachloral impurity).

5.3 *MASS SPECTROMETRY OF DITHIOPARACHLORAL*

The behaviour of dithioparachloral under electron impact is different from that of the trioxanes (Section 3.3), in that the molecular ion is observed at 70 eV. The mass spectrum of a pure sample of β-dithioparachloral is shown in Figure 5.1 and a fragmentation pattern is suggested in Scheme 5.2. The depolymerisation and dehydrohalogenation processes resemble those which occur during fragmentation of the trioxanes.

5.4 *STEREOISOMERISM OF DITHIO- AND TRITHIOPARACHLORAL*

Chattaway and Kellett (1929) have discussed the possible stereoisomers of dithioparachloral (Section 5.1). A more modern representation of the structures of these isomers is given in Scheme 5.3. If the *cis*-isomer (5.11) adopts a chair conformation, the 2-*trans*-isomer either of the twist conformations (5.12) or (5.13) and the 4-*trans*-isomer either of the twist conformations (5.14) or (5.15), all CCl_3 groups will be accommodated in unhindered positions. All other twist conformers of the 2-*trans*- or 4-*trans*-isomers are seriously strained by CCl_3 groups in ψ_{ax} positions. In both the present work and that of Chattaway and Kellett, only two of the three possible isomers of dithioparachloral were isolated.

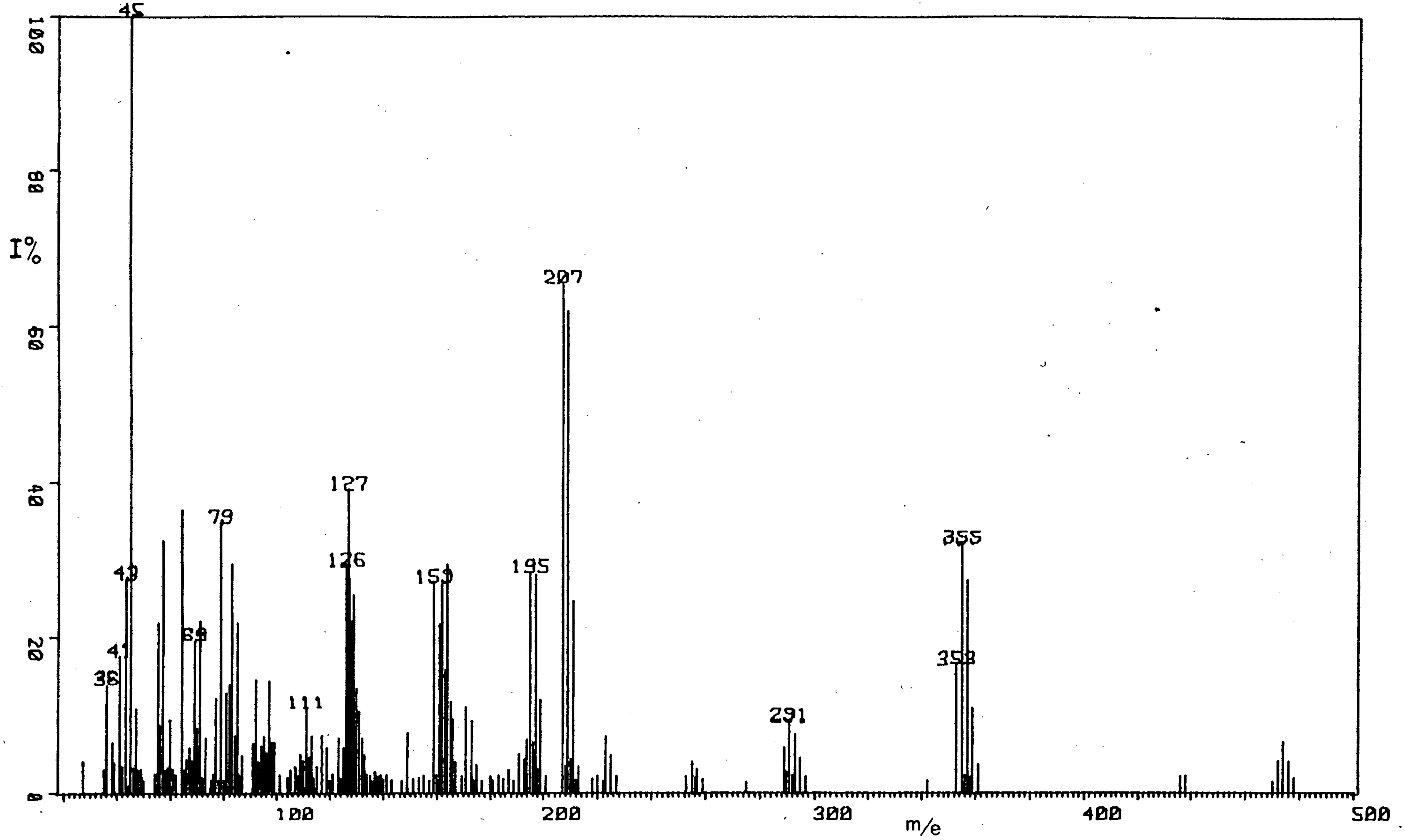
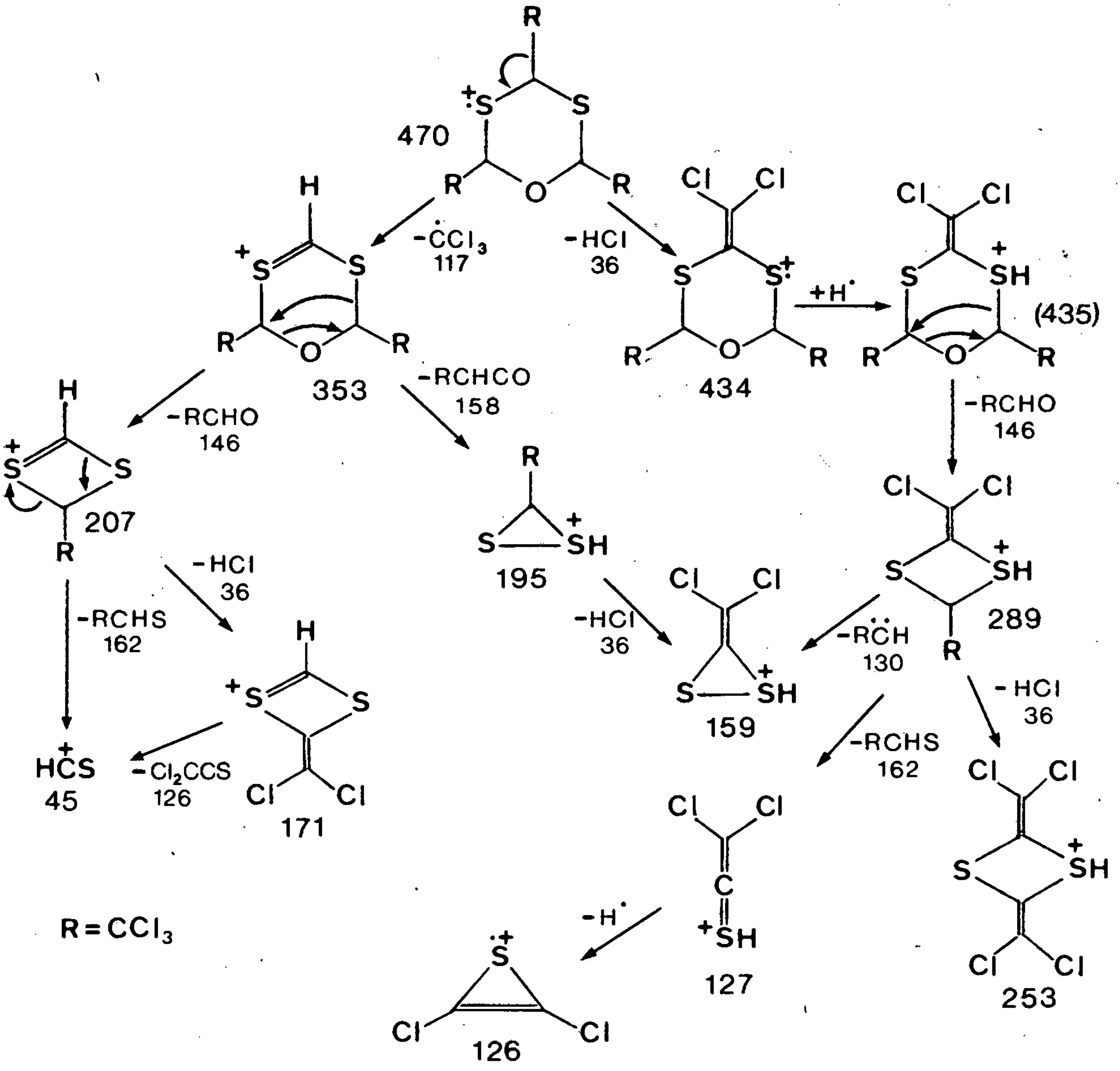
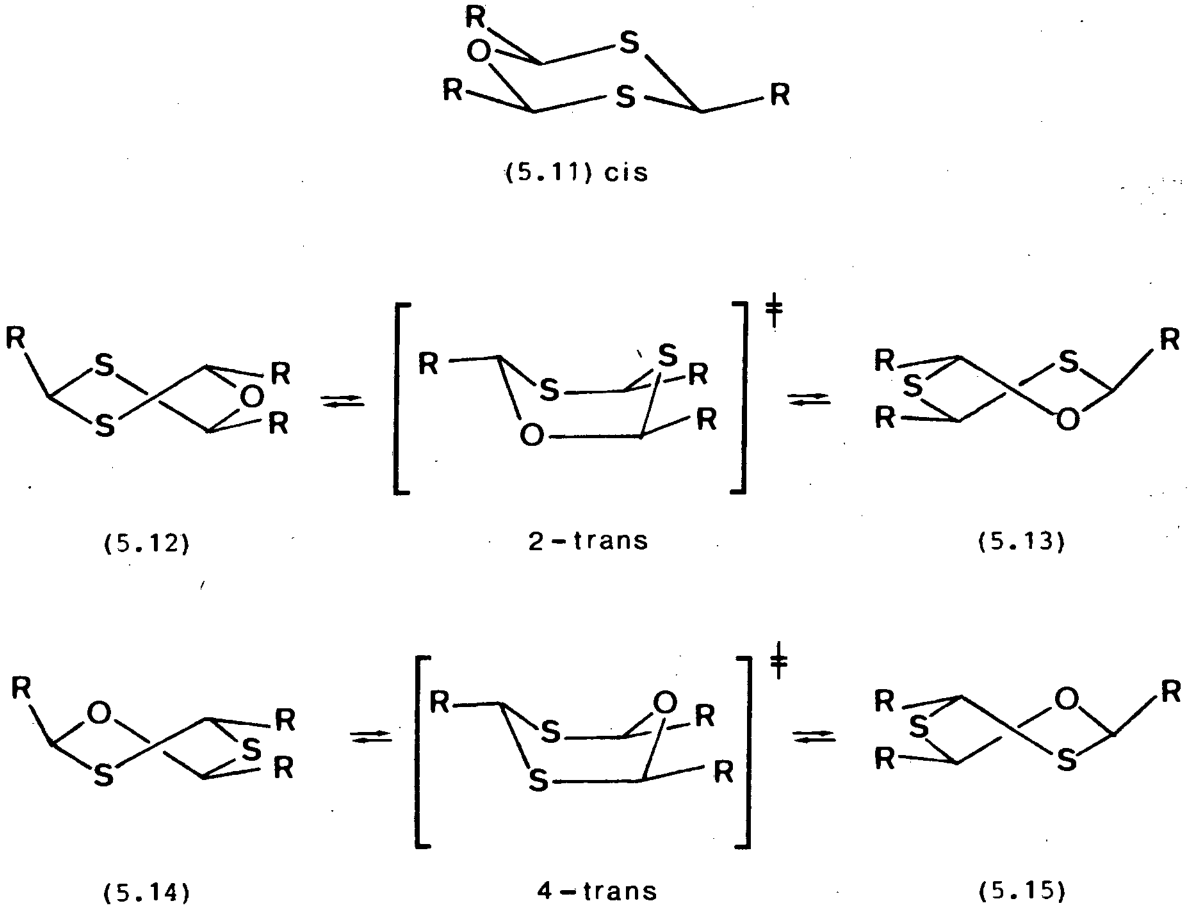


Figure 5.1. 70 eV mass spectrum of β-dithioparachloral.



Scheme 5.2. Mass spectral fragmentation pattern of β-dithioparachloral.



Scheme 5.3. Possible stereoisomers of dithioparachloral (R = CCl_3).

Since very few physical techniques were available to the early workers, the only stereochemical information they could deduce (from dehydrochlorination experiments; Section 5.6) was that one of their isolated products was the racemic mixture of the 2-*trans*- and 6-*trans*-isomers.

The ^{1}Hnmr spectra of α-dithioparachloral (with *cis*-trithioparachloral impurity) and β-dithioparachloral (with *trans*-trithioparachloral impurity) are shown in Figure 5.2. The three-line spectrum of β-dithioparachloral indicates that this isomer possesses no elements of symmetry, and must therefore, have the 2-*trans* configuration. In solution it probably consists of the twist forms (5.12) and (5.13) rapidly interconverting *via* the boat transition state (Scheme 5.3). The symmetry in the spectrum of the α-isomer shows that it could have either the *cis* structure or the 4-*trans* structure; the *cis*-isomer possesses a mirror plane and the average environment of the 2-proton in the rapidly interconverting enantiomeric twist forms (5.14) and (5.15) of the 4-*trans*-isomer, is the mirror image of that of the 6-proton.

The conformational behaviour of dithioparachloral is expected to be significantly different from that of parachloral, since C—S bonds are longer than C—O bonds by about 0.3 Å. Thus, annular bond eclipsing interactions in non-chair conformers and interactions between axial CCl_3 groups and *syn*-axial hydrogen atoms on chair conformers, are expected to be less severe in dithioparachloral than they are in parachloral. It is probable therefore, that the chair—non-chair energy difference is altered by the replacement of oxygen atoms in *cis*,*trans*-parachloral by sulphur atoms. The existence of a trans-annular hydrogen bond in the non-chair form of 4-*trans*-dithioparachloral is unlikely, since models suggest an O···H distance of about 3.0 Å between the oxygen atom and the 4-hydrogen atom in the boat conformer of this molecule.

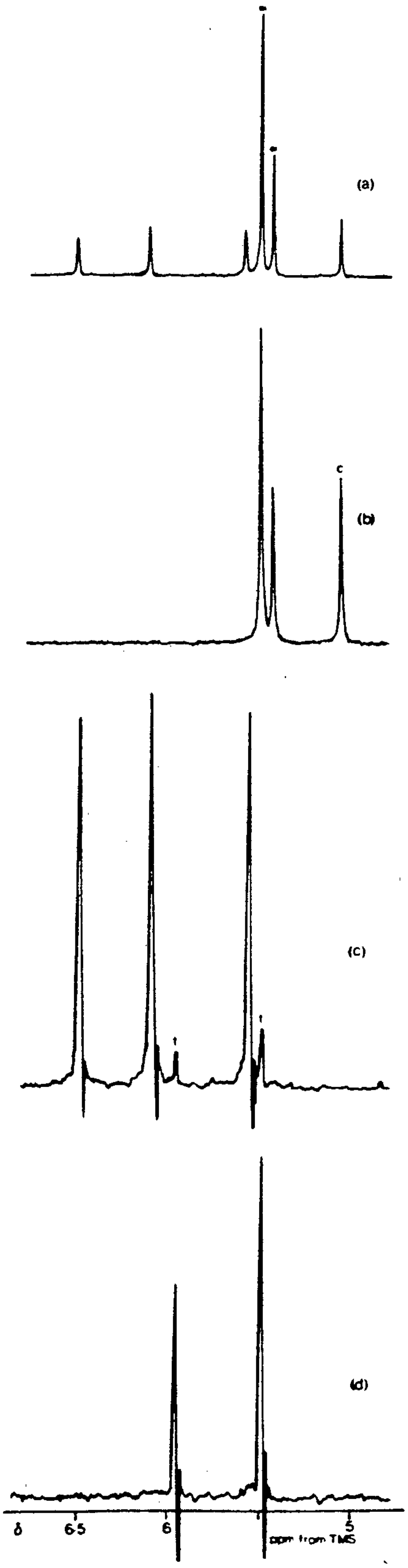


Figure 5.2. *¹Hnmr spectra of (a) a mixture of α- and β-dithioparachlorals and* cis-*trithioparachloral, (b) a mixture of α-dithioparachloral and* cis-*trithioparachloral, (c) β-dithioparachloral (with* trans-*trithioparachloral impurity) and (d)* trans-*trithioparachloral.*

Since the configuration of α-dithioparachloral could not be determined by ^{1}Hnmr, an *x*-ray crystallographic study of both isomers of dithioparachloral was undertaken by Dr. Anne Irving of this laboratory. Considerable difficulties were encountered and the work is still in the early stages.

5.4.1 *X-ray crystallography of β-dithioparachloral*

The chosen crystal of β-dithioparachloral was found to be unstable in the *x*-ray beam, resulting in a data collection of poor quality. The structure has been solved however, in the space group $Pbc2_1$ with an *R*-factor of 13%. The structural precision is correspondingly poor, but the configuration and conformation of the molecule is clear; β-dithioparachloral has the 2-*trans* configuration and exists in a twist conformation in the solid state (Figure 5.3). The space group is non-centrosymmetric, but both enantiomers are present. β-Dithioparachloral chooses the conformation (5.13) in the solid state. It is only in this conformation that the oxygen atom and the 4-hydrogen atom approach each other; in (5.12), H4 occupies an isoclinal position. This is perhaps indicative of a weak interaction between O1 and H4 in the solid state.

5.4.2 *Trithioparachloral*

Chattaway and Kellett (1929) isolated only one of the two possible isomers of this sulphur-containing analogue of parachloral. In the present work, one isomer has been isolated, and a small amount of the other has been obtained as a mixture with α-dithioparachloral. The two isomers of trithioparachloral are expected to have the *cis,cis*-chair structure (5.16) and the *cis,trans*-twist structure (5.17). In support of this, the ^{1}Hnmr spectrum of *cis,trans*-trithioparachloral (Figure 5.2(d)) consists of two signals of intensity ratio 1:2, probably arising from

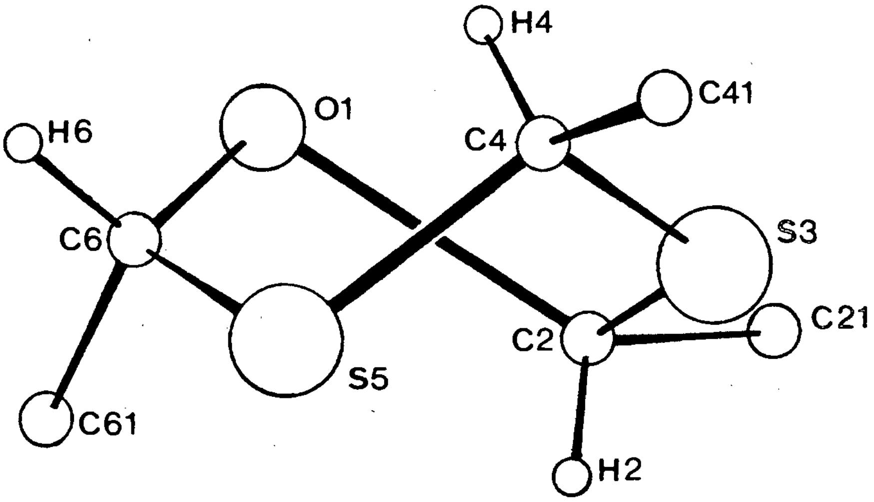
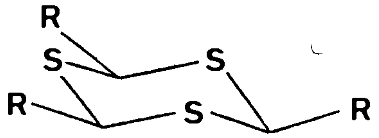
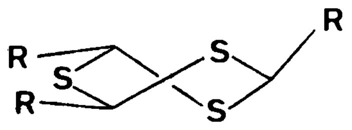


*Figure 5.3. Solid state structure of 2-*trans*-dithioparachloral.*



(5.16)

$R = CCl_3$



(5.17)

two rapidly interconverting enantiomeric twist conformers (5.17). The single signal thought to be due to the protons of *cis,cis*-trithioparachloral appears in Figures 5.2(a) and 5.2(b).

It is interesting to note that by fractional crystallisation, α- and β-dithioparachloral may be separated from each other with relative ease, as may *cis*- and *trans*-trithioparachloral. However, the separation of α-dithio- from *cis*-trithioparachloral and of β-dithio- from *trans*-trithioparachloral is more difficult. It is tempting to rationalise this observation by assuming that α-dithioparachloral has the *cis*-chair structure (5.11), for then it and *cis*-trithioparachloral would have identical structures (and hence similar solubilities) as do *trans*-trithio- and β-dithioparachloral, except for the identity of the heteroatoms. However, the argument is tenuous.

5.5 ^{1}H AND ^{13}CNMR OF PARACHLORAL, DITHIO- AND TRITHIOPARACHLORAL

The ^{13}C spectra of the dithio- and trithioparachlorals (Figures 5.4 and 5.5) are all in accordance with the respective structures proposed in Section 5.4. The assignment of signals was assisted by the great intensity differences between the signals from carbon atoms with protons

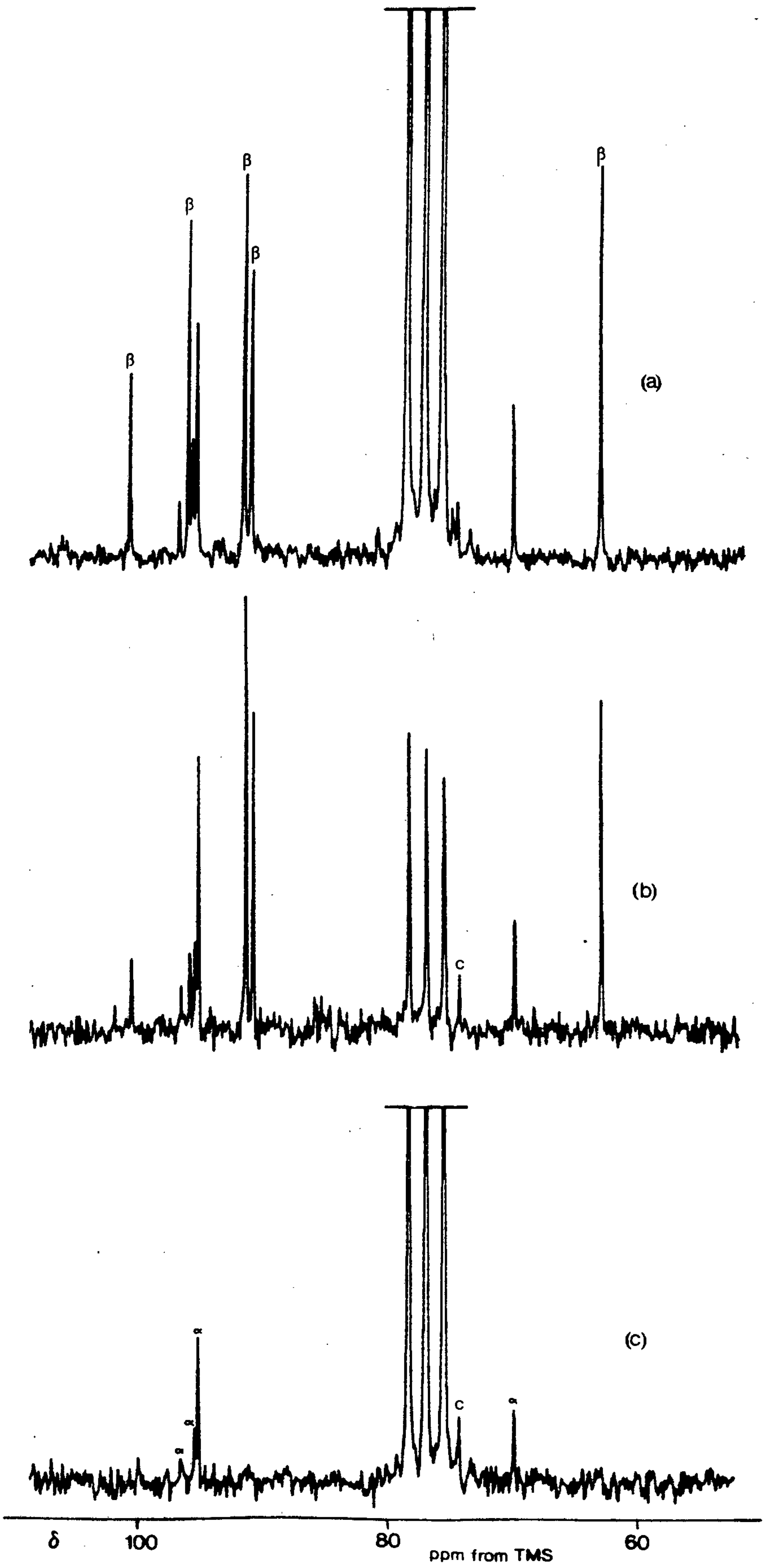


Figure 5.4. Broad band decoupled ^{13}Cnmr spectra of (a) a mixture of α- and β-dithioparachlorals (with cis-trithioparachloral impurity), (b) the same mixture, fully relaxed and (c) α-dithioparachloral (with cis-trithioparachloral impurity).

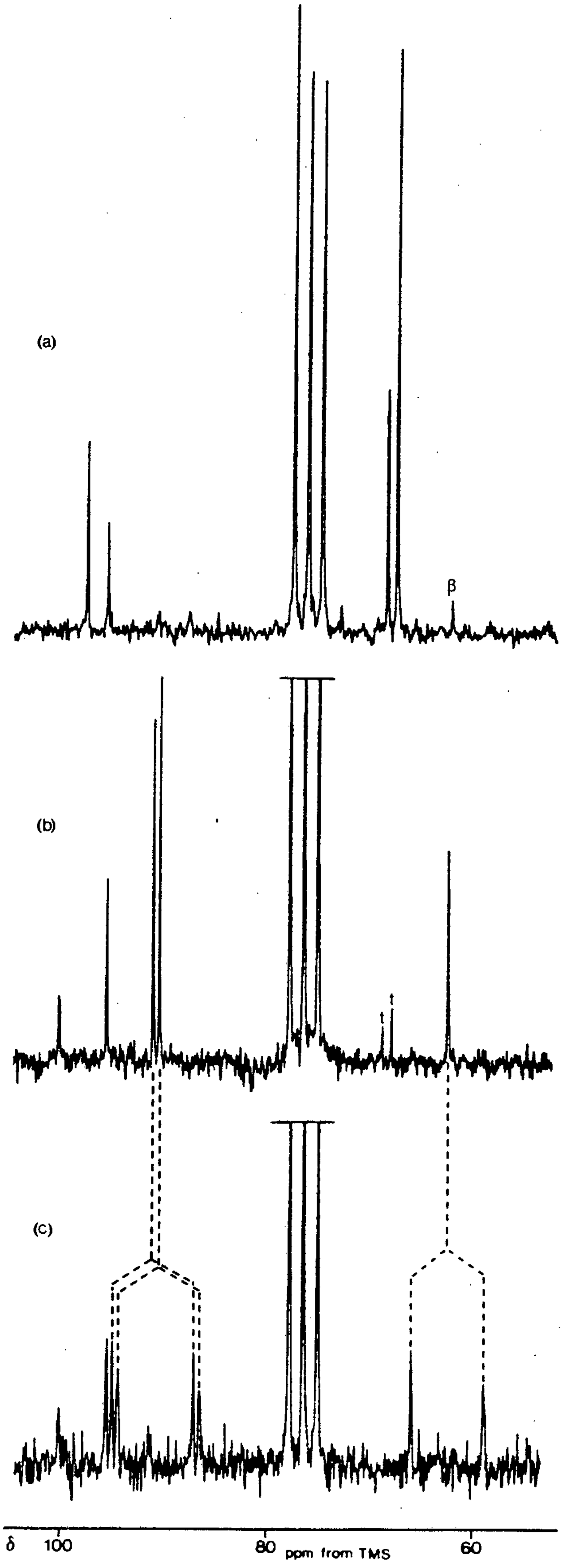


Figure 5.5. Broad band decoupled ^{13}*Cnmr spectra of (a)* trans-*trithioparachloral (with* β-*dithioparachloral impurity) and (b)* β-*dithioparachloral (with* trans-*trithioparachloral impurity). (c)* ^{1}*H-coupled spectrum of* β-*dithioparachloral.*

attached and those without. Figure 5.4(a) shows the ^{13}C spectrum of a roughly 1:2 mixture of α- and β-dithioparachloral. The fully relaxed spectrum of the same mixture, obtained by using chromium(III) acetylacetonate as a relaxation agent and allowing a longer delay time between pulses, is shown in Figure 5.4(b). Its ^{1}H spectrum provides evidence that this mixture contains a small amount of *cis*-trithioparachloral, and the signal at δ 74.0 ppm in Figures 5.4(a) and (b) is thought to be due to the equivalent ring carbon atoms of this molecule. The signal from its CCl_3 carbon atoms is evidently too weak to be observed above the noise.

The ^{1}H-coupled and decoupled ^{13}C spectra of β-dithioparachloral are compared in Figure 5.5. The $^{1}J_{^{1}H-^{13}C}$ coupling constants of C2 and C6 (177.4 Hz) are similar to those of the ring carbons in parabutylchloral (Table 3.2), but that of C4 in β-dithioparachloral (157.5 Hz) is significantly smaller. Numerical ^{1}H and ^{13}C chemical shift data is listed in Table 5.1.

5.5.1 *Some spectral comparisons*

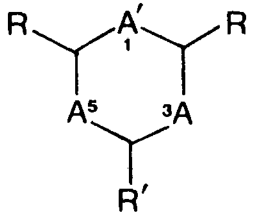
The quantity of nmr data available prompted a comparative study of the effects of structural changes on the ^{13}C and ^{1}Hnmr spectra of these oxygen- and sulphur-containing heterocycles (trianes).

The effect of change of substituent on the nmr spectra of the 1,3,5-trianes.

Cis-parachloral and both isomers of parabutylchloral have the same *cis*-chair structures. Their ^{13}C and ^{1}Hnmr spectra are compared in Figure 5.6. The chemical shifts of the ring carbon atoms and of the ring protons are insensitive to the change of substituent from CCl_3 to $CCl_2CHClCH_3$. The

Table 5.1

^{13}C and ^{1}Hnmr chemical shifts (ppm from TMS in CDCl$_3$) in heterocycles of the type



A	O		O		S		S		S	S
A'	O		O		S		O		O	O
R	CCl_3		$CH_3CHClCCl_2$		CCl_3		CCl_3		CCl_3	$:CCl_2$
R'	CCl_3		$CH_3CHClCCl_2$		CCl_3		CCl_3		$:CCl_2$	$:CCl_2$
isomer	*cis*	*trans*	RRR	RRS	*cis*	*trans*	α	2-*trans*	*trans*	
C2	100.7	99.6	100.0	100.4	74.0	67.7	94.9	91.1	92.2	139.6
C4	100.7	97.2	100.0	100.2	74.0	68.7	69.6	62.5	121.4	121.4
C6	100.7	99.6	100.0	99.8	74.0	67.7	94.9	90.5	92.2	139.6
C21	94.0	95.8	90.4	90.5		97.9	95.3	95.6	95.6	113.7
C41	94.0	94.8	90.4	90.5		95.9	96.3	100.3	114.7	114.7
C61	94.0	95.8	90.4	90.5		97.9	95.3	95.6	95.6	113.7
H2	5.47	5.67	5.61	5.66	4.98	5.47	5.46	6.46	6.15	
H4	5.47	6.11	5.61	5.62	4.98	5.94	5.39	5.54		
H6	5.47	5.67	5.61	5.58	4.98	5.47	5.46	6.07	6.15	

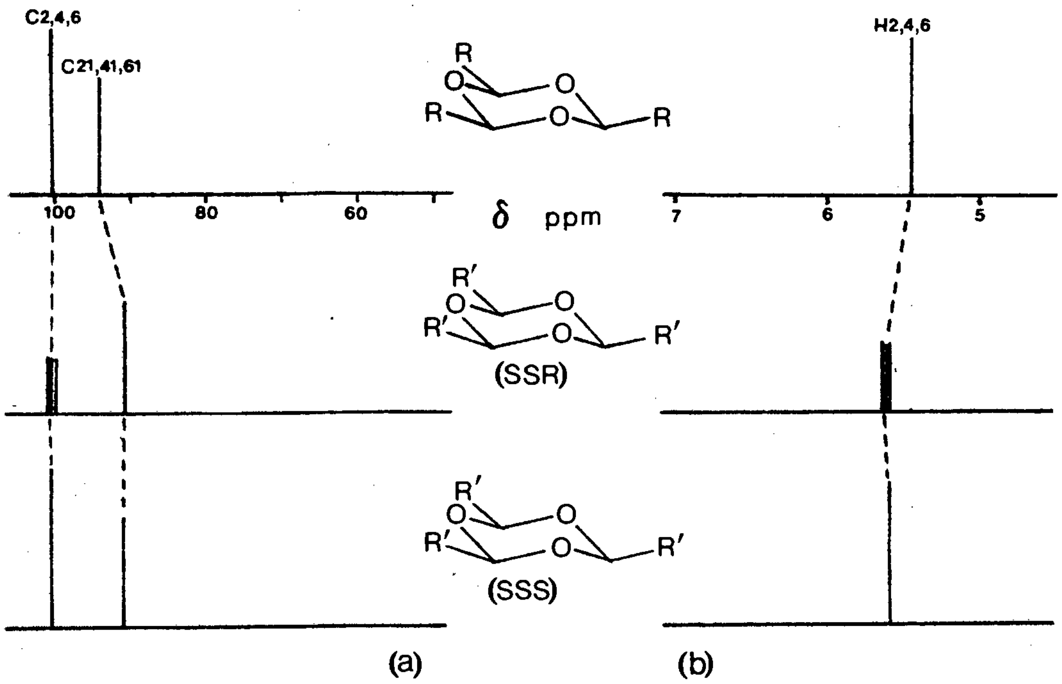


Figure 5.6. The effect of change of substituent on the (a) ^{13}Cnmr and (b) ^{1}Hnmr spectra of the 1,3,5-trianes (R = CCl_3, R' = $CCl_2CHClCH_3$).

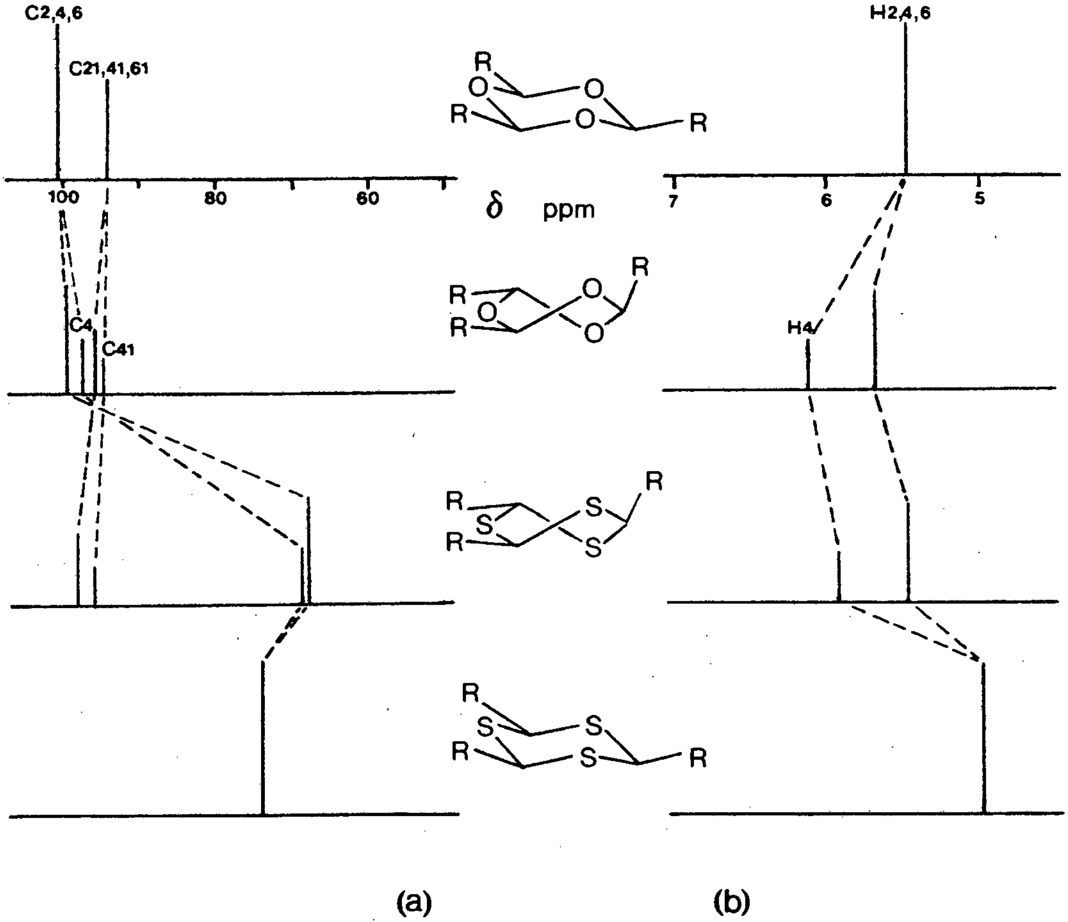


Figure 5.7. The effect of complete replacement of oxygen by sulphur on the nmr spectra of the 1,3,5-trianes (R = CCl_3).

signal from C21, C41 and C61, the carbon atoms attached to the ring in parachloral, is downfield from that in parabutylchloral, no doubt because of the extra electron-withdrawing chlorine atoms carried by the α-carbon atoms in the former compound.

The effect of complete replacement of oxygen by sulphur on the nmr spectra of the 1,3,5-trianes.

In Figure 5.7, the nmr spectra of the geometric isomers of parachloral are compared with those of trithioparachloral. Comparing the ^1H spectra of *cis*-parachloral and *cis*-trithioparachloral shows the effect of replacing all three oxygen atoms in the former compound with less strongly electron-withdrawing sulphur atoms; the ring proton signals shift upfield as expected. The comparison of spectra of the *trans*-isomers is not strictly valid however, since *trans*-parachloral is thought to contain a high proportion of the boat conformer in solution (Section 2.7). Nevertheless, the protons in *trans*-trithioparachloral do resonate upfield from the corresponding protons in *trans*-parachloral (Figure 5.7(b)).

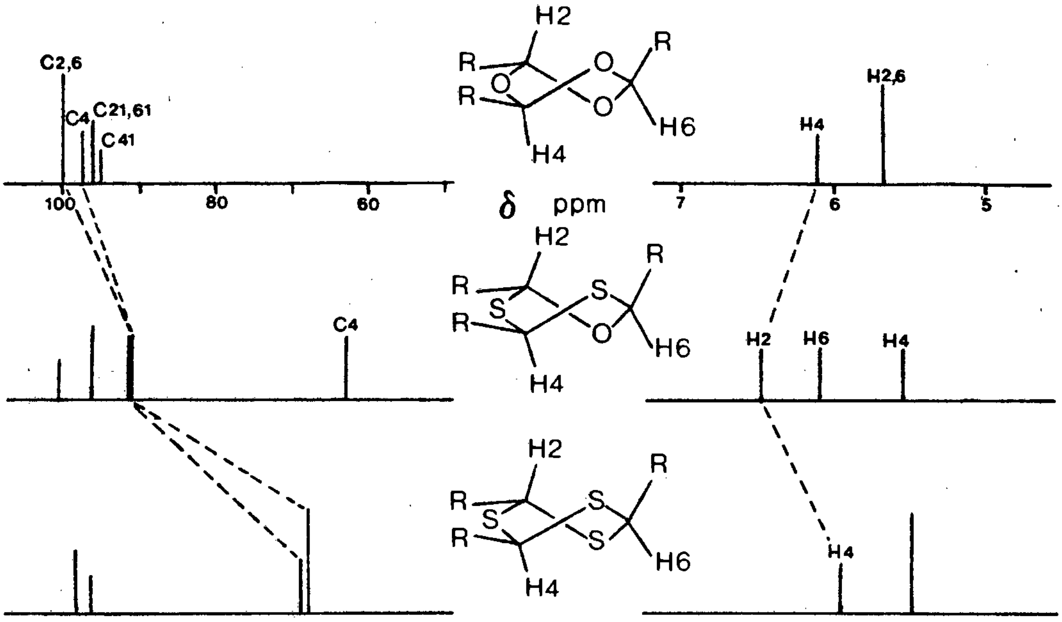
The ring protons in parachloral are less acidic than those in the trithio compound (Section 5.6), which are therefore more susceptible to hydrogen bonding with the solvent. Thus, ^1H chemical shifts, being subject to external influences, are not expected to be good indicators of changes occuring in the ring. Ring carbon atoms are probably more reliable witnesses to such changes, being less exposed to intermolecular influences. The effect of replacing the oxygen atoms in parachloral with sulphur atoms, is shown dramatically in Figure 5.7(a); the ring carbon atom resonances undergo an enormous upfield shift.

The effect of change of conformation on the nmr spectra of the 1,3,5-trianes.

The appearance of the ring carbon signals of the non-chair form of parachloral upfield from those of its chair form has already been discussed in the light of similar findings in other six-membered cyclic systems (Section 2.6.3). The same trend is observed in trithioparachloral (Figure 5.7). Furthermore, when either *cis*-chair structure adopts the *trans*-non-chair form, the ring proton signals shift downfield (Figure 5.7(b)).

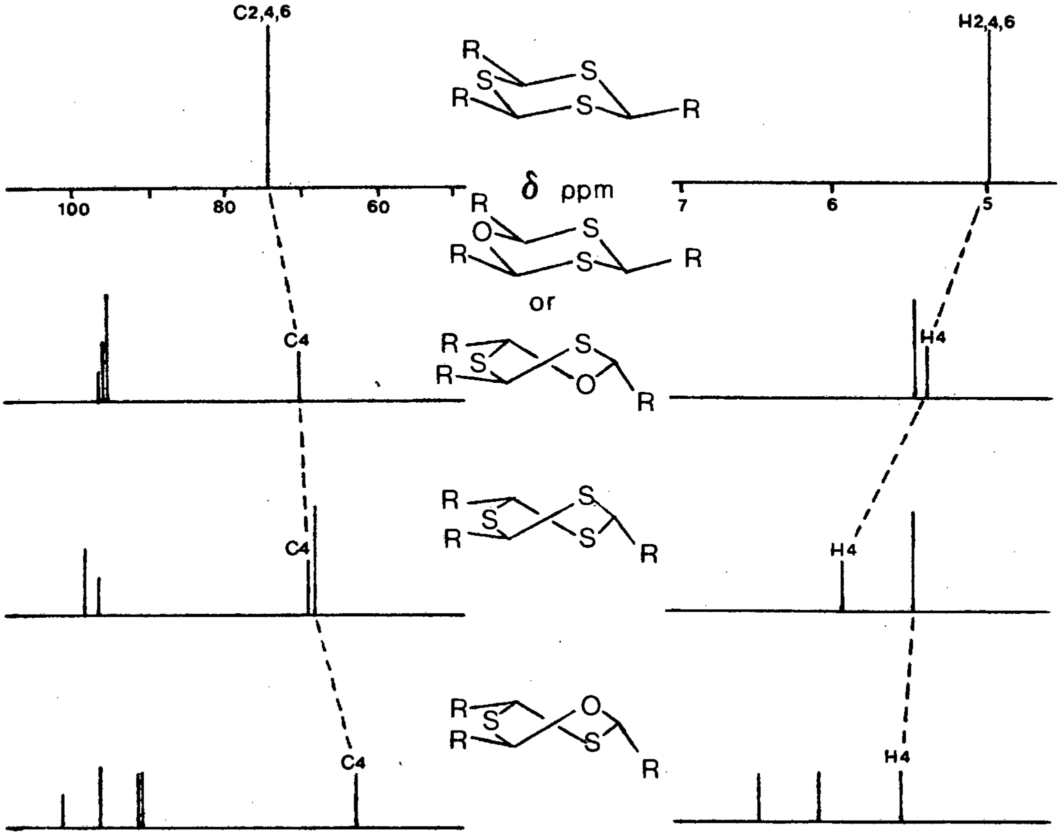
The effect of stepwise replacement of oxygen by sulphur on the nmr spectra of the 1,3,5-trianes.

The stepwise replacement of oxygen atoms in parachloral by less deshielding sulphur atoms, causes a stepwise upfield shift of the ring carbon signals (Figure 5.8). Care must be taken when comparing ^{13}C resonances from molecule to molecule. Firstly, only those isomers known to exist in non-chair conformations have been chosen for this comparison; *trans*-parachloral, 2-*trans*-dithio- and *trans*-trithioparachloral. As illustrated in Scheme 5.4, these *trans*-isomers consist of two twist conformers rapidly interconverting *via* a boat transition state (stable in the case of *trans*-parachloral). For the sake of consistency, the unique carbon atoms in each case are numbered C4 and the rings are numbered clockwise. C2, C4 and C6 in *trans*-parachloral are each flanked by two oxygen atoms, C2 and C6 in 2-*trans*-dithioparachloral by one oxygen atom and one sulphur atom, and all ring carbon atoms in *trans*-trithioparachloral by two sulphur atoms. Only those carbon atoms may be compared from molecule to molecule, which occupy the same positions in their respective rings. The position of a ring carbon atom in a twist conformer may be defined by its flanking heteroatoms and by the movement of its attached proton. For example, C6 in 2-*trans*-dithioparachloral is attached to H6 which oscillates between ψ_{ax} and I_c positions as



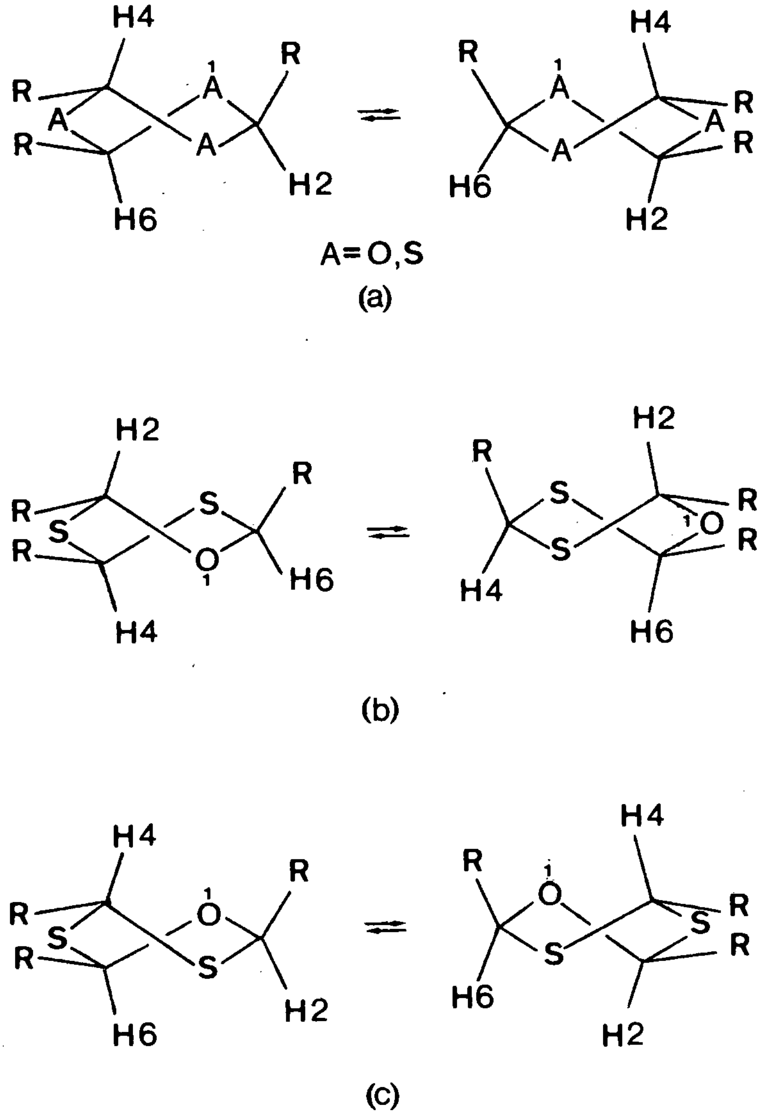
(a) (b)

Figure 5.8. The effect of stepwise replacement of oxygen by sulphur on the nmr spectra of the 1,3,5-trianes ($R = CCl_3$).



(a) (b)

Figure 5.9. Attempt to establish the configuration of α-dithioparachloral ($R = CCl_3'$).



C4(AA: ψ_{ax},ψ_{ax})
C2(AA: ψ_{ax},I_c)
C6(AA: ψ_{ax},I_c)

C4(SS: ψ_{ax},I_c)
C2(OS: ψ_{ax},ψ_{ax})
C6(OS: ψ_{ax},I_c)

C4(SS: ψ_{ax},ψ_{ax})
C2(OS: ψ_{ax},I_c)
C6(OS: ψ_{ax},I_c)

Scheme 5.4. Conformational equilibria in (a) trans-*parachloral and* trans-*trithioparachloral, (b) 2*-trans-*dithioparachloral and (c) 4*-trans-*dithioparachloral, showing hydrogen atom positions.*

twist-twist interconversion occurs. This carbon atom may therefore be designated C6(OS: ψ_{ax},I_c), where OS defines the flanking heteroatoms. It should be compared with the corresponding carbon atom C6 (equivalent to C2) in *trans*-parachloral, whose attached proton also oscillates between ψ_{ax} and I_c positions during twist-twist interchange. This carbon atom may be designated C6(OO: ψ_{ax},I_c). Thus, the variation of the chemical shifts of C6(OO: ψ_{ax},I_c), C6(OS: ψ_{ax},I_c) and C6(SS: ψ_{ax},I_c) in *trans*-parachloral, 2-*trans*-dithio- and *trans*-trithioparachloral respectively, provides a suitable description of the effect on the ring carbon atoms, of the stepwise replacement of oxygen atoms in parachloral by sulphur atoms (Figure 5.8). The same expected upfield shift is observed on comparison of the signals from C4(OO: ψ_{ax},ψ_{ax}), C2(OS: ψ_{ax},ψ_{ax}) and C4(SS: ψ_{ax},ψ_{ax}) in the same compounds.

An analagous trend is not observed in the corresponding ^{1}Hnmr spectra of these compounds, but as discussed already, the ring protons in these compounds are poor indicators of changes occuring in the rings. However, the comparison depicted in Figure 5.8(b) has been used to assign signals in the ^{1}H spectrum of 2-*trans*-dithioparachloral. In this compound, H4 is attached to the carbon atom (C4) flanked by two sulphur atoms, and is thus likely to give rise to the highest field resonance. In both *trans*-parachloral and *trans*-trithioparachloral, the unique protons H4 are those which occupy ψ_{ax} positions on both enantiomeric twist forms of the respective rings. In both cases, this proton resonates considerably downfield from the equivalent protons H2 and H6 (Figure 5.8(b)). Thus, it may be argued that of the two protons H2 and H6 in 2-*trans*-dithioparachloral, each flanked by an oxygen and a sulphur atom, H2 being the one which occupies ψ_{ax} positions on both twist forms of the molecule, gives rise to the lower field signal.

An attempt to establish the configuration of α-dithioparachloral.
A similar analysis of nmr data has been used in an attempt to establish the configuration of α-dithioparachloral. If this molecule has the *cis*-configuration, C4(SS) should occupy a similar environment to that of C4(SS) in *cis*-trithioparachloral. On the other hand, if α-dithioparachloral has the 4-*trans*-configuration, the environment of C4(SS: ψ_{ax},ψ_{ax}) should resemble that of C4(SS: ψ_{ax},ψ_{ax}) in *trans*-trithioparachloral. To check the hypothesis underlying this reasoning, the chemical shift of C4(SS: ψ_{ax},I_{c}) in 2-*trans*-dithioparachloral was compared with that of C2(SS: ψ_{ax},I_{c}) in *trans*-trithioparachloral. As Figure 5.9(a) shows, although C4 in α-dithioparachloral is much closer in chemical shift to C4 in *trans*-trithioparachloral than to C4 in its isomer, the large difference in chemical shift between C2 on *trans*-trithioparachloral and C4 on 2-*trans*-dithioparachloral undermines the hypothesis and allows no concrete conclusion to be drawn.

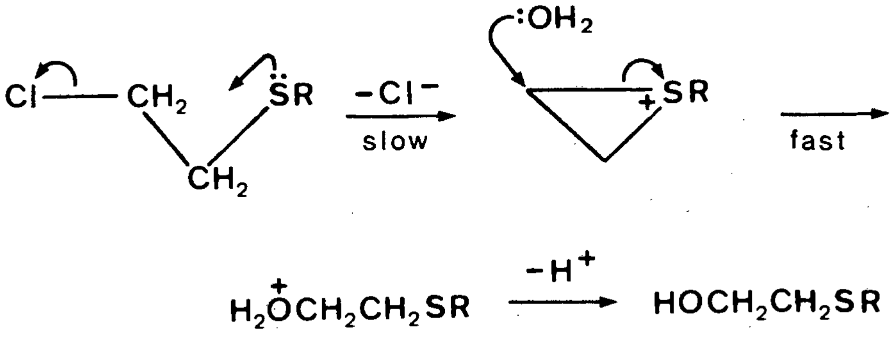
Figure 5.9(b) depicts a similar attempt using ^{1}Hnmr data. In this case, in support of the hypothesis, H4 in 2-*trans*-dithioparachloral resonates very close to H2 in *trans*-trithioparachloral but the chemical shift of H4 in α-dithioparachloral differs considerably from that of H4 in both *cis*- and *trans*-trithioparachloral. Obviously, such comparisons are naive and must be used with great caution. The determination of the configuration of α-dithioparachloral awaits a full *x*-ray crystallographic determination which will be carried out as soon as suitable crystals have been grown.

It is clear from Figures 5.7(a) and 5.8(a) that all the CCl_3 carbon atoms (C21, C41 and C61) resonate within a very narrow band. These carbon atoms must therefore be quite insensitive to the nature of the heteroatoms in the ring as well as to configurational and conformational changes in the ring.

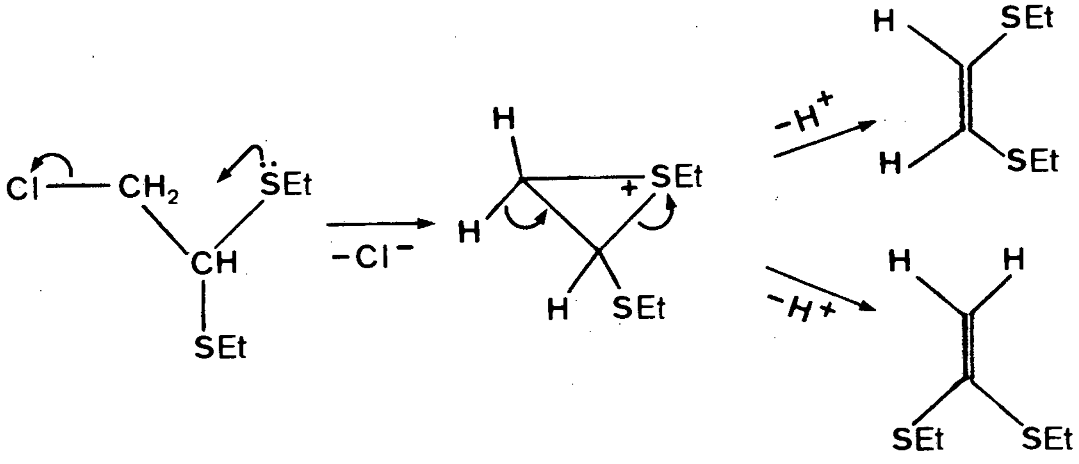
5.6 *DEHYDROCHLORINATION OF DITHIO- AND TRITHIOPARACHLORAL*

The $CHCCl_3$ groups lying between two sulphur atoms in dithio- and trithioparachloral undergo elimination of HCl under very mildly alkaline conditions. Chattaway and Kellett (1929) and other early workers (Bennett and Hock, 1925) offered the following description: "... chlorine atoms and bivalent sulphur atoms, when attached to adjacent carbon atoms, mutually affect one another's reactivity: the negative activity of the chlorine is accentuated, whilst the sulphur is rendered correspondingly inert, and very reluctant to assume a higher valency by oxidation or by addition of halogens or alkyl halides. Owing to the presence of large groups of chlorine atoms, this effect is very strongly marked in the thioparachlorals". A more modern explanation follows.

β-Halothioethers undergo hydrolysis much more rapidly than do their oxygen analogues. Their reactivity has been rationalised in terms of the formation of an episulphonium ion in the rate-determining step (Scheme 5.5; Brandsma and Arens, 1967). Furthermore, β-halothioacetals undergo spontaneous elimination of HCl with the formation of a rearranged product. This may also be explained by the formation of an intermediate episulphonium ion (Scheme 5.6). Formation of the product (5.18) could also be envisaged, especially from substrates with no β-hydrogen atoms. Thus, an analagous mechanism may be proposed to explain the easy elimination of HCl from the thioparachlorals (Scheme 5.7).

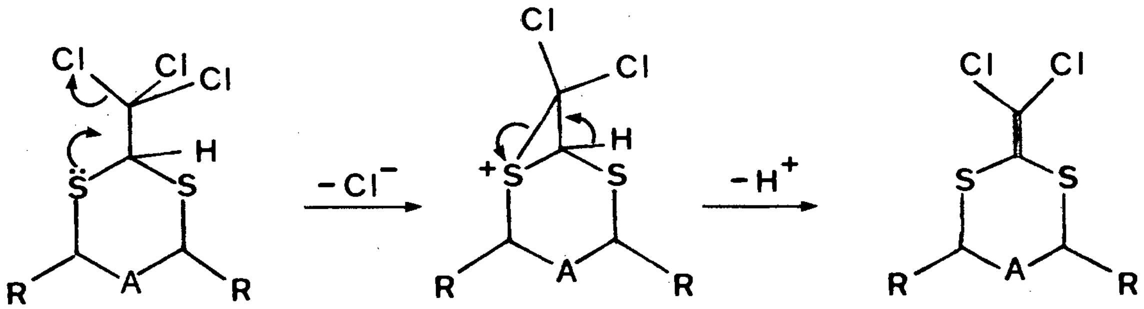


Scheme 5.5. *Hydrolysis of β-halothioethers.*



(5.18)

Scheme 5.6. *Dehydrochlorination of β-halothioacetals.*



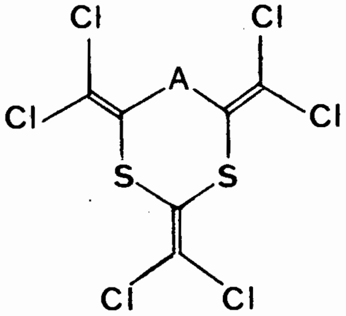
R=CCl$_3$ A=O,S

(5.19), A=O

Scheme 5.7. *Dehydrochlorination of dithio- and trithioparachlorals.*

The decreased tendency of the sulphur atoms in the thioparachlorals to undergo oxidation or to form adducts with alkyl halides, could result from the powerful electron-withdrawing action of the CCl_3 substituents on the polarisable sulphur electrons.

If trithioparachloral is treated with an alcoholic solution of potassium acetate (very feebly alkaline), three molecules of HCl are readily eliminated, giving 2,4,6-tris(dichloromethylene)-1,3,5-trithiane (5.20). If dithioparachloral is subjected to the same treatment, only the C4—C41 bond loses HCl with such ease, and the mildly alkaline conditions of a cold alcoholic solution of KCN are required to bring about the elimination of three molecules of HCl to give (5.21). The $CHCCl_3$ group in the 4-position in dithioparachloral has two alternative sites for the formation of an episulphonium ion, whereas those in the 2- and 6-positions having only one, lose HCl less easily.



(5.20) A = S

(5.21) A = O

Chattaway and Kellett (1929) showed that α- and β-dithioparachloral yield different forms of the dehydrochlorination product (5.19) when treated with alcoholic potassium acetate. They argued that since both *cis*- and 4-*trans*-dithioparachloral would give the same form of this compound, the *cis*-form, either α- or β-dithioparachloral must be the racemic 2-*trans*—6-*trans* mixture.

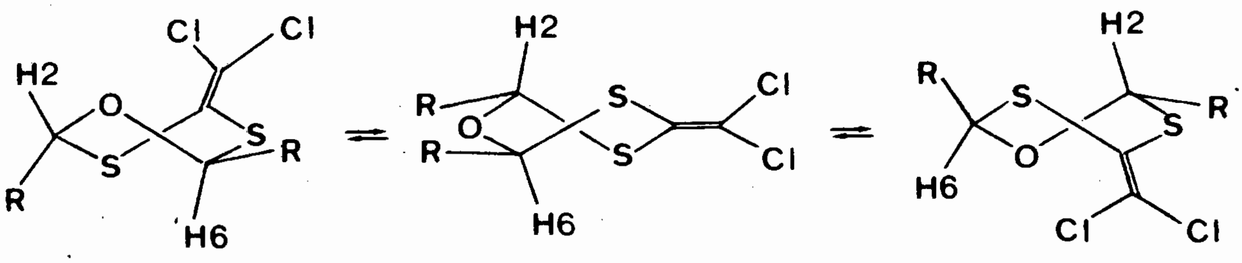
Following the method of Chattaway and Kellett, the mono- and tris-dehydrochlorinated forms of β-dithioparachloral were prepared by Professor H. Irving. The crystal structure of the former product has been determined by Dr. Anne Irving.

5.6.1 *Crystal structure of* trans-*2,6-bis(trichloromethyl)-4-dichloromethylene-1-oxa-3,5-dithiane*

Two views of the solid state conformation of *trans*-(5.19) are shown in Figure 5.10. The molecule retains the twist conformation of its parent, 2-*trans*-dithioparachloral. The ring is slightly flattened in the region of C4 because of the constraint imposed by the sp^2-hybridisation of this atom. The chair conformation of this molecule is destabilised by the strain which would result from an axial CCl_3 substituent.

5.6.2 ^{13}*C and* ^{1}*Hnmr of* trans-*2,6-bis(trichloromethyl)-4-dichloromethylene-1-oxa-3,5-dithiane and 2,4,6-tris(dichloromethylene)-1-oxa-3,5-dithiane*

The molecule *trans*-(5.19) possesses a potential two-fold rotation axis passing through O1, C4 and C41. However, as borne out by the torsion angles in Figure 5.10, this symmetry is not realised in the solid state. The ^{1}H and ^{13}Cnmr spectra of *trans*-(5.19) are presented in Figure 5.11. Apparently, in solution, the molecule undergoes rapid twist-twist interconversion between conformations (5.22), (5.23) and (5.24) so that H2



(5.22) (5.23) (5.24)

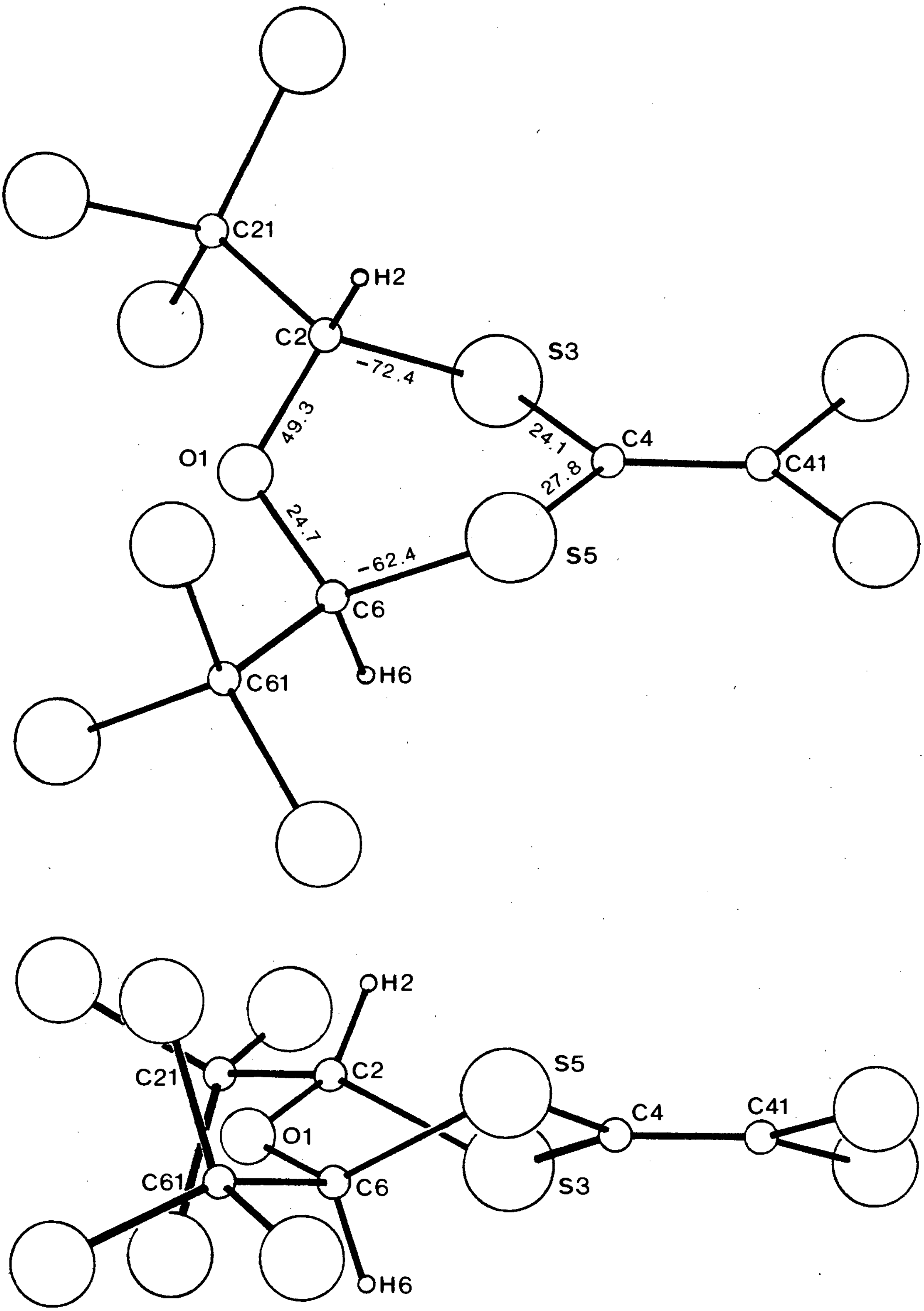


Figure 5.10. Two views of the solid state conformation of trans*-2,6-bis-(trichloromethyl)-4-dichloromethylene-1-oxa-3,5-dithiane showing torsion angles in the ring.*

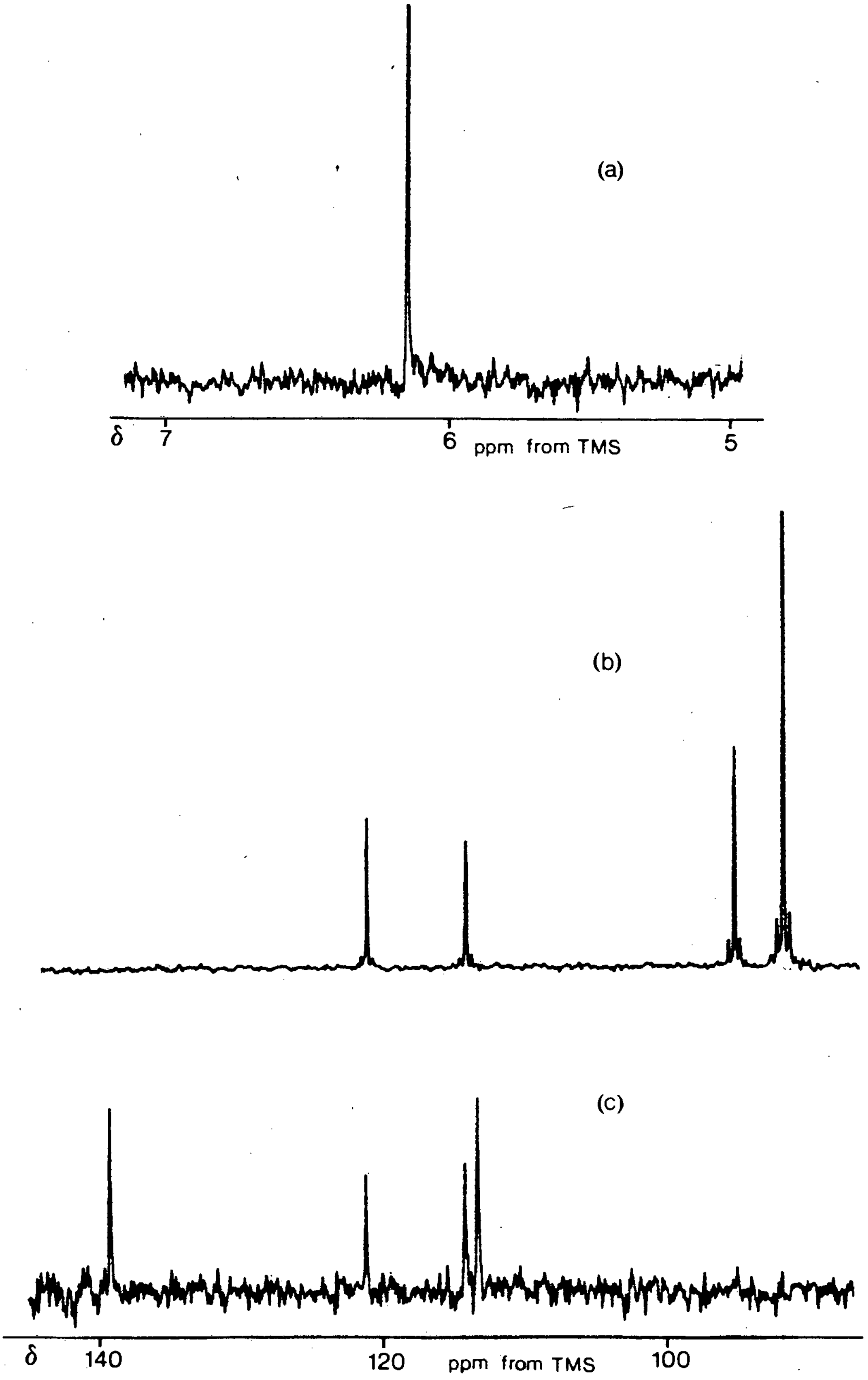


Figure 5.11. (a) ^{1}Hnmr spectrum and (b) broad-band decoupled ^{13}Cnmr spectrum of trans*-2,6-bis(trichloromethyl)-4-dichloromethylene-1-oxa-3,5-dithiane in $CDCl_3$. (c) Broad-band decoupled ^{13}Cnmr spectrum of 2,4,6-tris(dichloromethylene)-1-oxa-3,5-dithiane in $CDCl_3$.*

and H6 are equivalent protons and C2 and C6 are equivalent carbon atoms. The ^{13}C spectrum of (5.21) is shown in Figure 5.10(c). Numerical chemical shift data are listed in Table 5.1

*The effect of stepwise dehydrochlorination of 2-*trans*-dithioparachloral on its nmr spectrum.*

The ^{13}Cnmr spectra of 2-*trans*-dithioparachloral and its two dehydrochlorination products (5.23) and (5.21) are compared in Figure 5.12. The assignment of signals in the spectra of (5.23) and (5.21) is not straightforward. In the spectrum of (5.21), the lowest field signal must be due to C2 and C6, since these carbon atoms are expected to resonate downfield from C4 which lies between two sulphur atoms. Furthermore, it is possible that the signals from the three substituent carbon atoms lie close to each other, since these carbon atoms probably occupy similar positions on the flattened ring, and since they are expected to be quite insensitive to the nature of the heteroatoms (Section 5.5.1). Thus, the signal at δ 114.7 ppm is assigned to C41.

The trends which are observed in this series of spectra are satisfying. The first dehydrochlorination step causes the signals from C4 and C41 to shift far downfield as they are subjected to the strongly deshielding anisotropy of the carbon—carbon double bond. The signals from C2, C6, C21 and C61 are hardly affected by this change. Similarly, the signals from C4 and C41 are unmoved by the second dehydrochlorination step, whereas those from C2, C6, C21 and C61 experience large downfield shifts.

That C21 and C61 resonate at precisely the same chemical shift in 2-*trans*-dithioparachloral and in (5.23), and that the signals from C4 and C41 in (5.23) are identical to the corresponding signals in (5.21), surely

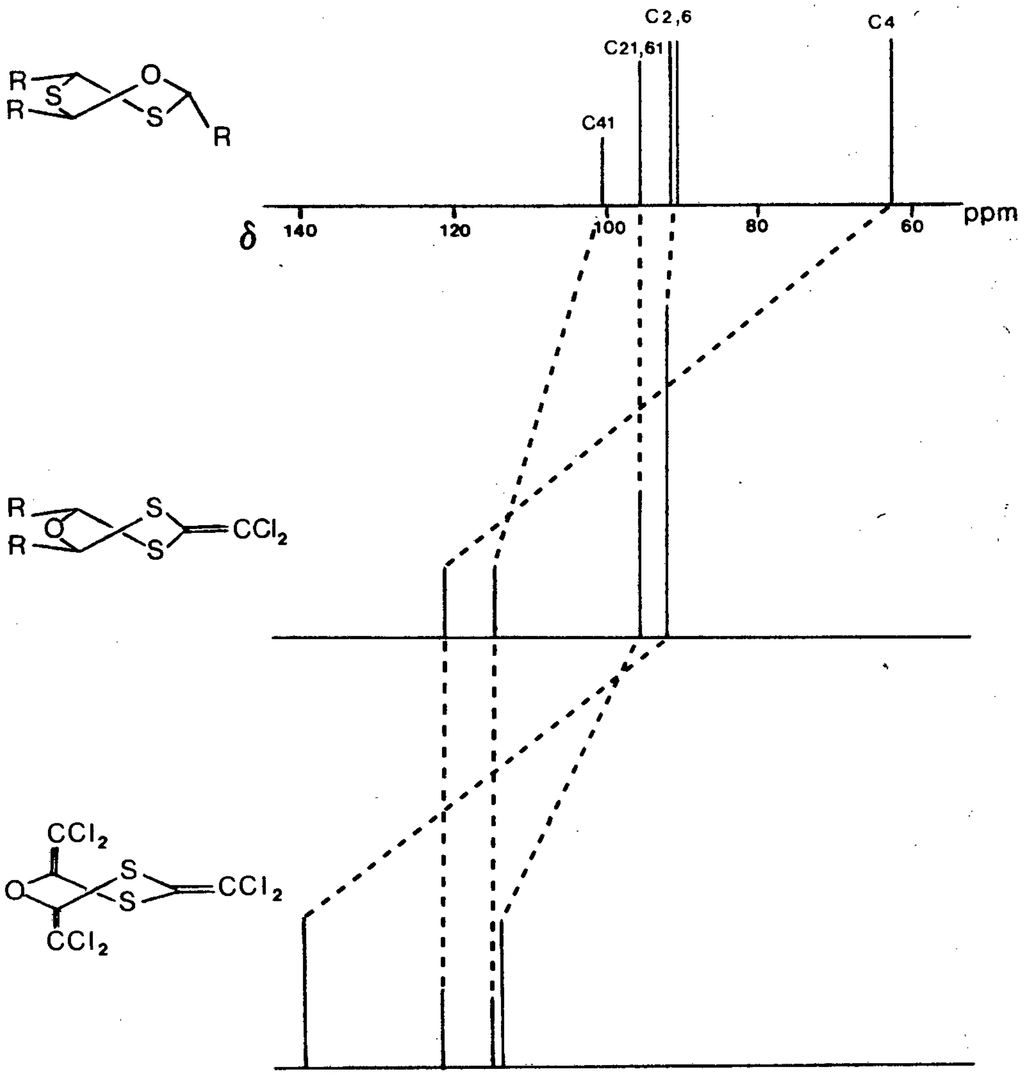


Figure 5.12. The effect of stepwise dehydrochlorination on the ^{13}*Cnmr spectrum of 2-*trans*-dithioparachloral (R =* CCl_3*).*

implies that the conformations of these compounds are very similar. Since 2-*trans*-dithioparachloral and (5.23) are both known to exist in twist conformations, the same appears to be true for (5.21), although in this case, the twist conformer must be noticeably flattened since the bond angles at the ring carbon atoms are expected to approach 120°.

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6 1,3,5-TRITHIANE 1,3,5-TRIOXIDES AS POTENTIAL METAL-SELECTIVE TERDENTATE LIGANDS

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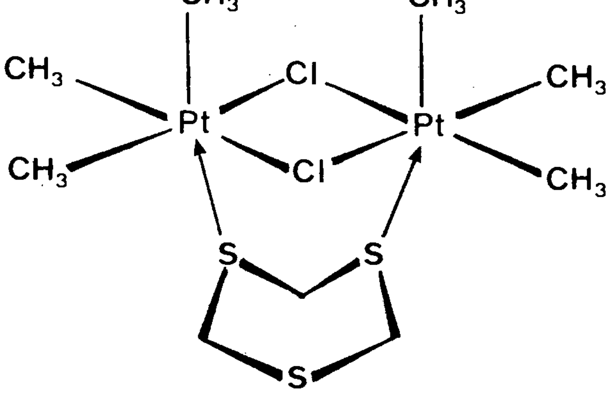
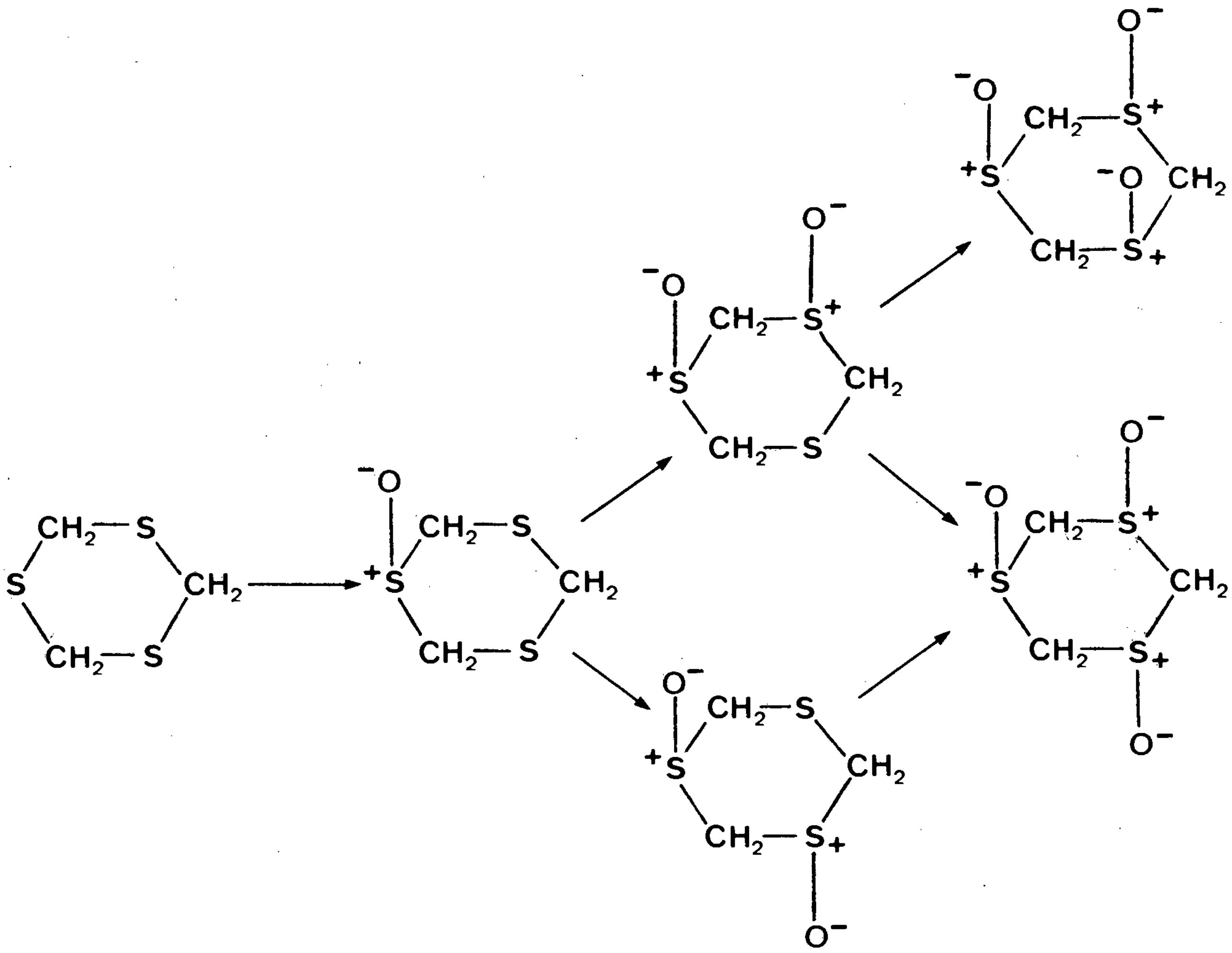
6.1 INTRODUCTION

Soon after optically active forms of certain sulphoxides, RR'SO, had been discovered (Harrison *et al.*, 1926), Bell and Bennett (1927) pointed out that the cyclic disulphoxide 1,4-dithiane 1,4-dioxide should have two isomers. After proving this to be so, they proceeded to isolate all possible sulphoxides of 1,3,5-trithiane, an impressive piece of experimental work which also constituted an exact determination of the configurations of these compounds (Scheme 6.1). Thus, the three-dimensional chemistry of sulphur became well established.

The idea of using 1,3,5-trithiane and its derivatives as ligands is not entirely unprecedented. The infrared spectra of complexes with the formulae $C_3H_6S_3 \cdot HgX_2$ and $C_3H_6S_3 \cdot AgX$ (X = halogen) have been discussed; in the former complex, mercury is thought to be tetrahedrally coordinated to two halogen atoms and two trithiane molecules, forming a polymeric structure (Dalziel *et al.*, 1966). An interesting dinuclear platinum complex (6.1) has been shown by *x*-ray diffraction to contain 1,3,5-trithiane in a boat conformation (Abel *et al.*, 1981). In the same study however, evidence was found that in the complex formed between



(6.1)



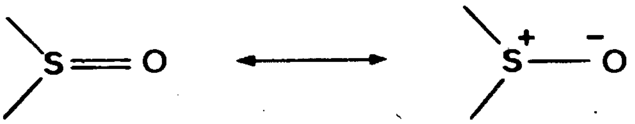
Scheme 6.1. Possible sulphoxides of 1,3,5-trithiane as seen by Bell and Bennett (1927).

platinum and *cis*-2,4,6-trimethyl-1,3,5-trithiane, the ligand is monodentate and retains the chair conformation.

Complexes with the formulae ML_6X_2 and ML'_nX_2, where M = Co(II), Ni(II), Cu(II), L = 1,3,5-trithiane 1-oxide, L' = *cis*- or *trans*-1,3,5-trithiane 1,3-dioxide, n = 2,3 and X = ClO_4^- , $CF_3SO_3^-$, have been examined by infrared spectroscopy and nmr, and found to be O-bonded sulphoxide complexes, although no precise structural information was reported (Nelson, 1973). Complexes of the formula $ML_6(ClO_4)_3$ where M = Sc(III), Ga(III), In(III) and L = 1-oxa-4-thiane 4-oxide have also been examined by infrared spectroscopy (Vincentini and De Lima, 1973).

6.2 *SULPHOXIDES AS LIGANDS*

Of the two canonical forms (6.2) and (6.3) of the sulphoxide moiety, the polar form (6.3) has been shown by *x*-ray spectroscopy to be the more



(6.2) (6.3)

realistic (Davies, 1981). An acceptable model describes oxygen as sp^2-hybridised; one sp^2-orbital overlaps with a sulphur sp^3-orbital, leaving two oxygen lone pairs (sp^2) for donation to a Lewis acid. Vacant, low-lying d-orbitals on sulphur are available for d_π-p_π overlap with the filled p-orbital on oxygen. The extent of d_π-p_π overlap depends on the strength of the Lewis acid to which the molecule bonds.

It has been found by *x*-ray crystallography, that coordination through oxygen or through sulphur little affects the geometry of the ambidentate sulphoxide ligand. In O-bonded complexes, M—O bonds are longer than the relevant covalent distances (Davies, 1981).

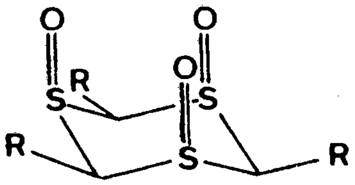
In general, sulphoxides bond to hard metals through oxygen, and to soft metals through either oxygen or sulphur. *X*-ray crystallography and infrared spectroscopy have been the most widely used techniques for determining the mode of coordination in sulphoxide complexes. For example, Cr(III), Mn(II,III), Fe(II,III), Co(II), Ni(II) and Cu(II) form O-bonded sulphoxide complexes, while for Mo(IV), Ru(III), Rh(I,II,III), Ir(I,III), Pt and Pd, both O- and S-bonded complexes have been reported (Davies, 1981).

6.2.1 *Potential of 1,3,5-trithiane 1,3,5-trioxides as ligands*

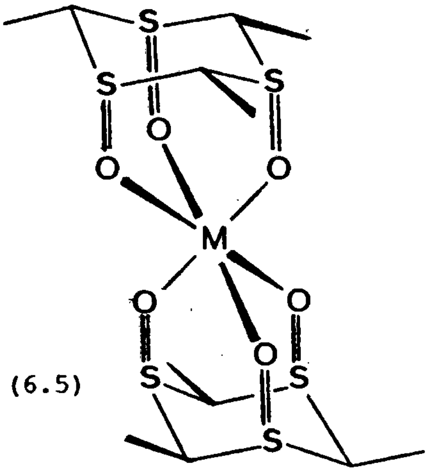
It was mentioned in Section 1.1 that the original aim of this project was to prepare a trisulphoxide of the type (6.4) as a potential terdentate ligand. It was encouraging to find that the sulphoxide group in thiane oxides seems to have an inherent preference for the axial orientation. For example, in thiane 1-oxide, the conformation with an axial sulphoxide group is prefered in solution (Lambert and Keske, 1966). Furthermore, *x*-ray diffraction has shown that in the solid state, *trans*-1,4-dithiane 1,4-dioxide adopts the chair conformation with both sulphoxide groups axially oriented (Shearer, 1959), while the *cis*-isomer chooses the chair conformation with one equatorial and one axial sulphoxide group (Montgomery, 1960).

In agreement, a molecular mechanics study suggested that in thiane 1-oxide, 1,4-dithiane 1-oxide, *trans*-1,4-dithiane 1,4-dioxide and *cis*-1,3,5-trithiane 1,3-dioxide, conformations with axially directed sulphoxide groups are the most stable (Allinger and Kao, 1976). However, the same study indicated that in 1,3-dithiane 1-oxide, 1,3,5-trithiane 1-oxide and *cis*- and *trans*-1,3,5-trithiane 1,3,5-trioxides, equatorial sulphoxide groups give rise to more stable conformations.

Thus, it appears that the axial-equatorial preference of oxygen in cyclic sulphoxides is highly variable, depending on the steric and electrostatic interactions present in each case. Nevertheless, there is a finite possibility that a 1,3,5-trithiane 1,3,5-trioxide can be prepared with three axially directed sulphoxide groups (6.4). It may be desirable to include fairly bulky substituents, R, to anchor the trithiane ring in the required chair conformation. However, these should not be so large as to interfere with subsequent coordination.



(6.4)



(6.5)

Conceivably, the molecule (6.4) could combine with a suitable metal to form a complex with the structure (6.5). It is possible to estimate the ideal size of the metal ion which would be expected to participate in such a complex. Assuming tetrahedral geometry in the ligand and $|C–S| = 1.82$ Å, the non-bonded distances (within each ligand) $|S\cdots S| = |O\cdots O| \approx 3.0$ Å. For $O\hat{M}O = 90°$, the distance $|M–O| \approx 2.1$ Å. The ligand is expected to be quite inflexible with respect to the size of metal ion which it accommodates, because of the rigidity of the chair structure on which it is built. Thus, a fair degree of selectivity is anticipated.

Some |M—O| distances obtained from *x*-ray crystallographic studies on O-bonded sulphoxide complexes are listed in Table 6.1. From this data, the metals Fe(III), Mo(VI), Rh(III) and Ru(II,III) can be expected to form stable complexes with the ligand (6.4), whereas Cu(II) may be too small and Ag(I), Hg(II) and Eu(III) too large to form complexes of great stablility.

6.3 PREPARATION OF 1,3,5-TRITHIANE 1,3,5-TRIOXIDES

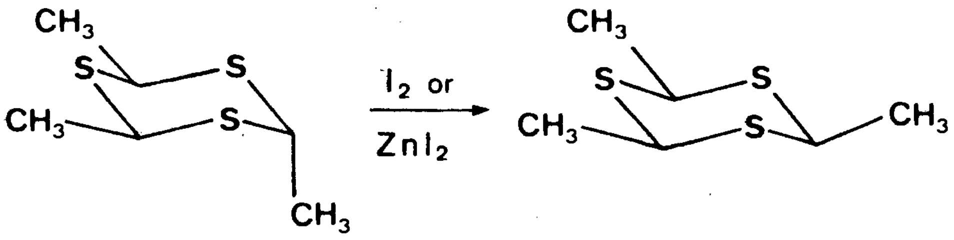
A mixture of *cis*- and *trans*-2,4,6-trimethyl-1,3,5-trithianes was kindly provided by Dr. K.R. Koch of this laboratory. The mixture was converted to the pure *cis*-isomer (6.6) by isomerisation with iodine (Scheme 6.2; Suyver, 1905). After recrystallisation from acetone, its purity was checked by m.p. (123-125°C), microanalysis (Found: C 40.1, H 6.8%. Calc. for $C_6H_{12}S_3$: C 39.96, H 6.71%), ^{1}Hnmr (Figure 6.1) and mass spectrometry (Figure 6.2 and Scheme 6.3).

Some of the many attempts made at the selective oxidation of (6.6) are described here. Although some did produce the trisulphoxide, and possibly even the conformer (6.4), a mixture of products usually resulted. Without due care, the trithiane may be over-oxidised to a variety of sulphones. There also arose the difficulty of how to identify the desired trisulphoxide if it should be formed. Figure 6.3 shows the possible trisulphoxides of (6.6). Although ^{1}Hnmr may be used to distinguish between the more symmetric isomers and those of lower symmetry, a convenient method to differentiate between (6.7) and (6.8) does not present itself so easily. Techniques based on infrared frequency shifts and ^{1}Hnmr coupling constants, for recognising equatorial from axial sulphoxide groups (Cairns *et al.*, 1964; Khan *et al.*, 1975), are unsuitable for the

Table 6.1

Some M—O distances obtained from x-ray crystallographic studies on O-bonded sulphoxide complexes (Davies, 1981).

Metal	|M—O|	Metal	|M—O|
Fe(III)	2.006(6)	Rh(III)	1.990
Cu(II)	1.955(4)	Ag(I)	2.358
Mo(VI)	2.17	Hg(II)	2.54
Ru(II)	2.142(3)	Hg(II)	2.58(1)
Ru(III)	2.050(7)	Eu(III)	2.40



Scheme 6.2. Isomerisation of trans- *to* cis-*2,4,6-trimethyl-1,3,5-trithiane.*

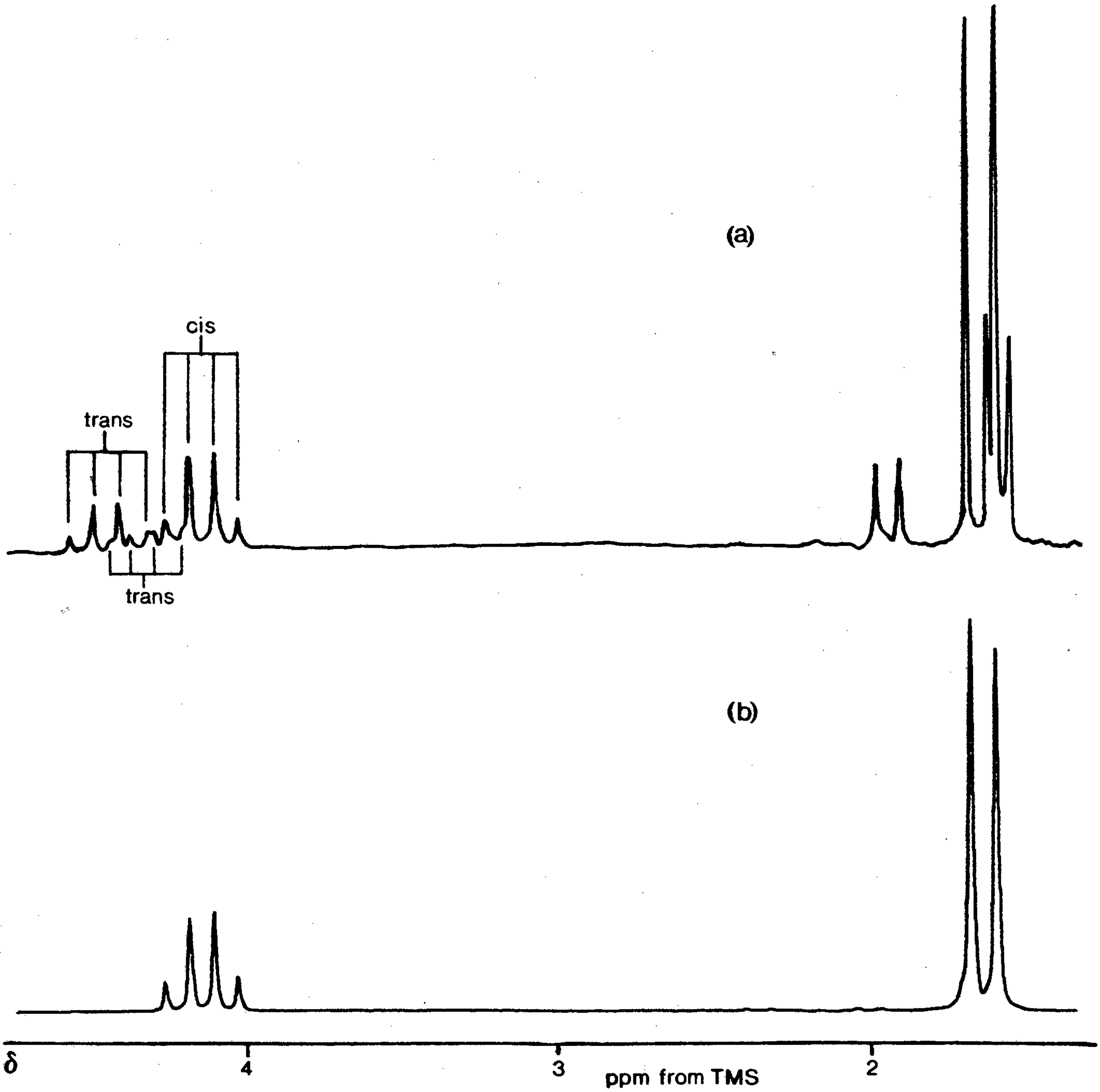


Figure 6.1. (a) ^{1}Hnmr spectrum of a mixture of cis- *and* trans-*2,4,6-trimethyl-1,3,5-trithianes in CDCl$_3$. (b) After treatment of same with I$_2$.*

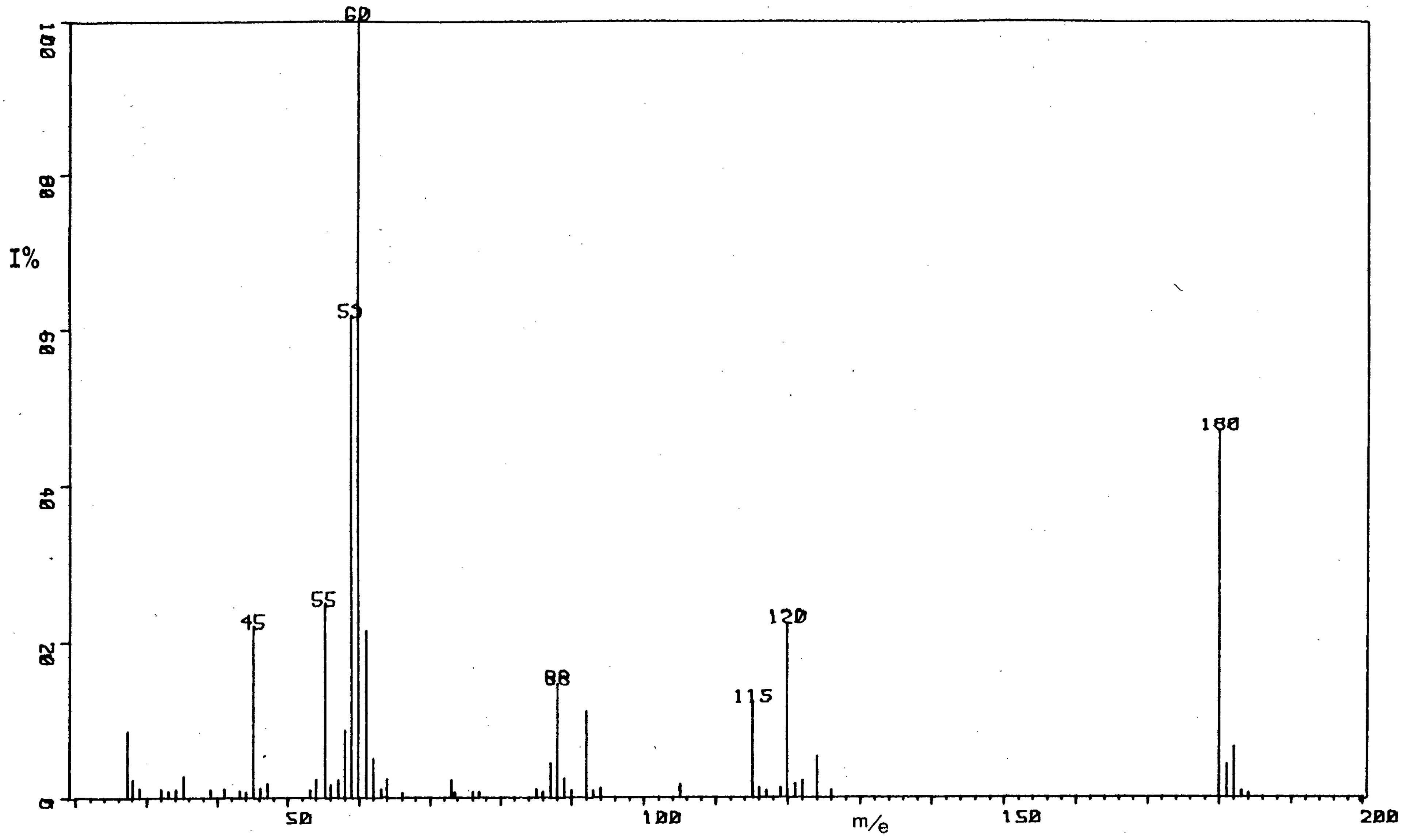
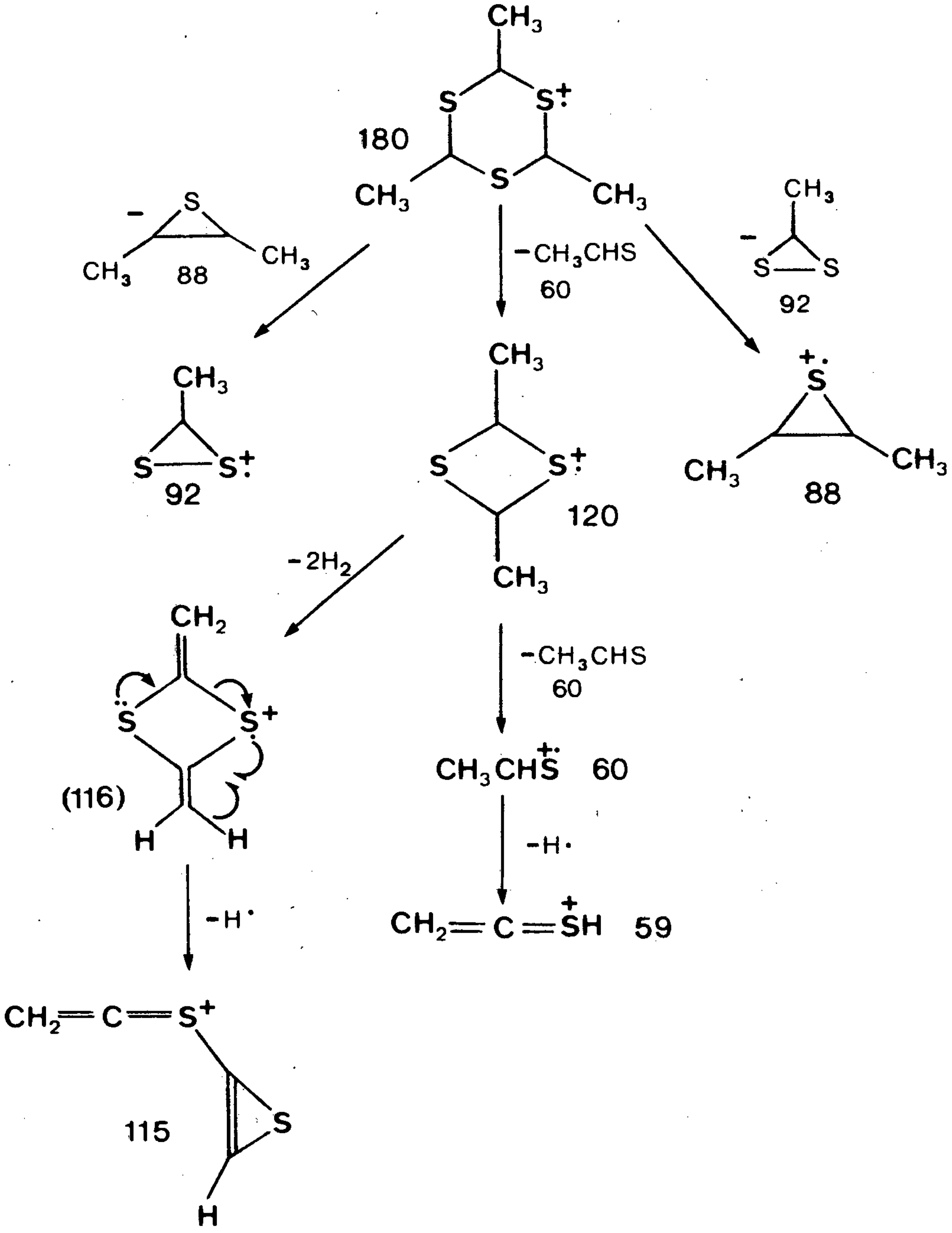
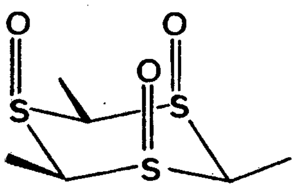


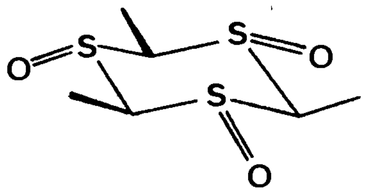
Figure 6.2. 70 eV mass spectrum of cis-2,4,6-trimethyl-1,3,5-trithiane.



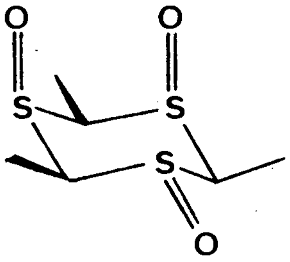
Scheme 6.3. Proposed mass spectral fragmentation of cis-2,4,6-trimethyl-1,3,5-trithiane.



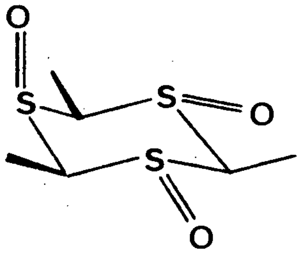
(6.7)



(6.8)



(6.9)



(6.10)

Figure 6.3. Possible trisulphoxides of cis-*2,4,6-trimethyl-1,3,5-trithiane.*

present compounds. Short of *x*-ray crystallography, perhaps dipole moment measurement would be the most convenient and convincing tool. Alternatively, a technique based on the coupling constants between methyl protons and ring protons, or those between ring protons and ring carbon atoms could possibly be developed.

6.3.1 Peroxide oxidation of (6.6)

30% H_2O_2 (29.4 mmoles) in glacial acetic acid (10 mℓ) were added with stirring over a period of 10 min, to a solution of (6.6) (9.81 mmoles) in glacial acetic acid (50 mℓ). After stirring for 24 h at room temperature, the acetic acid was removed on a rotary evaporator, leaving a white crystalline product. Three recrystallisations from ethanol yielded a product melting at 162-172°C; microanalysis showed only trioxides of (6.6) to be present (Found: C 31.6, H 5.4%. Calc. for $C_6H_{12}S_3O_3$: C 31.68, H 5.30%). Tlc on silica gel plates with 13% ethanol/benzene revealed three components which were then partially separated on a column (Ø25mm x 300 mm) packed with deactivated silica gel (containing 25% m/m water), and eluted with 13% ethanol/benzene. The column produced three distinct fractions, two of which were shown by ^{1}Hnmr to contain many components. The third gives a fairly simple spectrum (Figure 6.4) pointing to either of the structures (6.9) or (6.10).

6.3.2 Bromine oxidation of (6.6)

Br_2 (27.3 mmoles) in CCl_4 (50 mℓ) was added slowly (10 drops min^{-1}) with stirring to a solution of (6.6) (8.48 mmoles) in CCl_4 (50 mℓ) in an ice bath. Slow oxidation prevents sulphone formation and perhaps encourages selectivity. The mixture was allowed to stir overnight at room temperature after which, the excess Br_2 was destroyed with DMSO. The mixture was then shaken for 2 h with 1M NaOH solution (25 mℓ) to

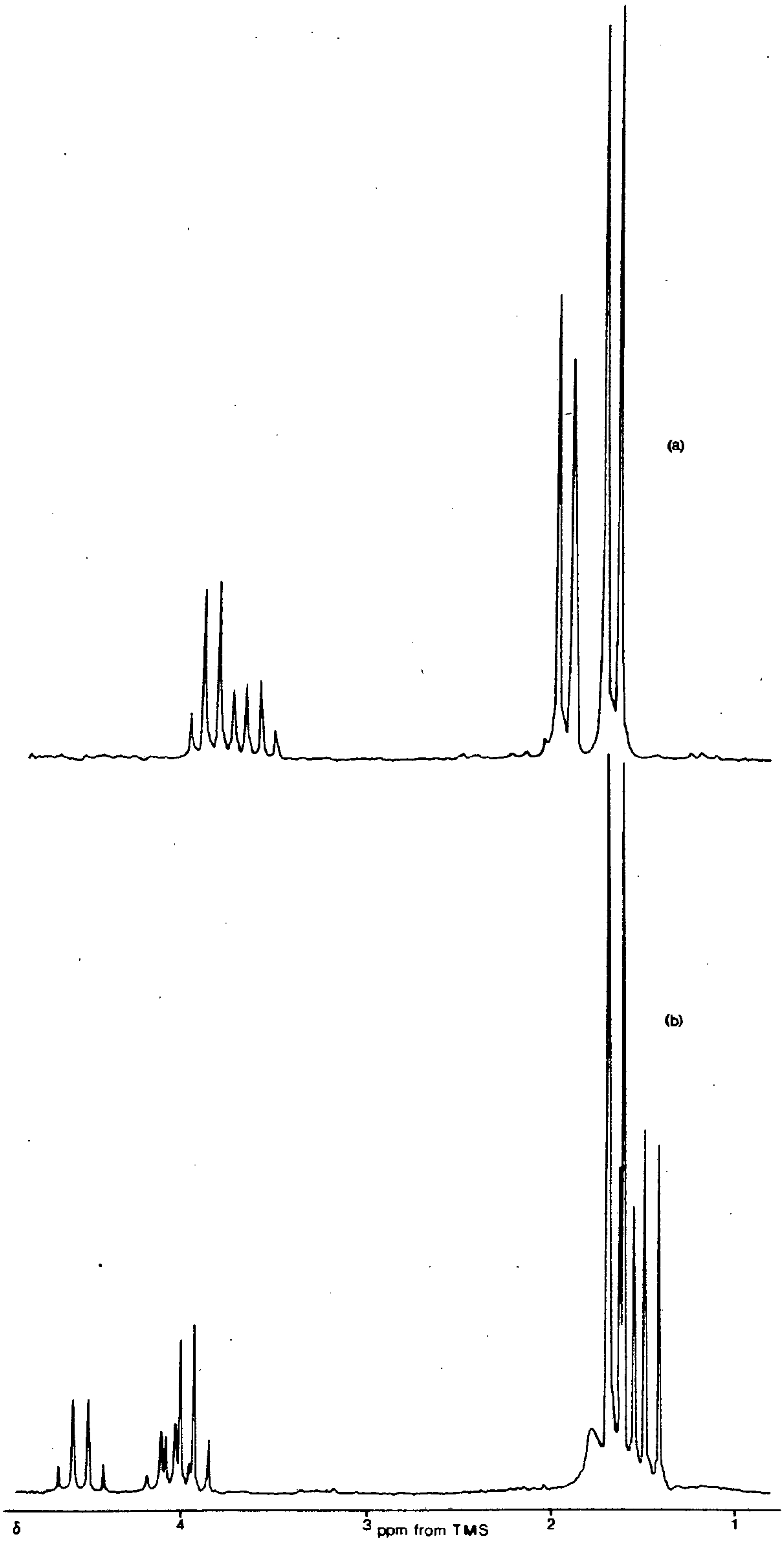


Figure 6.4. Product of (a) peroxide-oxidation and (b) TBAPI oxidation of (6.6).

hydrolyse the intermediate adduct. The organic layer was separated and the solvent removed, leaving a very complex mixture of products.

6.3.3 Tetrabutylammonium periodate oxidation of (6.6)

TBAPI has been found to be an excellent selective oxidant for alkyl and aryl sulphides, producing good yields of sulphoxides (Santaniello *et al.*, 1980). Following their method, (6.6) (1.54 mmoles) was added to TBAPI (4.61 mmoles) in $CHCl_3$ (9 mℓ). The solution which became yellow immediately, was refluxed for 4 h. The reaction mixture was then passed down a short silica gel column to remove polar tetrabutylammonium salts, and the solvent removed on a rotary evaporator, leaving a sticky yellow product. Recrystallisation from hot water gave an oily product whose ^{1}Hnmr is relatively simple (Figure 6.4). However, no solid could be obtained.

6.4 CONCLUSION

Much work remains to be done on this section of the project. TBAPI is perhaps the most hopeful oxidising agent of those tried. Successful oxidations of sulphides to sulphoxides have been performed without danger of over-oxidation, by passing a solution of the sulphide down a column of sodium metaperiodate adsorbed onto silica gel (Liu and Tong, 1978). The gentleness of this method is appealing.

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7

CONCLUSION

Until this decade, chemical intuition, coupled with the results of such inferential techniques as dipole moment measurement, infrared and nmr spectroscopy, led chemists to believe that *trans*-parachloral existed in a chair conformation, supporting an axial trichloromethyl group. Although, with recent advances in conformational analysis, some might have predicted a twist conformation for this trioxane, the crystallographic proof of its preference for the classical boat conformation in the solid state, came as a complete surprise.

This is a common scientific story, and serves to emphasise the degree of caution which must be exercised when interpreting experimental data. It also illustrates the power of *x*-ray crystallography which, although limited to the solid state, probably heads the list of definitive techniques for structure elucidation. Another witness to this power is α-dithioparachloral, whose configuration could not be established by chemical methods, nor by simple nmr considerations, but will certainly be revealed by an *x*-ray crystallographic study.

Further investigations in the following areas could help to solve some of the problems and unanswered questions arising from this work:

(i) A ^{13}C or 270 MHz ^{1}Hnmr temperature study of α-parachloral might provide positive evidence for the existence of its chair form and allow measurement of the chair—non-chair energy difference.

(ii) The intramolecular hydrogen bond in α-parachloral might be detected in a more comprehensive infrared study.

(iii) The variation in size along the series CF_3, CCl_3, CBr_3, CI_3 is vast, and since very little is known about the trioxanes prepared from haloaldehydes besides chloral, a comparative conformational study of these relatives of parachloral may prove rewarding.

(iv) The crystal structure of *cis*-chloralide should show whether this compound, like the *cis*-1,3-dioxolan-4-one (4.18), adopts the O1-envelope conformation, thereby shedding more light upon the factors which determine conformation in these heterocycles.

(v) An interesting phenomenon which presented itself during the study of chloralide and which deserves further investigation, is the observed increase in carbonyl stretching frequency with decreasing ring size in cyclic ketones (Section 4.6).

(vi) The continuing crystallographic study of the dithioparachlorals and their dehydrochlorination products should reveal the configuration of α-dithioparachloral, and provide a useful addition to the growing class of six-membered cyclic systems which prefer non-chair conformations.

(vii) A conformational analysis of *trans*-trithioparachloral might show whether or not its chair conformer exists in the solid state or in solution. It would be of interest to discover the effects on conformational equilibria, of replacing the oxygen atoms in α-parachloral with sulphur atoms.

(viii) The successful preparation of the triaxial trisulphoxide of a substituted trithiane would require the development of a technique to distinguish between all-axial and all-equatorial isomers.

(ix) Once prepared, the chemistry of these ligands would be many-faceted. Such topics as the crystallography of some of their metal complexes, an investigation of metal-selectivity and a study of their analytical applications, could provide a wealth of research possibilities.