



**Studies on photochromic and potentially
mesogenic mercury(II) dithizonates**

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MASTER OF SCIENCE

by

NATALIE LYN CROMHOUT
B.Sc. (Hons) *Natal*

Department of Chemistry
University of Cape Town
Rondebosch
7700
South Africa

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Abstract

ABSTRACT

Studies on Photochromic and Potentially Mesogenic Mercury(II) Dithizonates

The 4-(4'-n-alkoxybenzylideneanilino)mercury(II) dithizonates, $C_nH_{2n+1}OC_6H_4CH=NC_6H_4-Hg(HDz)$ ($n = 1, 4, 12, 14$ or 18), were prepared by complexation of dithizone (1,5-diphenylthiocarbazone, H_2Dz) with the corresponding 4-(4'-n-alkoxybenzylideneanilino)mercury(II) acetates. The 4-(4'-n-alkoxybiphenyl)mercury(II) dithizonates, $C_nH_{2n+1}OC_6H_4C_6H_4-Hg(HDz)$ ($n = 4, 5, 10, 14$ or 18), were similarly prepared by reaction of dithizone with the appropriate 4-(4'-n-alkoxybiphenyl)mercury(II) bromides, although the latter compounds, derived from the 4-n-alkoxy-4'-bromobiphenyls, were not isolated. The preparation of the 4-(4'-n-octyloxyazobenzene)mercury(II) dithizonate, $C_8H_{17}OC_6H_4N=NC_6H_4Hg(HDz)$, from 4-n-octyloxy-4'-bromoazobenzene was attempted but the chosen synthetic method was not successful. The thermal behaviour of those series of compounds isolated was investigated by polarized optical microscopy and differential scanning calorimetry. The organomercury(II) acetates displayed a limited, poorly-defined mesomorphism and the type of any mesophase formed remains unidentified. The 4-n-alkoxy-4'-bromobiphenyls (alkoxy = $C_nH_{2n+1}O$, $n = 3-5, 10-12, 14-16$ or 18) exhibited liquid crystalline behaviour within a broad temperature range for the compounds with $n \geq 10$ and the nature of the mesophases was tentatively assigned as smectic D and C. The 4-n-alkoxy-4'-bromoazobenzenes (alkoxy = $C_nH_{2n+1}O$, $n = 5, 10, 12$ or 14) showed monotropic ($n = 5, 10$ or 12) or enantiotropic ($n = 14$) nematic and smectic A mesophases. However, none of the dithizonate derivatives was mesomorphic and this was attributed to the geometry of the dithizonate ligand. The organomercury(II) dithizonates were photochromic in organic solvents, displaying reversible colour changes from yellow to blue on irradiation with visible light. The visible absorption spectra of these solutions were recorded and appeared to be independent of the nature of the long-chain organic ligand. This photochromism was not observed in the solid state.

Abbreviations used in Text

ABBREVIATIONS USED IN TEXT

b.p.	=	boiling point
COSY	=	correlated spectroscopy
c.p.	=	clearing point
dec.	=	decomposition
DMF	=	dimethylformamide
DMSO	=	dimethylsulfoxide
DSC	=	differential scanning microscopy
HDz	=	dithizonate anion
H ₂ Dz	=	dithizone
I	=	isotropic liquid
<i>J</i>	=	coupling constant
K	=	crystalline phase
m.p.	=	melting point
<i>m/z</i>	=	mass-to-charge ratio
N	=	nematic mesophase
N*	=	chiral nematic mesophase
NMR	=	nuclear magnetic resonance (m = multiplet, s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet)
ppm	=	parts per million
S	=	smectic mesophase (S _A = smectic A, S _B = smectic B, S _C = smectic C, S _F = smectic F, S _I = smectic I, S _G = smectic G)
TG	=	thermogravimetry
THF	=	tetrahydrofuran
TLC	=	thin-layer chromatography

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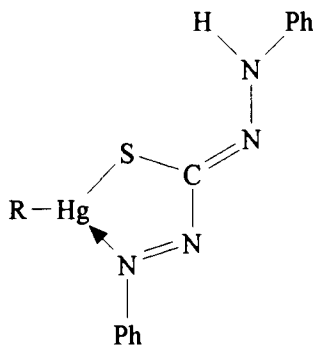
Chapter One

Introduction

CHAPTER 1

INTRODUCTION

The objective of the work reported in this dissertation was to synthesize liquid crystalline materials incorporating the photochromic mercury(II) dithizonate system **1**.



1

This chapter aims to introduce the subject of liquid crystals, with emphasis on the metal-containing systems. The criteria to be considered in the design of a mesogenic molecule will be discussed, in terms of which the compounds synthesized in this study were chosen. The photochromism of the metal dithizonates will be briefly reviewed and the particular advantages offered by the mercury complexes described.

Liquid crystals

The liquid crystalline phase is a fourth state of matter which may be observed as an intermediate phase between the solid crystal and the liquid states – these intermediate phases are called mesophases and the molecules which give rise to them are termed mesogens.

Liquid crystals have been defined as ‘orientationally ordered liquids’ or ‘positionally disordered crystals’.¹ In the conventional crystalline solid the molecules are

positionally fixed in a regular three-dimensional array; in the liquid phase only a very short-range orientational order may exist between anisotropic molecules. Liquid crystals are characterized by the fact that the long-range positional ordering of the solid is either absent or significantly reduced, while a degree of orientational order is maintained. Since some manner of shape anisotropy is required to generate such a structure it can be expected that macroscopic properties such as refractive index, electric conductivity and permittivity, and elasticity are also anisotropic. Furthermore, because of the removal of one or more degrees of order, the mesophase is mobile or viscous – otherwise a property only of the liquid state – and hence the application of external fields can easily induce changes in the above macroscopic properties.

In fact, liquid crystals uniquely combine the mechanical behaviour of liquids with the anisotropic physical properties of a crystal. It is the exploitation of these features which has led to the widespread application of liquid crystalline materials in such diverse technologies as electro-optic displays,²⁻⁴ temperature-sensing devices⁴⁻⁶ and high-performance polymers.⁷

The vast majority of liquid crystalline materials finding use in such applications are organic compounds, the synthesis of metal-containing liquid crystals – metallomesogens – being a relatively new area of the chemistry of liquid crystals, with most of the work having been carried out only since the early 1980's. The subject has recently been comprehensively reviewed.^{1,8-10}

The introduction of a metal centre having a large and polarizable concentration of electron density has the potential to affect many of the anisotropic properties associated with liquid crystals, and some data have already been amassed quantifying the enhanced linear polarizability¹¹ and increased birefringence¹² of a number of metal complexes compared with the free mesogenic organic ligands. Furthermore, the coordination of a metal can generate geometries and hence shapes not easily

accommodated in purely organic systems.¹ The oxidation states of many transition metals can give highly coloured compounds which may be used to advantage in so-called guest-host display devices;¹³ many have unpaired electrons and exhibit paramagnetism and even ferromagnetism, features¹⁴ which further extend the range of useful physical properties of metallomesogens.

Before further discussion of the molecular structure–property relationships of metallomesogens it is pertinent to introduce some of the terminology and classifications applied to liquid crystal systems.

Liquid crystals are broadly divided into two classes, *viz.* lyotropic and thermotropic, according to the manner in which the mesophase is generated.

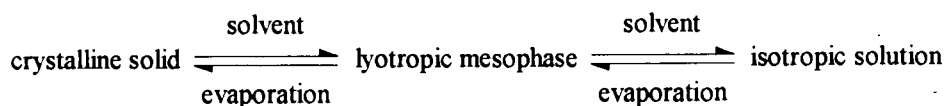
Lyotropic liquid crystals

Lyotropic mesophases are exhibited by surfactant amphiphiles such as sodium stearate **2**, in which a polar end group is attached to a non-polar hydrophobic chain.¹



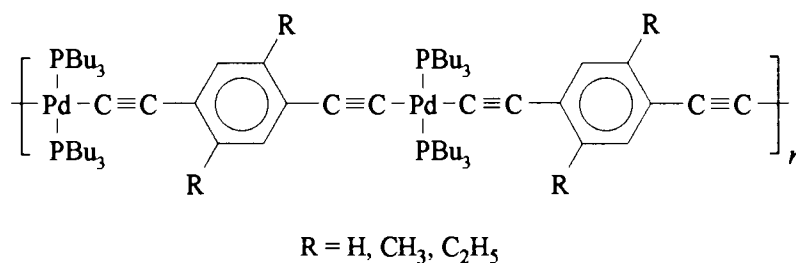
2

When such a compound is dissolved in a solvent (typically water) the molecules organize into micelles so as to minimize the unfavourable interactions between the solvent and the long alkyl chains. At a certain concentration and temperature the micelles further organize into ordered arrays and it is these arrays which constitute the lyotropic liquid crystal phase. In an excess of solvent the micelles are dispersed to give the isotropic liquid. The phase changes can be summarized as in Scheme 1.²



Scheme 1

Certain rigid polymers are also known to form mesophases in aqueous and non-aqueous solvents, one such example being the alkynyl palladium complexes **3**, which form lyotropic mesophases in trichloroethylene.¹⁵



3

However, few other lyotropic metallomesogens (except those of the alkali and alkaline earth metals)¹⁶ have been prepared and these systems are not discussed further.

Thermotropic liquid crystals

Most metallomesogens are thermotropic, where the mesophase arises as a result of a change in temperature. The solid transforms to the liquid crystal at the melting point and then passes to the isotropic liquid at a higher temperature called the clearing point, where the terminology reflects the fact that the mesophase often appears turbid, whereas the true liquid is optically clear.⁸

If the mesophase is manifested in both the heating and cooling processes it is said to be enantiotropic and is thermodynamically stable. A monotropic phase is unstable with respect to the crystalline solid and is obtained only on supercooling from the isotropic liquid.

Thermotropic liquid crystals are further subdivided into two main groups based on molecular structure. It was recognized soon after the discovery of liquid crystals that rigid, elongated molecules were of a shape suitable to give rise to a mesophase: such rod-like or calamitic molecules can readily gain translational freedom but maintain rotational or orientational order.¹⁷ More recently, similar behaviour has been observed in discotic or disc-like molecules.¹⁸ In both cases the molecules can be described as cylinders with a large shape anisotropy: in calamitic compounds the axial component is larger than the radial components (Fig. 1a), while the reverse holds for discotic molecules (Fig. 1b).¹

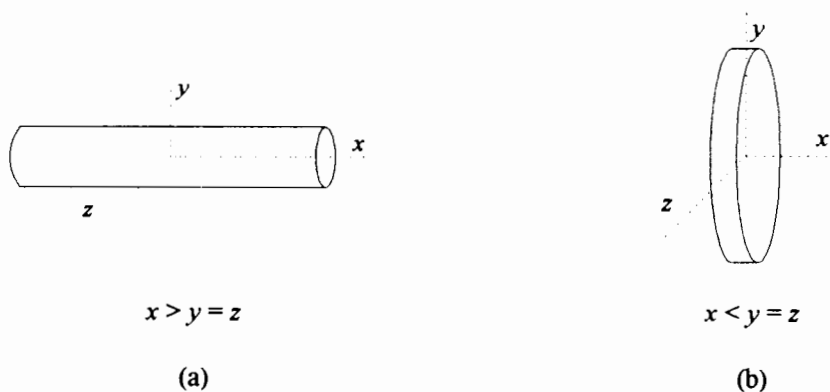


Fig. 1 Geometrical models of (a) calamitic and (b) discotic mesogens.

Depending on the degree of order exhibited by the molecules of the mesophase, three further sub-classes of liquid crystal may be defined: the nematic, chiral nematic and smectic mesophases.

Calamitic mesogens

Considering first the calamitic systems, the above three classes can be distinguished by different arrangements of essentially parallel, rod-like molecules.

Nematic mesophases

The nematic, designated N, is the simplest of the mesophases in that its constituent molecules exhibit only short-range orientational order. The molecules are preferentially aligned with their long axes parallel to one another, but because of thermal motion this direction of alignment is only an average property and varies from point to point in the sample. The local direction of the preferred axis is described by a unit vector \mathbf{n} called the director (Fig. 2).

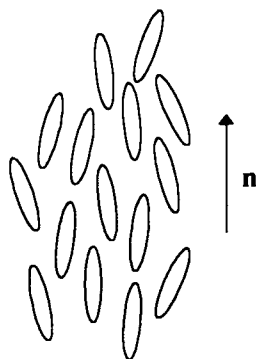


Fig. 2 Schematic representation of the nematic calamitic phase.

There is no long-range correlation between the centres of mass of the molecules, which can translate freely. This fact determines the fluid nature of the mesophase, whereas the directional property described above, in a specially uniformly aligned sample (this is achieved by chemical and mechanical pre-treatment of the substrate),¹⁹ results in a large anisotropy of refractive index, or birefringence, given by:

$$\Delta n = n_{\parallel} - n_{\perp}$$

where n_{\parallel} and n_{\perp} are the refractive indices measured parallel and perpendicular to the nematic director \mathbf{n} . Typically $\Delta n \approx 0.25$,⁴ amongst other factors, the birefringence determines the contrast and angle of view of a liquid crystal display.²⁰

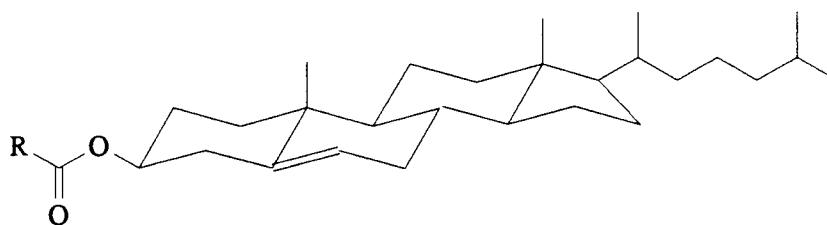
Similarly, the electric permittivity is also anisotropic:

$$\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$$

It is the anisotropy of particularly these two properties, coupled with the fluidity, that accounts for the ease with which the nematic mesophase may be re-oriented by an electric or magnetic field and which has led to the extensive use of these materials in electro-optic display devices. A particularly straightforward discussion of the specifics of device construction and the technological applications of liquid crystals can be found in ref. 2.

Chiral nematic mesophases

If a racemate exhibits a nematic phase then the enantiomerically pure material (or a mixture containing an excess of one enantiomer) will give rise to the chiral nematic phase, abbreviated N* and historically called the cholesteric phase because it was first observed in the derivatives, **4**, of cholesterol.²¹



R = Ph or Me

4

The molecular organization of this phase is described with reference to Fig. 3. The structure consists of nematic layers: the local direction of alignment of the molecules in any given layer is very slightly rotated with respect to that in an adjacent layer such that the net effect is for the director to precess through the phase describing a helix, which may be right- or left-handed depending on the chirality.²² A full rotation of \mathbf{n} is

completed through a distance p called the pitch, which may vary from about 200 nm to infinity, for different substances.²³

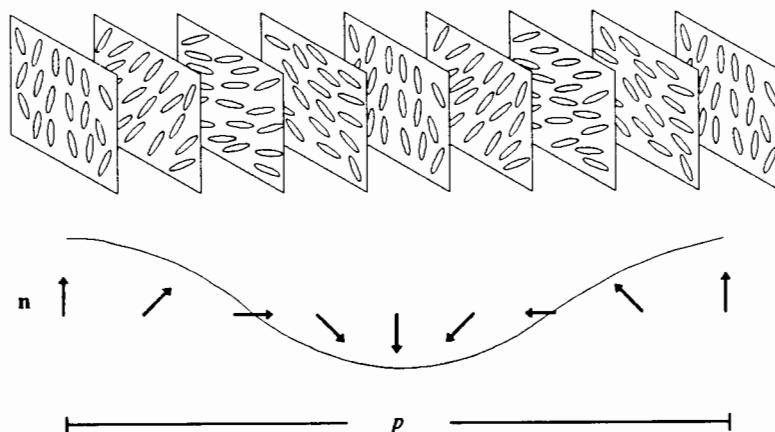


Fig. 3 Schematic representation of the chiral nematic phase showing the layered structure, the helical twist of the directors, \mathbf{n} and the pitch length p .

This progressive deviation from the statistically parallel alignment of the nematic phase is a consequence of the asymmetry of the intermolecular force fields;² thus in the racemate the twist averages to zero giving a nematic of infinite pitch.

The helix pitch-length is often of the order of a wavelength of visible light and the planes can give rise to a selective Bragg-type reflection of light: cholesteric liquid crystals often have vivid iridescent colours.⁵ Changes in the pitch with temperature lead to changes in the colour of the reflected light, which is the basis of the use of these N* materials in thermometry and thermal imaging.^{5,6}

From the above discussion it follows that a given substance will not exhibit both nematic and chiral nematic phases; however, both phases are commonly observed in association with the third and final class of liquid crystal, *viz.* the smectic.

Smectic mesophases

The smectic phases are more highly ordered than the nematic phase and are usually the lower temperature modifications in systems exhibiting both smectic and nematic (or N*) structures. (So-called re-entrant phenomena are known in which the cooling of a smectic phase can lead to the formation of a less ordered nematic, N_R.)²⁴

Smectic mesophases are lamellar in nature: they are characterized by a degree of positional correlation of the molecules into layers in addition to the orientational ordering already described for nematics. Direct evidence for this layered structure is seen in X-ray diffraction patterns where a sharp reflection is observed at small Bragg angles corresponding to the layer thickness.

Two major smectic classes are recognised:

- (i) The true liquid crystal smectic phases which are discussed below and in which there is little or no correlation of structure between the layers. Interlayer diffusion of the molecules is therefore facile and the phases have low viscosity (although necessarily greater than that found in nematics).
- (ii) The crystal-type phases in which the layers are built up regularly so that the molecular centres lie on a two-dimensional lattice. These phases have a restricted molecular mobility and greater viscosities and are really a kind of 'soft crystal'.²

Subdivisions within the above two categories depend upon the molecular packing and direction of tilt within the layers; many structural variants (polymorphs) are obviously possible.

In the simplest structure, called the smectic A phase, denoted S_A (the subscripts here and below indicate the chronological order of discovery of the phases) and represented

schematically in Fig. 4a, the layers are, on average, perpendicular to the director n . The S_C phase (Fig. 4b) is obtained when the average direction within each layer is tilted at some angle to the normal.

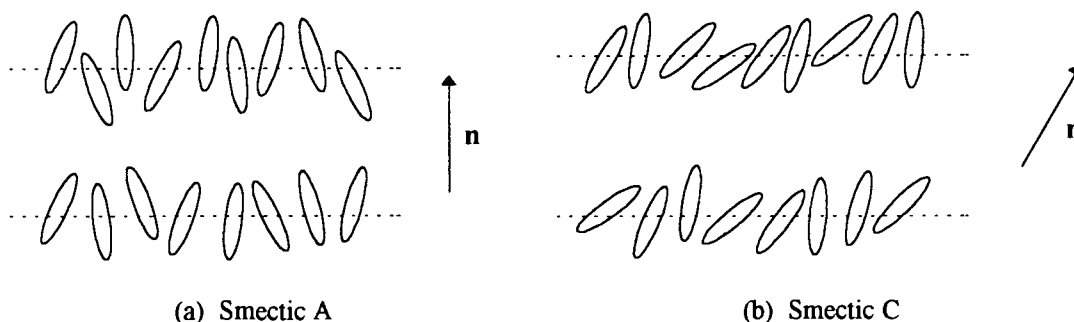
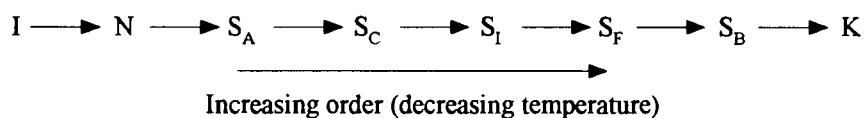


Fig. 4 Schematic representation of the S_A and S_C calamitic phases.

The S_B phase is a more highly ordered modification of the smectic A in that within each layer the molecules are positioned at sites which describe a hexagonal lattice. Again tilted variations are possible: thus the S_I phase may be regarded as an S_B phase in which the molecules are on average inclined towards a vertex of the hexagonal lattice; in the S_F phase this tilt is directed towards the lattice edge.

Chiral modifications of the tilted phases (S_C^* , S_I^* and S_F^*) can also exist in the case of enantiomorphic molecules. In these phases the tilt angle is the same in each layer but the tilt direction precesses and traces a helical path through a stack of layers.²⁵

The normal thermodynamic ordering of the liquid crystal mesophases between the extremes of the totally disordered isotropic liquid I and the solid crystal K is given in Scheme 2.¹⁰



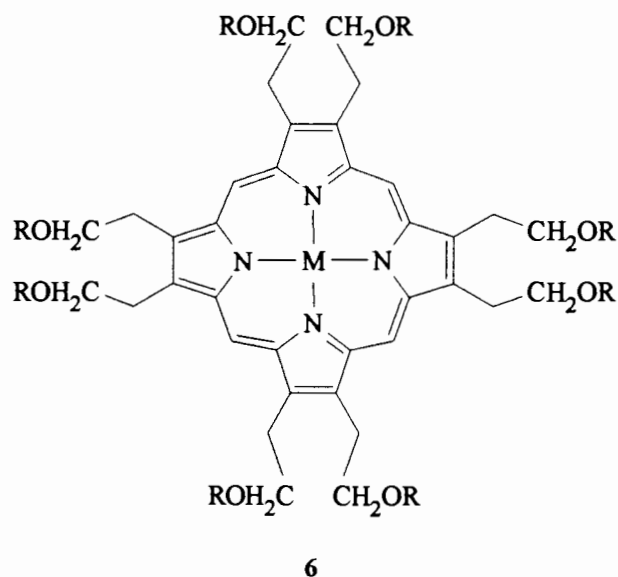
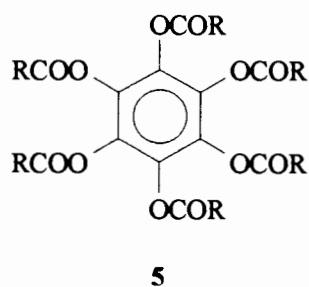
Scheme 2

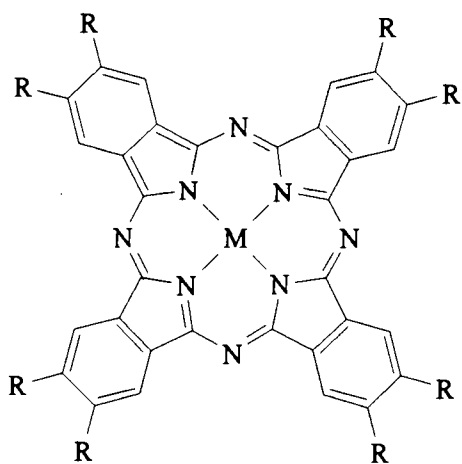
With the possible exception of certain intersmectic transitions all phase changes are first order. The enthalpy change associated with the K to N transition, ΔH_{KN} , is usually an order of magnitude greater than the change ΔH_{NI} observed at the clearing point.^{26,27} Typically ΔH_{NI} is about 2% of ΔH_{KN} .¹⁷ The heat change associated with smectic–smectic or smectic–nematic transitions can be extremely small.¹⁷

The nature and number of the mesophases formed by any given compound must be determined experimentally, although some predictions are possible.

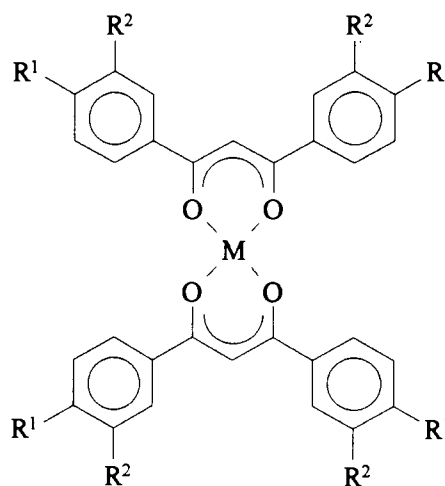
Discotic mesogens

Whereas calamitic molecules are defined by their elongated, rod-like structure, discotic molecules usually have a flat, plate-like core surrounded by at least four, but usually six or more peripheral chains. The first observation of discotic behaviour was reported for the hexa-acyl derivatives **5** of hexahydroxybenzene.²⁸ Many metallomesogens, for example the porphyrin **6**,²⁹ phthalocyanine **7**³⁰ or even β -diketonate **8**³¹ complexes, also form discotic phases.





7



8

Nematic mesophases

In contrast to calamitic phases, discotics correlate their short axes (refer to Fig. 1) and two distinct structural types are known. The nematic discotic phase, N_D (illustrated schematically in Fig. 5) is directly analogous to the nematic calamitic, but materials showing this phase are quite rare.¹⁰

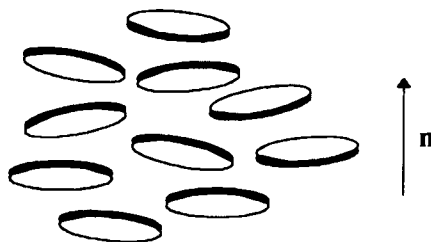


Fig. 5 Schematic diagram of the nematic discotic phase.

Columnar mesophases

More common are the various columnar phases, in which the disc-like molecules stack irregularly in columns so that the different columns constitute a two-dimensional array and the phases have translational periodicity in two dimensions but retain a liquid-like disorder in the third. The two-dimensional network of such a phase can be rectangular, hexagonal or oblique.

In this work a liquid crystalline material based on a discotic molecule was not considered and these systems are not discussed further.

Intermolecular forces in liquid crystals

In the mesophases described above, each molecule interacts with its neighbours *via* forces which depend on the mutual orientations of the molecules. In the case of calamatic mesogens a parallel alignment of the molecular long axes optimally minimizes the intermolecular repulsive forces; such an arrangement also enhances the pair attractions.²⁷

The Helmholtz energy A is a balance between the total interaction energy E and the temperature-weighted entropy TS :

$$A = E - TS$$

As the temperature of the isotropic liquid is lowered it can happen that the decrease in E arising from the parallel ordering of the molecules will become sufficient to offset the decrease in S attendant upon this alignment and a stable mesophase will result.²⁷

For this situation to be achieved before the freezing (liquid \rightarrow solid) temperature is reached the intermolecular potential must be properly anisotropic. The magnitude of this potential is similarly critical: the intermolecular interactions must be strong enough to induce orientational order but sufficiently weak so that, as the solid crystal is heated, a liquid crystalline state can be reached below temperatures which could either cause decomposition of the molecule or melting straight to the liquid phase.¹

Mesogenic molecules must meet a series of structural and electronic requirements if the above conditions are to be fulfilled. For organic molecules the particular structural

features which can be expected to confer liquid crystallinity are well established in the literature.³²⁻³⁴

The basic requirements for a metal complex to show mesomorphism are similar to those for many organics because the ligands occupy much of the space around the metal and, at least in a first approximation, dominate the molecular interactions.⁹

The following discussion of the criteria for design of a calamitic metallomesogen is therefore initially focused on the architecture of the organic ligands.

Design of a calamitic mesogen

The required anisotropic molecular potential depends on dispersion forces supported by permanent and induced dipoles – consequently almost all mesogenic molecules possess permanent dipolar groups and all have a high anisotropy of polarizability. This latter feature determines the magnitude of the induced dipoles and is most readily achieved by the conjugation of aromatic rings: the prototype liquid crystalline species are therefore based on cores of biphenyl, azobenzene, azomethine, naphthalene, *etc.* With only a few exceptions³⁵ calamitics containing only a single benzene unit have too low a molecular anisotropy to display liquid crystalline properties.

The general structure of a calamitic mesogen is often modelled as shown in Fig. 6.

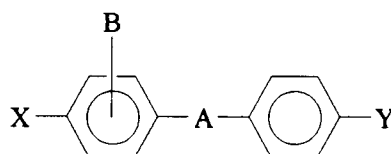


Fig. 6 Generalized model of a calamitic mesogen.

The double 1,4-disubstituted benzene ring system is highly polarizable and at the same time determines the basic rod-shaped structure. However, heteroaromatic and even cycloaliphatic rings such as bicyclooctane have also been successfully incorporated³²⁻³⁴ and very recently a calamitic hydrogen-bonded system has been reported.³⁶

In the model depicted in Fig. 6 at least one of the terminal groups X or Y on the long axis of the molecule is an n-alkyl or n-alkoxy chain to promote phase stability through a mutual affinity of neighbouring chains and to maintain the desired geometrical anisotropy, whilst the other is often a small polarizable group such as -CN, -NO₂ or -OCH₃, which further extends the length of the molecule without affecting its width.

By varying the number of carbon atoms in the terminal chain a series of homologues can be built up. Longer terminal groups prevent the molecules from sliding and therefore favour the formation of smectics over nematics. However, these groups tend to coil with increasing length, thus generally hindering a parallel alignment. It follows that the clearing temperatures of smectics in a homologous series will generally rise with increasing chain length to reach a maximum at a moderate chain length (often 10 to 12 carbons) and then decrease to a nearly constant value for very long chains.³³

The bridging group A in Fig. 6 must preserve the overall molecular linearity and at the same time extend the conjugation of the system; examples of such groups are C≡C, CH=CH, CH=N and N=N, as found in, respectively, tolanes, stilbenes, azomethines and azobenzenes. Obviously only the *trans* isomers maintain the necessary elongated configuration and the above bridging groups force the 1,4-axes of the benzene rings to lie parallel, as illustrated for the stilbene in Fig. 7. For this reason angular monatomic bridging groups such as >O , >NH , >CH_2 and >CO are to be avoided in the design of a mesogen.³³

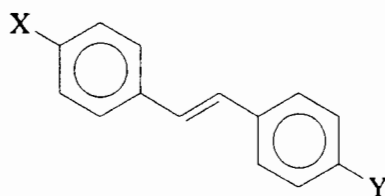


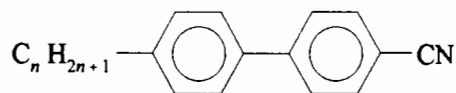
Fig. 7 *Trans* isomer of a stilbene derivative.

The effect of placing lateral substituents (B in Fig. 6) in the core structure of the mesogen is to decrease the molecular length-to-width ratio. The result is usually deleterious and acts either to decrease the mesophase range or to suppress mesophase formation altogether. The introduction of such substituents into the core structure is a complication which was not considered in this work.

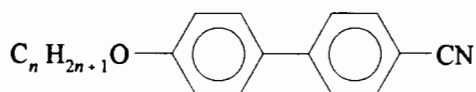
Metallomesogens

The most obvious route to a metal-containing liquid crystal is the linear coordination of long, rigid, monodentate organic ligands to a metal centre.

Consider, for example, the 4-alkyl- and 4-alkoxy-4'-cyanobiphenyls, **9** and **10**, respectively.



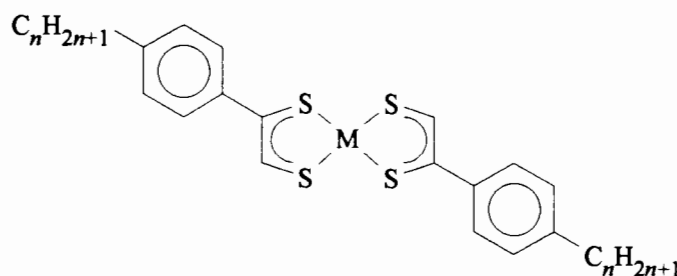
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These molecules conform closely to the model depicted in Fig. 6, but where the linking group A is a direct bond between the two aromatic rings. These cyanobiphenyls were

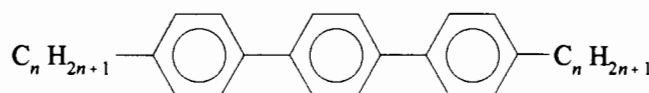
The square-planar bis(dithiolene) complexes **12**, the synthesis of which in 1977 marked the practical beginnings of the recent interest in metal-containing liquid crystals, were also designed to mimic known organic mesogens.³⁹



M = Ni, Pt or Pd

12

It was proposed that the two fused five-membered $\overline{\text{M-S-C-C-S}}$ rings would act in total as a single aromatic ring, making the complexes analogous to the 4,4"-dialkylterphenyls **13**, which form smectic phases when $n = 3-18$.⁹

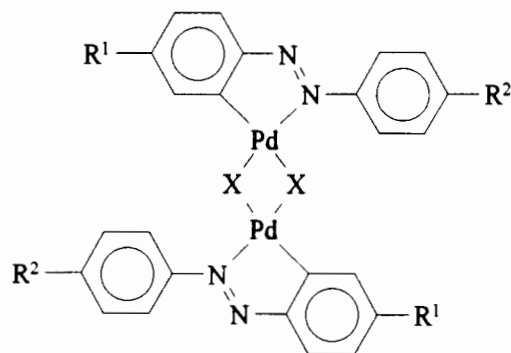


13

The nature of the metal was found to have a profound effect on the mesomorphism of the complexes **12**. Both the nickel and platinum derivatives formed nematic and smectic mesophases: those with $n = 4$ or 5 showed only nematic and those with $n > 6$ showed only smectic mesophases. However, the palladium analogues were not mesomorphic; a definitive explanation for this unexpected observation has not been advanced.⁹

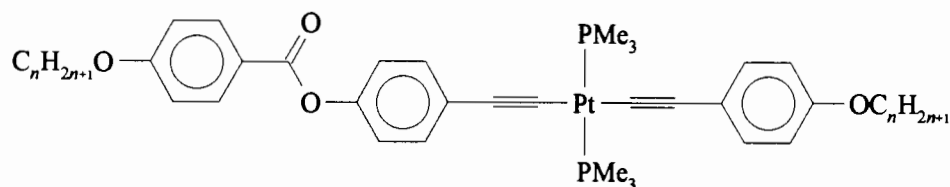
The metal complexes described above serve to highlight some general features of metallomesogens which are worth emphasizing.

Firstly, these compounds, **11** and **12**, are representative of most metallomesogens synthesized to date in that they are conventional coordination complexes. Comparatively few organometallic mesogens are known, mainly the *ortho*-metallated palladium complexes such as **14**⁴⁰ and certain acetylides such as the platinum(II) complexes **15**,⁸ which show smectic A and nematic phases when $n = 8$ or 12 .



X = Cl or Br

14

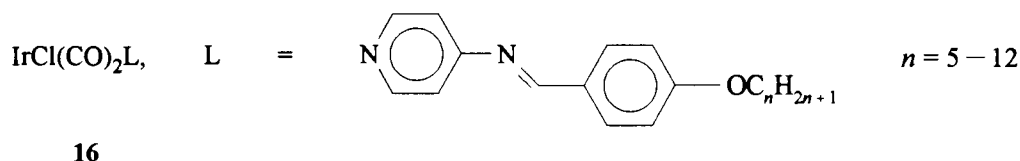


15

The majority of calamitic metallomesogens have been based on metals with d^8 - d^{10} electronic configurations which exhibit a linear or square-planar geometry, the latter exemplified by structures **11** and **12**. The metals Ni^{II} , Pd^{II} , Pt^{II} , Rh^{I} , Ir^{I} , Au^{III} , Cu^{II} , Ag^{I} , Au^{I} and Zn^{II} therefore feature prominently since materials containing these metal cores will most readily satisfy the basic requirements for a calamitic mesogen. In many of these compounds the metal atom is often (though not necessarily) at or near the centre of gravity of the molecule.

The above complexes also illustrate one final point. It is broadly true that the anisotropic dipole-dipole and dispersion forces responsible for the liquid crystalline behaviour of a mesogenic organic ligand are not necessarily destroyed on coordination to a metal (and indeed in some cases the resulting mesophases are identical to those of the free ligand). It is also true that the metal can have a profound effect on the mesomorphism.

The high polarizability associated with the metal centre has already been mentioned and the consequent increase in dipole interactions is well-illustrated by the fact that the introduction of a metal atom into a non-mesogenic ligand can induce mesophase formation as was found for the iridium complexes **16**.⁴¹



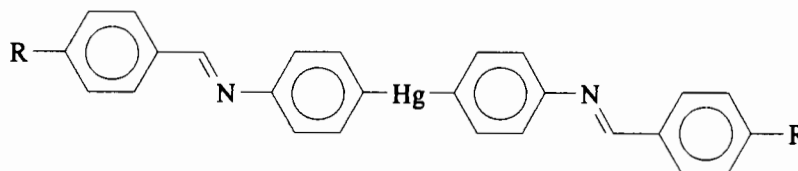
Whereas for organic molecules the problem is frequently a need to increase intermolecular interactions to produce liquid crystallinity, in the case of metallomesogens it is often necessary to prevent these interactions from being so strong as to lead to undesirably high melting points.¹

The melting points of the $[\text{MCl}_2(\text{NCC}_6\text{H}_4\text{C}_6\text{H}_4\text{R})_2]$ complexes **11**, for example, are very much higher than those of the free ligands (**9** and **10**), so that at the mesophase temperature the inherent lability of the M-N bond results in partial decomposition.²⁰ Most physical applications of liquid crystalline materials require taking the compound through to the isotropic state¹ and where the clearing point is too high, as is the case for many metallomesogens, severe decomposition is often the result.

Since molecules of reduced symmetry usually pack less efficiently and with a concomitant decrease in intermolecular interactions, an asymmetrical complex having two or more different ligands will often exhibit a significantly lower melting point than a symmetrical system.⁹ Ligands which bind strongly to the metal confer greater stability on the complex and chelating ligands are useful in this regard.

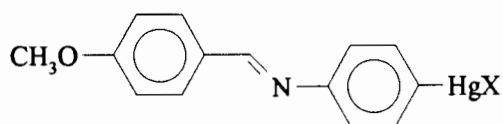
In the light of the above, it seemed feasible to investigate a potentially mesogenic system based on the organomercury(II) dithizonate complexes **1**. The choice of metal here was dictated by the photochromic properties of the dithizonate system; these are described later.

The first reported metallomesogens were, indeed, the organometallic mercury(II) derivatives **17**, prepared by Vorländer in 1923⁴² by the condensation of bis(4-aminophenyl)mercury with aromatic aldehydes.



17

Derivatives with R = H, CH₃ and CH=CH₂ were obtained and all show smectic phases. The related compounds **18** are also mesogenic.⁴² However, none of these compounds is thermally stable; it was hoped that coordination of the bidentate dithizonate ligand would confer stability, allow the mesomorphism to be retained and, in addition, make the resultant material photochromic.



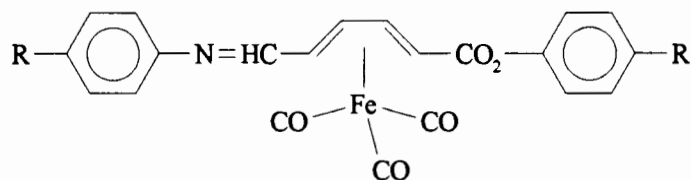
X = Cl or OAc

18

The d^{10} electronic configuration of the Hg^{II} ion affords no crystal field stabilization and the stereochemistry of its compounds depends on such factors as the size and polarizing power of the metal and the steric requirements of the ligands.¹ The two-coordinate, linear geometry favoured by Hg^{II} and evident in the above compounds **17** and **18** is, in principle, ideally suited to give calamitic metallomesogens.

Complexation of the dithizonate ligand gives rise to an unusual three-coordinate geometry at the metal centre (see below)⁴³ which at first sight, and in view of the preceding discussion, might be expected to militate against the appearance of any liquid crystalline behaviour. However, despite the already mentioned emphasis on linear and square-planar geometries, there are many examples that suggest that metal-containing mesogens can tolerate greater deviations from linearity than is the case for purely organic systems.

The tricarbonyliron(0) butadiene derivatives **19**⁴⁴ and the ferrocenyl Schiff bases **20**⁴⁵ both exhibit structures in which parts of the molecule project out of the plane which the long chains ideally define, and yet both are liquid crystals.¹

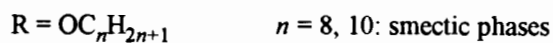
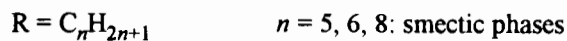
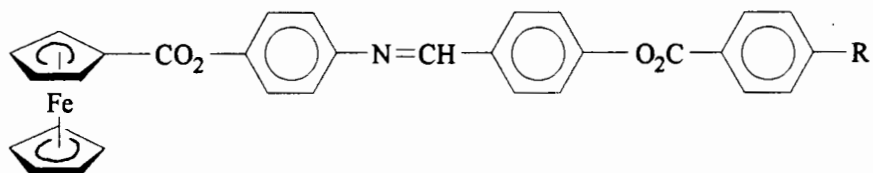


R = OC_nH_{2n+1}

$n = 6 - 10$: nematic phases

$n = 9 - 12$: nematic and/or smectic phases

19



20

The di- μ -acetato palladium complexes derived from the 4,4'-bis(alkoxybenzylidene)azines (Fig. 9) exhibit nematic and/or smectic C mesophases depending on the group R. The bridging acetato ligands require the complexes to be non-planar and a novel 'open-book' structure has been proposed.⁴⁶

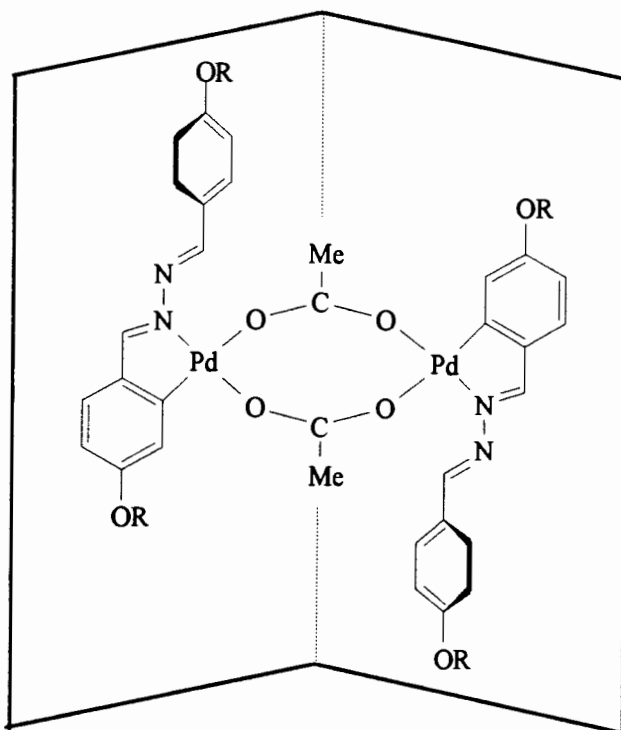
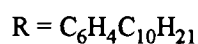
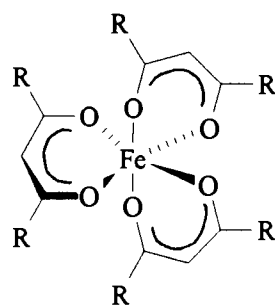


Fig. 9 Schematic structure of the *trans*-isomer of the μ -acetato palladium azine complexes.

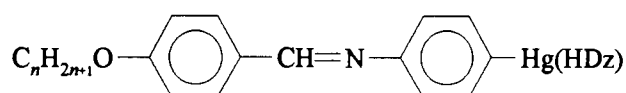
Finally, a single instance of an octahedral metallomesogen, the iron(III) tris- β -diketonate **21**, has been reported although its mesomorphism is admittedly unconfirmed.⁴⁷



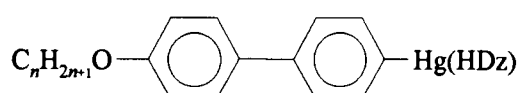
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Organomercury(II) dithizonates

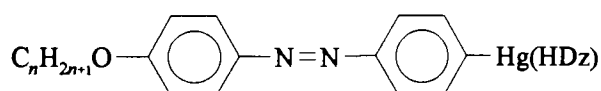
The organomercury(II) dithizonates $RHg(HDz)$ prepared in this study were chosen so that the group R conformed as closely as possible to the model calamitic mesogen described by Fig. 6. The syntheses of the Schiff bases **22**, the biphenyls **23** and the azobenzene derivatives **24**, and the elaboration of homologous series within these classes were all attempted in the hope that the mesomorphism already observed in the Schiff base compound **18** would be retained in the dithizonates **22** and that the similar series **23** and **24** would also exhibit liquid crystalline behaviour.



22



23



24

Since phenylmercury(II) dithizonate may be regarded as the core structure from which the potentially mesogenic molecules in this study were built up, the molecular geometry of this compound is now described in some detail.

Structure of phenylmercury(II) dithizonate

A perspective view of the molecular structure of phenylmercury(II) dithizonate is given in Fig. 10.⁴³

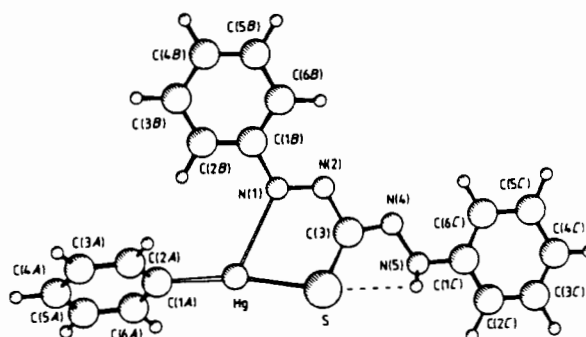


Fig. 10 Molecular structure of PhHg(HDz) with atomic nomenclature.⁴³

The Hg atom exhibits planar, irregular three-coordination, the geometry at the metal centre being described as approximately T-shaped, with the dithizonate ligand acting as a bidentate chelate coordinating through a strongly covalent Hg–S bond (2.37 Å) and a weaker dative Hg–N bond (2.65 Å).

The bond lengths in the dithizonate ligand reveal extensive delocalization of π electrons within the N–N–C–N–N chain; furthermore, the entire ligand is very nearly coplanar and the conjugation of the chelate ring is extended to the two phenyl groups, B and C. The third phenyl ring, A, is twisted by 59° out of the plane defined by the rest of the molecule; in this way steric interaction with the phenyl ring B is minimized. That this latter ring does not twist out of the plane in the opposite direction is attributed to the electron delocalization throughout the dithizonate ligand.

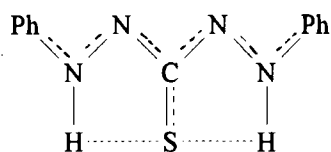
The imino proton participates in a weak intramolecular hydrogen bond to the sulfur atom; although the H \cdots S distance (~ 2.4 Å) favours a strong intramolecular hydrogen bond, the stereochemistry of the sp²-hybridized N(5) atom precludes linearity of the N(5)–H \cdots S angle and consequently the hydrogen bond formed is considerably weakened. Nevertheless, this interaction effectively fixes the dithizonate residue into an *anti* (disposition of anilino and phenylazo groups relative the formal C=N double bond),⁴⁸ *s-trans* (relative the C-N bond)⁴⁸ configuration.

It should be evident that, in the solid state at least, the dithizonate ligand presents a flat and fairly rigid structure (because of extensive electron delocalization) and a comparison with the cholesterol derivatives **4** is perhaps instructive since here just such a flat and rigid system (because of the all *trans-transoid* ring fusion) is found to give rise to mesomorphic materials.

The purpose of introducing the dithizonate group was to produce a photochromic liquid crystal and this chapter will now turn to a discussion of the spectroscopic properties of the metal dithizonates.

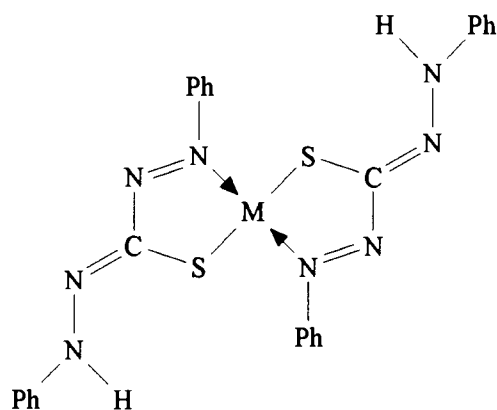
Photochromism of metal dithizonates

Dithizone (abbreviated here as H₂Dz), is formally a 1,5-diphenylthiocarbazone and is sometimes also named as a 1,5-diphenyl-3-thioformazan. The solid state and solution structure has only fairly recently been unequivocally established as **25**.⁴⁹ Dithizone gives highly coloured complexes with many heavy metals and has long been used in analytical chemistry as a reagent for the determination of trace metals.⁵⁰



25

The solution spectra of these metal bis-dithizonates, $M(\text{HDz})_2$, **26**, are characterized by a single intense absorption band in the visible spectrum located between 450 and 550 nm.⁵¹ The transitions involved are primarily associated with the delocalized electronic system of the ligand, as evidenced by the high molar absorption coefficients of the bands ($\epsilon = 10^4\text{--}10^5 \text{ m}^2 \text{ mol}^{-1}$), their relative independence of the nature of the metal and the existence of a band of similar wavelength in the parent dithizonate anion.⁴⁹



$M = \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Pt}^{\text{II}} \text{ and } \text{Pd}^{\text{II}}$ square-planar

$M = \text{Hg}^{\text{II}} \text{ and } \text{Zn}^{\text{II}}$ tetrahedral

26

The photochromism of the bis-dithizonate complexes was first reported⁵² for the mercury(II) species, solutions of which in benzene or chloroform were observed to change from the usual orange-yellow colour to an intense blue on irradiation by visible light, the normal form having a strong absorption band at 485 nm in chloroform ($\epsilon = 7050 \text{ m}^2 \text{ mol}^{-1}$) which was replaced in the activated form by a band at 604 nm (Fig.

11). The yellow coloration was found to return slowly in diffuse daylight or in the dark and the sequence of colour changes could be repeated indefinitely.

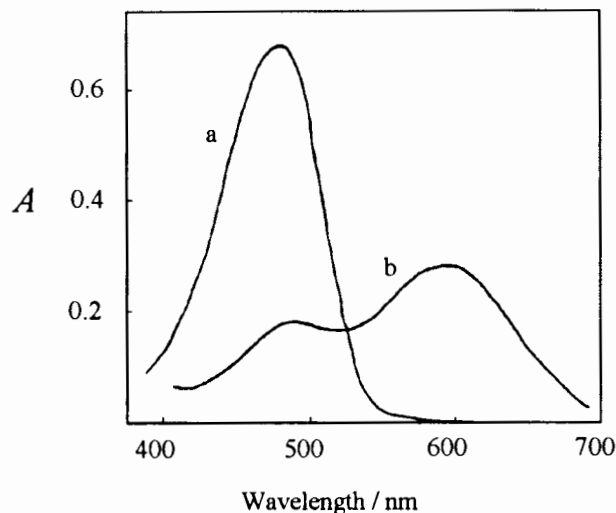


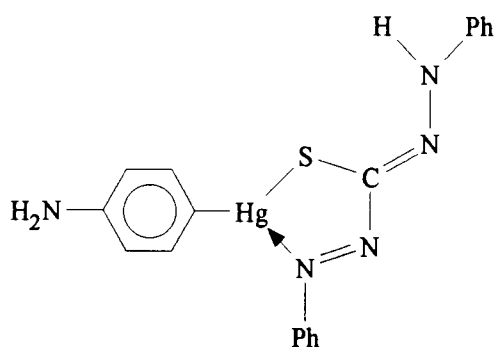
Fig. 11 Spectra showing the photochromism of mercury(II) bis(dithizonate): (a) before and (b) after irradiation with visible light.⁵¹

This reversible photochromism is now known⁵¹ to be a general feature of all primary metal dithizonates **26** but the thermal return reaction is usually too rapid to allow visual observation of a colour change and only in the case of the mercury(II) complex, where the half-life of the blue form is of the order of a minute, is this back reaction sufficiently slow for conventional measurements. The half-lives of the cadmium or lead dithizonates, for example, are less than one second even when cooled to $-80\text{ }^{\circ}\text{C}$.⁵¹

The percentage conversion for the mercury(II) species is also markedly high: with intense illumination a steady-state system can be achieved at $25\text{ }^{\circ}\text{C}$ in benzene in which 80–90% of the total mercury complex exists as the activated blue form. Under comparable conditions the steady-state concentration of the activated Cd or Pb complexes has been calculated as not more than 0.1%.⁵¹

Furthermore, of some 24 metal dithizonates that have been investigated,⁵¹ only mercury(II) bis(dithizonate) is photochromic in the solid state: a colour change from orange through brown to violet was observed on irradiation of a solid sample with visible light. Return to the orange colour was slow, taking several hours.

A number of studies^{51,53} have shown that mercury is unique in conferring both high conversion and slow thermal return rates on the photochromic dithizonate system. These properties are retained and even enhanced in the organomercury(II) derivatives $\text{RHg}(\text{HDz})$, which are subject of this work. For example, the half-life of methylmercury(II) dithizonate in dichloromethane at room temperature is 50 minutes and the percent conversion is estimated at nearly 100, the same data for 4-aminophenylmercury(II) dithizonate **27** being $t_{1/2} = 51.3$ minutes with again 100% conversion.⁵³

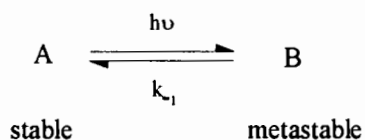
**27**

For these reasons, and because of the potential for photochromism in the solid state, mercury was the metal of choice in this study.

Mechanism of the photoisomerization

The photochromism of the metal dithizonates in solution is a unimolecular process and appears to conform to the simple model of Scheme 3 in which the forward reaction is a

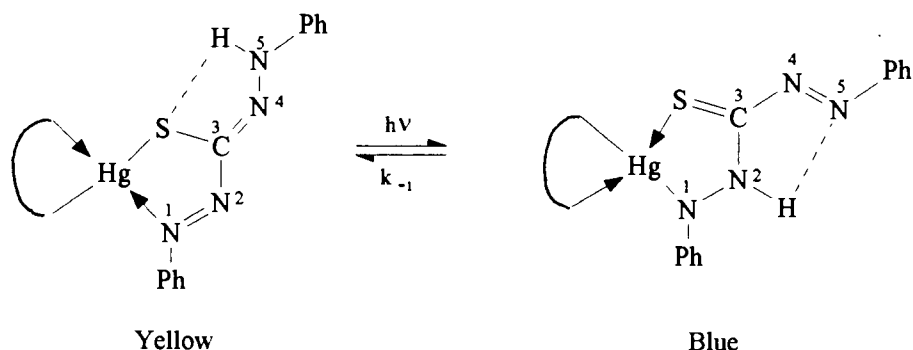
strictly photochemical process dependent only on the intensity of the activating light, whereas the back reaction occurs thermally and identically in both light and dark, this latter fact indicating the absence of a photochemical return pathway.⁵¹ The position of the photoequilibrium at any given time is therefore a function of both the temperature and the activating light intensity.



Scheme 3

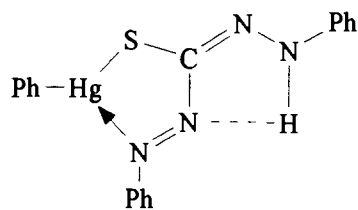
Photochromic systems are frequently characterized by spectral and kinetic behaviour which is critically dependent on environmental conditions. The thermal return rate of the metal dithizonate system is very dependent on the proton-transfer ability of the medium;⁵¹ the strongest photochromic effects are observed in dry, non-polar solvents such as benzene, toluene, carbon tetrachloride or chloroform. Protic solvents are notable for their effect in accelerating the back reaction: the addition of a few drops of ethanol to a solution of $\text{Hg}(\text{HDz})_2$ in toluene reduced the half-life from 30 seconds at 25 °C to less than 1 second at 0 °C.⁵¹

Free-radical species are not implicated in the photochromic reaction.⁵¹ This fact, together with the sensitivity of the system to acids and bases, suggests that the photochromic process is ionic. From kinetic and spectrophotometric studies, Meriwether *et al.*^{51,54} proposed the equilibrium shown in Scheme 4, where the structure of only one of the ligands is shown in detail. An *anti-syn* isomerization about the formal C=N bond and an N(5) to N(2) proton transfer were suggested and the observed pH and solvent sensitivity of the photochromic reaction was explained by assuming that a molecule of water (or a second molecule of the complex) acts as a proton bridge by means of which the hydrogen transfer is effected.



Scheme 4

However, very recently, single crystals of the activated blue form of phenylmercury(II) dithizonate have, for the first time, been isolated in this laboratory and the structure determined by X-ray crystallography as **28**.⁵⁵ This result requires a re-evaluation of the mechanism of photoisomerization, and other workers in this laboratory are pursuing this aspect.



28

In summary, the photochromic mercury(II) dithizonates possess several unique characteristics which could be usefully incorporated into a mesogen: activation by visible light, large differences in the spectra of the stable and metastable states (*i.e.* large colour changes), favourable photoconversions, the absence of complicating side reactions which are responsible for the fatigue of a photochromic system, and long-term stability towards visible and near-UV light of wavelength longer than about 350 nm.

Photochromic liquid crystals

The concept of combining photochromic and liquid crystalline properties is of practical interest because of possible applications in optical recording as well as display devices,⁵⁶ and the suitability of mercury(II) bis(dithizonate) as a reusable optical recording medium for use in optical data processing applications has already been established.⁵⁷

The reversible transformations of molecular structure exhibited by photochromic molecules can affect the type of mesophase of a liquid crystal,⁵⁶ *i.e.* can induce an isothermal phase change in an otherwise thermotropic mesogen. For example, the photo-induced isomerization of *trans*-azobenzene dissolved in a cholesteric liquid crystal has been reported to change the mesophase from one exhibiting a light-scattering texture to the almost transparent nematic phase,⁵⁶ the application to optical devices is obvious. Reversible colour changes in the cholesteric reflection bands of a chiral nematic (N*) material mixed with stilbene or azobenzene on selective UV irradiation of such mixtures have been reported.⁵⁸ The colour images arise from a modification of the cholesteric pitch caused by the *cis-trans* isomerization of the photosensitive dopant molecule.

As in the two examples described above, most studies to date have involved photochromic molecules dissolved in a liquid crystalline matrix and the efficacy of the interaction is often strongly dependent on the affinity of the photoresponsive system with the host mesogen.^{56,59} It therefore seemed an appealing challenge to attempt to combine the two phenomena of photochromism and liquid crystallinity in a single molecule.

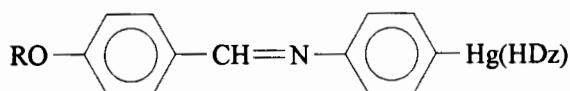
Chapter Two

Results and Discussion

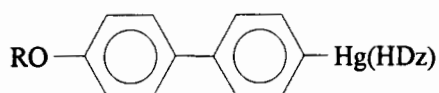
CHAPTER 2

RESULTS AND DISCUSSION

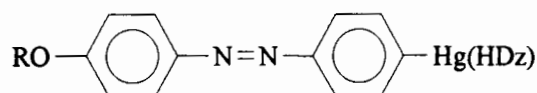
This chapter describes the preparative work involved in the synthesis of the 4-(4'-n-alkoxybenzylideneanilino)- and 4-(4'-n-alkoxybiphenyl)mercury(II) dithizonates, **22** and **23**, respectively, as well as the attempted synthesis of the 4-(4'-n-alkoxyazobenzene)mercury(II) dithizonates **24**.



22



23



24

The techniques of optical microscopy and thermal analysis, by means of which the mesomorphic properties of a compound are investigated, are then introduced and the results of their application to the compounds synthesized in this work are discussed.

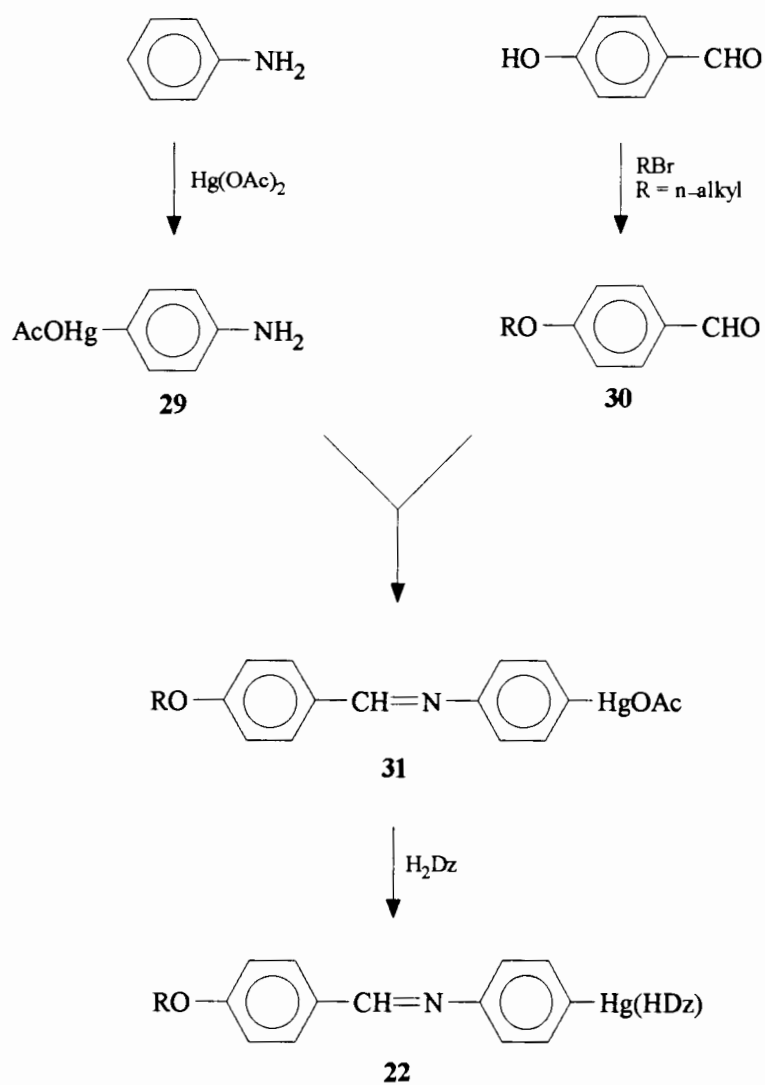
Finally, the visible solution spectra of the long-chain organomercury(II) dithizonates **22** and **23** are presented, and it will be seen that although these compounds themselves did not exhibit any mesomorphic behaviour, they did display photochromic properties.

Synthetic studies

Preparation of the azomethine series

The preparation of the Schiff base dithizonates **22** was the obvious starting point for this work: the mesomorphism of the 4-(4'-methoxybenzylideneanilino)mercury(II) acetate **18** had previously been reported⁴² and it was hoped that coordination of the dithizone would preserve the liquid crystalline properties, if not in the derivative of **18** then at least in the longer alkoxy chain homologues. Because the terminal ether function has been identified as a particularly effective group in stabilizing mesophase formation,³³ the introduction of an alkoxy chain rather than the corresponding alkyl group was attempted here and in the later series of compounds.

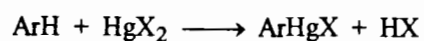
The most direct route to compounds containing the azomethine linkage, $-\text{CH}=\text{N}-$, is the condensation of an aldehyde and a primary amine,⁶⁰ which was the method employed by Vorlander⁴² in his preparation of the metallomesogens **17** and **18** although his paper does not report any experimental details. The synthetic route chosen was therefore the convergent one outlined below (Scheme 5) in which the mercury atom is first introduced into the amine and the latter then condensed with a *para*-substituted *n*-alkoxybenzaldehyde **30** to give the Schiff base derivative **31**. The final step in Scheme 5 describes the coordination of dithizone **25** giving the required organomercury(II) dithizonate **22**.



Scheme 5

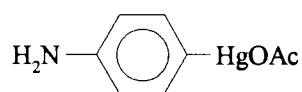
Synthesis of 4-aminophenylmercury(II) acetate 29

The direct electrophilic aromatic mercuriation of arenes by simple mercury salts (Eqn. 1) is one of the most important routes to organomercurials.⁶¹ Although isomeric mixtures are often obtained the pure isomers can usually be separated by recrystallization.



Eqn. 1

4-Aminophenylmercury(II) acetate **29** was prepared from aniline and mercury(II) acetate *via* this route and according to published methods.^{62,63} The pure *para*-isomer was isolated by filtration after a reaction time of 3 hours and was obtained in considerably higher yield than that reported in the original literature (83 vs. 57%).⁶²

**29**

The melting point of **29** has been variously reported in the literature: the original paper by Dimroth⁶² gives a temperature of 166–167 °C, this is misquoted in ref. 63 as 67 °C, while a more recent work⁶⁴ gives 148 °C. The melting point of the product obtained in this study was 158–160 °C; this is exactly the temperature range reported by Dimroth for the *ortho*-compound which he found precipitated in low yield from the filtrate on standing.

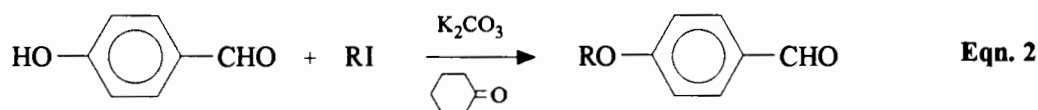
However, the product isolated here was unambiguously established as the *para*-isomer by ¹H NMR spectroscopy, which clearly showed the signals characteristic of a *para*-disubstituted benzene ring, *i.e.* a set of two doublets with a coupling constant *J* of 8.5 Hz which is in the range expected for *ortho* ¹H–¹H coupling.⁶⁵

A small amount of material was isolated from the filtrate but NMR spectroscopy again showed this to be the *para*-isomer **29**, with a melting point of 155–158 °C. A melting point for the *ortho*-compound was therefore not determined but a value of 166–167 °C is suggested if it is assumed that the melting points of the *ortho*- and *para*- isomers were inadvertently interchanged in the original paper⁶² and that this error has been perpetuated in the review literature.

The 4-aminophenylmercury(II) acetate was of only limited solubility in most organic solvents and attempts at recrystallization were unsuccessful. However, NMR spectroscopy revealed a satisfactorily pure compound and this product was therefore taken straight through to the second step of the synthesis, *viz.* condensation with the 4-n-alkoxybenzaldehydes.

Synthesis of the 4-n-alkoxybenzaldehydes 30

The preparation of these benzaldehydes was first attempted according to the method of Gray and Jones (Eqn. 2):⁶⁶ a solution of the n-alkyl halide, in this case iododecane, and 4-hydroxybenzaldehyde in cyclohexanone was refluxed with anhydrous potassium carbonate. The reaction was monitored by thin-layer chromatography (TLC) for the disappearance of the aldehyde and appeared to be complete after 1.5 hours; isolation of the product by distillation yielded a yellow fraction at 176–180 °C / 4 mmHg and a considerable quantity of an orange-coloured residue which began to char on further heating.



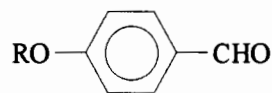
The yellow product obtained above was identified as the required dodecyloxybenzaldehyde by ¹H NMR spectroscopy. However, the yield of 26% was unacceptably low. Gray and Jones⁶⁶ reported the synthesis of a series of 4-n-alkoxybenzaldehydes with yields in the range 65–75%, though decreasing below 60% for the longer-chain ethers, where the high boiling points (230 °C/ 3 mmHg and 240 °C/ 2 mmHg for the hexa- and octadecyl ethers respectively) resulted in charring.

The above preparation is essentially an example of the Williamson ether synthesis involving the direct nucleophilic displacement of the halogen in the alkyl halide by an

aryloxide ion generated by reaction with a base,⁶⁷ in this case potassium carbonate. These reactions may also be carried out using potassium carbonate in acetone or acetonitrile, or with the base sodium hydride in dimethylformamide (DMF).⁶⁷ These polar aprotic solvents render both the attacking base and the deprotonated substrate more reactive since they do not solvate carbanions or other anions.⁶⁸ The bromides are the alkyl halides of choice since they are more reactive than alkyl chlorides and less susceptible to dehydrohalogenation than alkyl iodides.⁶⁷

Reaction with sodium hydride in DMF was therefore investigated and proved to be more successful in terms of yield than the method first attempted using potassium carbonate in cyclohexanone. The alkyl bromide was added to a solution of 4-hydroxybenzaldehyde in DMF; reaction was complete within 1 to 2 hours at elevated temperatures (100–110 °C) and it was discovered that the products could be precipitated from solution by the addition of hexane, thus avoiding the need for distillation of these very high-boiling compounds.

The 4-n-alkoxybenzaldehydes **30a–c** were obtained as waxy solids of melting points 20–23, 33–34 and 45–48 °C respectively (lit.,⁶⁶ 24, 34 and 49 °C respectively) and were characterized by NMR spectroscopy.



R

30 a C₁₂H₂₅

b C₁₄H₂₉

c C₁₈H₃₇

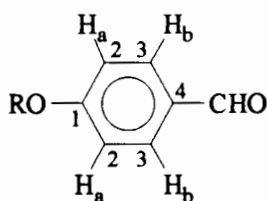
The ¹H NMR signals for most of the methylene groups in the long alkoxy chain overlapped in the range 1.27–1.38 ppm; only the two methylene units most closely bonded to the oxygen atom were observed separately. The chemical shift of the

methylene group directly adjacent to the oxygen atom in the product was some 0.7 (^1H) and 34 (^{13}C) ppm downfield of the shift observed in the starting material where this group is bonded to bromine. The ^{13}C assignments given in Chapter 3 (Experimental) for the carbon atoms of the aromatic ring were made by comparing the observed values with those calculated from tabulated data⁶⁹ using Eqn. 3

$$\delta_{\text{C}}(k) = 128.5 + \Sigma A_i \quad \text{Eqn. 3}$$

where $\delta_{\text{C}}(k)$ is the chemical shift of the ring carbon k , 128.5 is the ^{13}C chemical shift for benzene and the additivity parameter A_i is the increment to be added for a substituent in the i th position.⁷⁰ For these purposes the long alkoxy chains, RO-, in the molecules **30** were approximated as a methoxy group since this was the only ether functionality for which the data A_i were available. Nevertheless, agreement between the calculated and observed values was very close and the peaks were sufficiently separated to allow an unambiguous assignment of all the ring carbon atoms: the results are collected in Table 2.

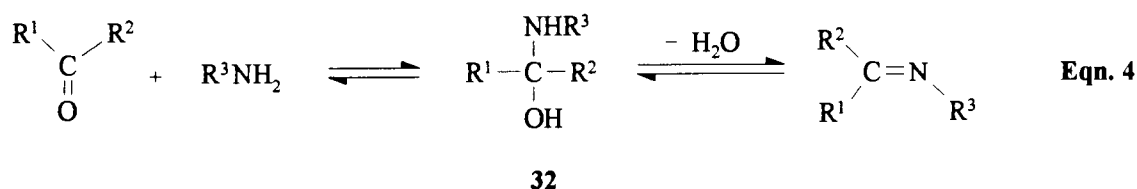
Table 2 Calculated ^{13}C chemical shifts for the aromatic carbon atoms 1–4 and their observed values.



Carbon atom	$\delta_{\text{C}} / \text{ppm}$	
	Calculated (R = CH ₃)	Observed (R = C ₁₂ H ₂₅)
C ₁	164.7	164.3
C ₂	115.0	114.7
C ₃	130.6	131.9
C ₄	129.4	129.7

Synthesis of the Schiff-base mercury(II) acetates 31

The reaction of primary amines such as **29** with aldehydes or ketones gives imines according to the general Eqn. 4.^{60,71} Reaction proceeds through an *N*-substituted hemiaminal **32**, which then loses water to give the product.

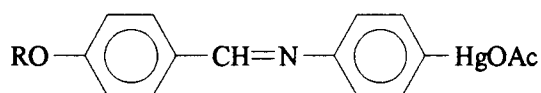


With simple R groups these products usually decompose or polymerize rapidly unless there is at least one aryl group on the nitrogen or carbon atom, in which case the imines are quite stable and are usually called Schiff bases.⁶⁰ Ketones are generally less reactive than aldehydes in the formation of imines and the position of the equilibrium in Eqn. 3 must often be shifted by the removal of water either with a drying agent, with molecular sieves or by azeotropic distillation.⁶⁰ On the other hand, the condensation of aromatic aldehydes with primary amines often proceeds directly to completion without requiring dehydrating agents.⁷²

Reaction of 4-methoxybenzaldehyde (anisaldehyde) with 4-aminophenylmercury(II) acetate **29** was therefore first attempted in refluxing toluene: the aldehyde was added to a suspension of the amine in toluene and the mixture heated at reflux temperature for 8 hours. However, no visible reaction was observed, the amine remained undissolved and analysis of the reaction mixture by TLC did not detect the presence of any product. This preparation was therefore attempted in refluxing benzene with provision in the form of a Dean and Stark trap for the azeotropic removal of water to force the equilibrium in Eqn. 4 to the right; again, however, the amine remained unchanged in suspension, no reaction product was detected by TLC, and no water was observed to have collected in the trap.

Because the limiting factor in the above procedures appeared to be the solubility of the 4-aminophenylmercury(II) acetate, the concentration of which in solution was always too low to permit the reaction to proceed at a satisfactory rate if, indeed, at all, and because of the similarly low solubility of this amine in most other organic solvents, it was decided to investigate the possibility of a solid state reaction to form the required Schiff bases **31**. The 4-methoxybenzaldehyde was accordingly added to a finely powdered sample of the amine **29** in a small open flask and this mixture heated at 155 °C. A pale yellow colour was immediately noticed as the amine appeared to melt, a vapour was observed to escape the flask and fine droplets of a liquid, which was assumed to be water, condensed at the mouth. After less than two minutes at 155 °C the mixture abruptly solidified and heating was then discontinued. The solid product was recrystallized from dichloromethane and identified as the required Schiff base **31a** by ¹H NMR spectroscopy.

The above procedure proved suitable for the small-scale preparation (*ca.* 1.0 g) of all the imines **31a–e**. The removal of the water, by evaporation from the open reaction flask at elevated temperatures, was effective in driving the reaction to completion and the imines were obtained in yields of 75 to 88%.



	R	R
31 a	CH ₃	d C ₁₄ H ₂₉
b	C ₄ H ₉	e C ₁₈ H ₃₇
c	C ₁₂ H ₂₅	

The ¹H and ¹³C assignments given in Chapter 3 (Experimental) for the compounds **31a–e** are referenced to the arbitrary numbering system shown in Fig. 12; similar

numbering of the aromatic rings was applied to all the compounds prepared in this work.

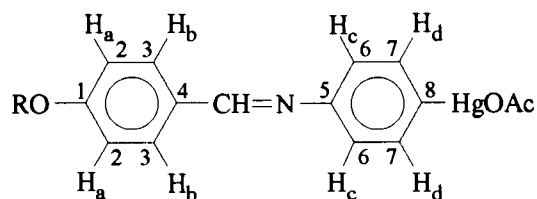


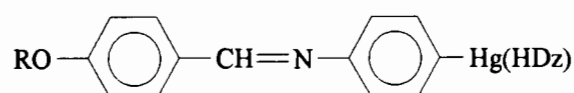
Fig. 12 H and C numbering of the compounds **31** for the purposes of NMR assignment

The ^1H NMR spectra of the compounds **31a–e** show the typical resonances expected for two *para* disubstituted benzene rings: the protons H_a and H_b are coupled together in a pattern which appears superficially like an AB system, *i.e.* a set of two doublets which are relatively widely spaced ($\delta_{ab} = 0.85$ ppm; $J_{ab} = 8.8$ Hz), but which exhibit a fine structure. The complexity arises from the fact that the pairs of H_a nuclei (and similarly for the H_b, H_c and H_d protons) are not magnetically equivalent and the system is more properly named as an AA'BB' system.⁷³ The nuclei H_c and H_d likewise give rise to a set of two doublets but these are much more closely spaced ($\delta_{cd} = 0.12$ ppm; $J_{cd} = 8.5$ Hz). The assignment of the above protons was based on the appearance of the spectrum (mutually coupled doublets 'point' to one another) and the values of the coupling constants, and was confirmed by a 2D COSY experiment.

The resonance for the azomethine proton of the compounds **31a–e** appeared in the range 8.26–8.34 ppm. In the case of **31a** a small signal representing some 28% of the larger resonance at 8.26 ppm, was observed at 8.37 ppm. This was assumed to arise from the azomethine proton of the less stable *cis* isomer which was expected to be present in only small quantities. In the case of the longer chain homologues **31b–f** this peak was barely visible and these products were therefore assumed to be almost pure *trans* isomers which is the configuration required for a mesogenic molecule.

Synthesis of the 4-(4'-n-alkoxybenzylideneanilino)mercury(II) dithizonates 22

The organomercury(II) dithizonates **22a–e** were prepared according to literature methods:^{74,75} stoichiometric ratios of the imines **31** and dithizone **25** were stirred together in a 1 M aqueous ammonia–chloroform extraction system for 15 minutes. The effect of the base is to singly deprotonate the dithizone molecule and the resulting metal dithizonates were obtained as bright red solutions in the organic solvent. These products were isolated and recrystallized from benzene–hexane to give dark-red, microcrystalline solids. The yields were relatively low but in the range typically reported for mercury(II) dithizonates, viz. 55–70%.⁷⁴



	R		R
22 a	CH ₃	d	C ₁₄ H ₂₉
b	C ₄ H ₉	e	C ₁₈ H ₃₇
c	C ₁₂ H ₂₅		

The aromatic proton and carbon numbering system applied to the dithizonates **22** for the purposes of NMR assignment, is defined in Fig. 13. The same numbering of these atoms was applied to the 4-(4'-n-alkoxybiphenyl)mercury(II) dithizonates **23** in which the azomethine linkage is simply replaced by a single bond.

The assignment of the aromatic ¹H and ¹³C resonances of the dithizonate moiety was achieved by comparison with the NMR spectra of ethylmercury(II) dithizonate in which the only aromatic signals are those due to the dithizonate and which was especially synthesized for this reason. For the sake of consistency and ease of comparison, the aromatic proton and carbon atoms of this compound were also

numbered as shown in Fig. 13 although, of course, the atoms H_a-H_d and C_1-C_8 are then absent.

The assignment of the resonances due to the protons H_h (Fig. 13) in ethylmercury(II) dithizonate was based on a weak coupling of these protons to the imino hydrogen, $-NH-$, which was observed in a 2D COSY experiment, and the remainder of the assignments then followed from a careful correlation of the cross-peaks in the COSY spectrum.

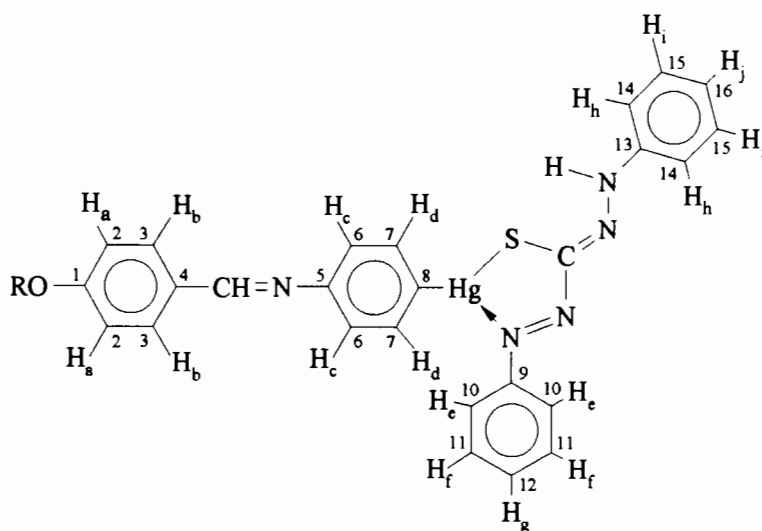
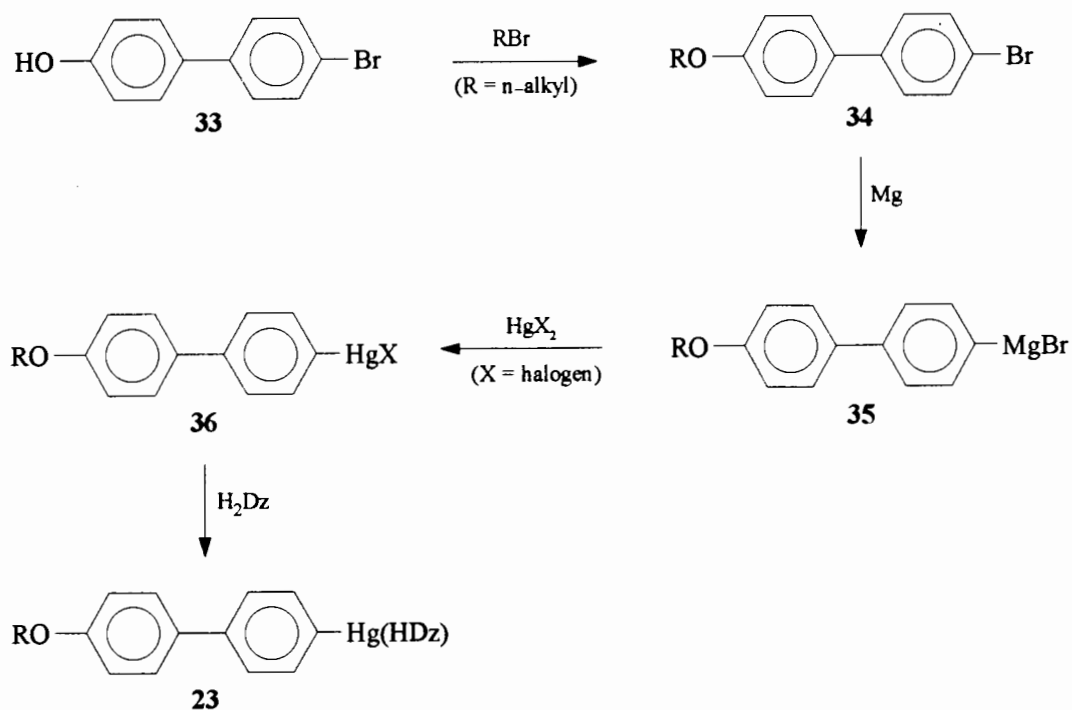


Fig 13 H and C numbering of the compounds **22** for the purposes of NMR assignment.

Preparation of the biphenyl series

The key feature in designing the synthesis of the 4-(4'-n-alkoxybiphenyl)mercury(II) dithizonates **23** was the necessity of introducing a single mercury atom into the biphenyl nucleus at a position *para* to a long alkoxy chain so as to generate a molecule having the required elongated, linear geometry. The proposed synthetic route was therefore as outlined in Scheme 6, starting from the commercially available and relatively inexpensive 4-bromo-4'-hydroxybiphenyl **33**.



Scheme 6

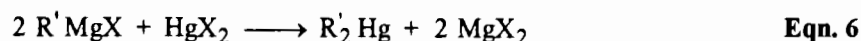
The first step here is the protection of the hydroxyl group as the ether. This prevents reaction of magnesium at this site and, at the same time, conveniently introduces the long alkoxy chain important in the construction of a mesogenic molecule.

Reaction of the 4-alkoxy-4'-bromobiphenyls **34** with magnesium was expected to give the Grignard reagents **35**. These organomagnesium halides are not isolated and usually react smoothly with mercury(II) halides according to Eqn. 5.⁷⁶



It is generally stipulated in the literature that the halogen atoms X in Eqn. 5 should be identical in both reaction partners,^{76,77} although alkylmercury chlorides have been prepared in this laboratory from the corresponding alkylmagnesium bromides and mercury(II) chloride without difficulty and in good yield.⁷⁸ However, the Grignard reagent must be formed separately and any unreacted metallic magnesium then removed by filtration through glass wool, lest it reduce the mercury(II) halide.⁷⁶ The

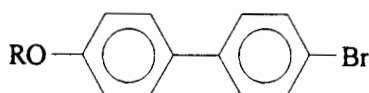
molar ratios of the two reagents are also important: in the presence of a two-fold excess of the Grignard reagent the diorganomercury(II) compounds are obtained (Eqn. 6).⁷⁶



The final step in Scheme 6 is the coordination of dithizone **25** to give the required product **23**.

Synthesis of the 4-n-alkoxy-4'-bromobiphenyls 34

The ethers **34a–j** were prepared in high yield (80–90%) and purity by reaction of **33** with sodium hydride and the appropriate alkyl bromide in DMF. Reaction was usually complete after 1 hour at near-reflux temperatures and the product was precipitated out of solution by pouring onto crushed ice and isolated by filtration. This material was recrystallized from methanol (**34a–c**) to give a fine, white powder or from chloroform (**34d–j**) to give large, semi-translucent, white plates.



	R		R
34 a	C ₃ H ₇	f	C ₁₂ H ₂₅
b	C ₄ H ₉	g	C ₁₄ H ₂₉
c	C ₅ H ₁₁	h	C ₁₅ H ₃₁
d	C ₁₀ H ₂₁	i	C ₁₆ H ₃₃
e	C ₁₁ H ₂₃	j	C ₁₈ H ₃₇

The thermal behaviour of these compounds proved interesting (see later) and for this reason as many of the ethers as possible were prepared in an attempt to build up a

homologous series for investigation, although not all the necessary alkyl halides were available and a complete series is lacking. Not all these compounds were taken through to the second step of the synthesis.

Synthesis of the 4-(4'-n-alkoxybiphenyl)mercury(II)halides 36

All attempts to form the intermediate Grignard reagents **35** were unsuccessful. Reaction was first attempted between 4-bromo-4'-dodecyloxybiphenyl **34f** and magnesium turnings in diethyl ether and then repeated using the propoxy homologue **34a**, lest the reactivity (or lack thereof) proved to be a function of alkyl chain length, together with a very much more finely divided grade of magnesium which, insofar as it presents a greater surface area, was expected to be more reactive. In both cases crystals of iodine were added in an attempt to initiate reaction⁷⁹ and the mixtures were heated at reflux for periods in excess of a day.

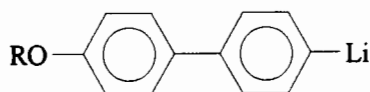
However, no reaction was observed and the magnesium metal appeared bright and unaffected, while in the second experiment described above the metal was also recovered quantitatively by filtration, confirming the absence of any reaction.

Reaction of 4-bromo-4'-propoxybiphenyl **34a** and magnesium was also attempted in tetrahydrofuran, which is a more polar solvent than diethyl ether and often effective where diethyl ether is not,⁸⁰ but again without effect.

A great many organic halides are unreactive towards magnesium under the standard Grignard reaction procedure and a number of techniques have been developed to overcome this. Among them is the method of 'entrainment' in which an excess of magnesium is treated with a mixture comprising one equivalent of the organic halide corresponding to the desired Grignard reagent and one or more equivalents of some other organic halide such as ethyl bromide, which reacts readily with magnesium and

serves to activate the metal surface.⁸¹ The use of highly pre-activated magnesium powders such as Rieke's magnesium⁸² is a second option.

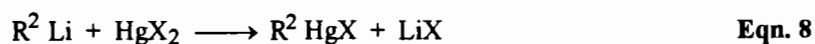
However, before either of these methods was investigated, it was decided to explore rather the preparation of lithiated derivatives **37** of the bromobiphenyl ethers since such species are also purported to react easily with mercury(II) halides^{83,84} and the required organolithium reagents (n-butyllithium, methyllithium, *etc.*) were readily available in the laboratory.

**37**

The lithium-halogen exchange reaction, Eqn. 7, is usually rapid even at low temperatures.⁸⁴ The position of the equilibrium depends on which of the two organic fragments R¹ or R² is better able to stabilize the charge of the lithium.



As with the organomagnesium halides described previously (Eqn. 5) the lithiated species R²Li are not isolated but reacted *in situ* with the mercury(II) halide (Eqn. 8). Here, however, it is not required that the halogen atoms X in Eqns. 7 and 8 be the same.



In the initial studies, a solution of 4-bromo-4'-propoxybiphenyl **34a** in THF was cooled to below -70 °C using a dry ice-acetone bath. A slight excess (1.2 equivalents) of n-butyllithium was then added and the mixture was allowed to stir for 30 minutes. One

equivalent of mercury(II) chloride was then introduced in a single portion either as the solid or dissolved in THF and the reaction mixture was allowed to come slowly to room temperature. Some 30 to 45 minutes after the addition of the mercury(II) chloride traces of metallic mercury were observed and these increased with time while the solution took on a greyish colour. The reduction of the mercury(II) was indicative of a failed reaction and these reaction mixtures were not worked up.

A number of parameters can be varied in the above reaction procedure and it was decided to investigate these systematically in the hope of successfully preparing the required organomercury(II) derivatives **36**.

The solvent was first changed to diethyl ether and the reactions were repeated as described above, but with similar results.

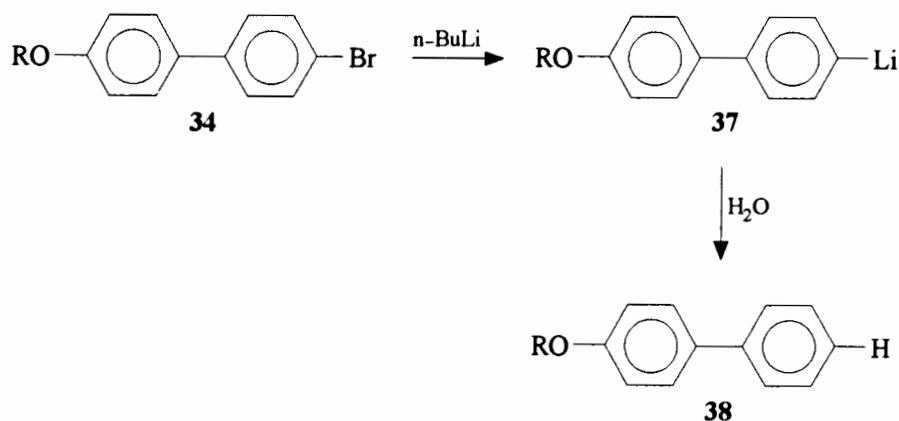
Attention was next focused on the temperature at which the reaction was performed. Reactions with n-butyllithium and similar organolithiums are invariably carried out at low temperature to protect such functional groups as C=O and C≡N, which are able to react with the lithiated species.⁸⁴ Such functionalities are not present in the biphenyl systems under consideration although it should be mentioned in this context that competitive metallation of *ortho*-hydrogen atoms made acidic by the adjacent halogen atom can occur as an alternative to metal-halogen exchange. This side-reaction can be reduced by using low temperatures and electron-donating solvents such as ethers rather than hydrocarbons. However, while metallation of *ortho*-hydrogens is especially common for fluoro- and also chloro-arene compounds, it is only occasionally observed for the bromo derivatives even at elevated temperatures.⁸⁴

There did not therefore appear to be any compelling reason to conduct further reactions at low temperatures and an experiment was performed at room temperature. An equivalent of n-butyllithium was added to a solution of the biphenyl **34a** in THF at

room temperature and the mixture was stirred for 30 minutes; a slightly murky solution was obtained. A solution of mercury(II) chloride in THF was added to this and the reaction mixture was left to stir at room temperature. A pronounced green colour was observed as well as a considerable deposit of metallic mercury. Thin-layer chromatography showed a complex mixture of compounds, separation of which was not attempted. It is possible that some of these products were the result of coupling reactions (Eqn. 9) and since such coupling is more probable in THF than in the less polar diethyl ether,⁸⁴ subsequent reactions were performed in the latter solvent.



At this stage it was decided to investigate separately the first of the two reactions described by Eqns 7 and 8 and a control experiment was set up in order to determine whether the lithiated biphenyl derivative **37** was in fact formed under the reaction conditions employed. Because of the difficulty of isolating such lithiated species, further reaction with water was attempted (Scheme 7); the expected product of lithium-hydrogen exchange is the 4-alkoxybiphenyl **38**, formation of which may be easily established by ¹H NMR spectroscopy.



Scheme 7

A slight excess of n-butyllithium was therefore added to a solution of 4-bromo-4'-propoxybiphenyl **34a** in diethyl ether at room temperature, the mixture stirred for 30 minutes and then quenched by the addition of one mole equivalent of water. A fluffy white precipitate was instantly formed and the ^1H NMR spectrum of this product clearly showed the collapse of the signals due to the H_c , H_d system (refer to Fig. 12) to a multiplet integrating for 5 protons and attributable to the phenyl group in **38**.

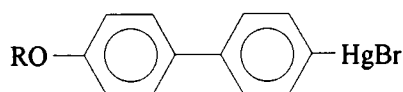
The reactivity of the starting material **34a** towards bromine-lithium exchange and the integrity of the rest of the molecule after treatment with n-butyllithium at room temperature were thus established. The failure to prepare the required mercurated derivative **36** must therefore lie in the methodology of the reaction between the lithiated biphenyl **37** and the mercury(II) salt.

It was decided to investigate a method of inverse addition whereby the 4-alkoxy-4'-lithiobiphenyl **37** was added slowly to a solution of mercury(II) chloride, with the rationale that, in the presence of an excess of the mercury salt, the preferred reaction would be attack of this species on the organolithium rather than reduction of mercury(II). Because of the extreme air-sensitivity of organolithium derivatives, the solution containing this species was transferred *via* a metal cannula under a positive pressure of nitrogen to the solution of the mercury(II) chloride. A white precipitate formed immediately on addition and this mixture was stirred for 4 hours at room temperature without the appearance of any metallic mercury. Filtration of the solid material was complicated by its extremely fine particle size and the filtrate always appeared slightly cloudy as some of the precipitate was not retained by the filter paper. However, the product, when isolated in the solid state, appeared to be unstable with portions of the material becoming an orange-brown colour.

For this reason preparation of the organomercury(II) bromide was attempted. The reaction just described was repeated except that the lithiated biphenyl **37** was added to

a solution of mercury(II) bromide instead of mercury(II) chloride. Filtration of the resulting solid was again difficult but this time the product did not visibly deteriorate in air.

The organomercury(II) derivatives **36a–e** were all prepared according to the above method, *i.e.* addition of a solution of the appropriate 4-alkoxy-4'-lithiobiphenyl **37**, prepared by reaction of 4-alkoxy-4'-bromobiphenyl **34** with *n*-butyllithium at room temperature in diethyl ether, to a solution of mercury(II) bromide also at ambient temperature in diethyl ether.



	R		R
36 a	C_4H_9	d	$C_{14}H_{29}$
b	C_5H_{11}	e	$C_{18}H_{37}$
c	$C_{10}H_{21}$		

The most critical factor in the preparation appears to be the method of reagent addition but the temperature is also important: this was confirmed in an experiment performed as described above but at a temperature of $-78\text{ }^\circ\text{C}$, for which the yield of the organomercury(II) bromide was much reduced. The use of mercury(II) bromide in place of the chloride would also appear to be necessary from the preceding discussion but it is possible that a sufficiently pure sample of the organomercury(II) chloride would, in fact, be air-stable.

Considerable effort was expended in attempting to obtain pure samples of the organomercury(II) bromides. The crude products were always obtained together with a contaminant which melted between 214 and $223\text{ }^\circ\text{C}$ and a small amount of a second, much higher-melting compound (m.p. $> 380\text{ }^\circ\text{C}$). The latter material was possibly the

by-product lithium bromide (lit.,⁸⁵ m.p. 550 °C) and the former was assumed to be unreacted mercury(II) bromide (lit.,⁸⁵ m.p. 236 °C), the melting point of which was lowered in the mixture, although analysis of the reaction by TLC before work-up had failed to detect any of this starting material. However, subsequent reaction (see below) confirmed this second assumption.

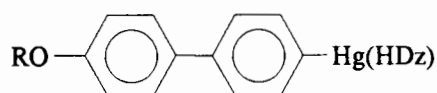
The crude material was profoundly insoluble in all common organic solvents and mixtures thereof. In dimethylsulfoxide (DMSO) the solid turned black and a degree of dissolution seemed to occur but this proved inadequate for the purposes of NMR spectroscopy. This insolubility precluded purification by either chromatography or recrystallization. Extraction of the contaminants into hot methanol in which both mercury(II) bromide and lithium bromide are soluble was also not successful and involved the loss of some material because of the difficulties of filtration already described. Purification by vacuum distillation was attempted but control of temperature and pressure was not fine enough to effect separation of the required product and the mercury(II) bromide, although the sublimed material did appear to be free of the second, higher-melting contaminant which remained unsublimed as a brown residue in the cold-finger apparatus.

No analytical or spectroscopic data for the organomercury(II) bromides **36a–e** is therefore presented. In fact, their successful preparation is only proved by the success of subsequent reaction with dithizone to give the corresponding organomercury(II) dithizonates.

Synthesis of the 4-(4'-n-alkoxybiphenyl)mercury(II) dithizonates 23

The complexation with dithizone **25** to give the compounds **23a–e** was performed in dichloromethane using the base triethylamine to deprotonate the ligand; this method⁸⁶

is quicker and more convenient than the method of extraction with aqueous ammonia used previously.



R

R

23 a C₄H₉ **d** C₁₄H₂₉

b C₅H₁₁ **e** C₁₈H₃₇

c C₁₀H₂₁

In a typical procedure, the crude organomercury(II) bromide **36** (X = Br) was suspended in the solvent and one equivalent (calculated by assuming a 100% purity of the mercurated starting material) of the solid dithizone was added directly to give a dark red, turbid mixture. On addition of only two or three drops of triethylamine, a clear, red solution was obtained, containing a small amount of undissolved brown material. The latter was assumed to be triethylamine hydrobromide (white when pure) mixed with perhaps some lithium bromide and mercury(II) bromide; it was removed by filtration. Analysis of the filtrate by thin-layer chromatography revealed two products; these appeared as two red spots on the TLC plate, with the intensity of the lower spot, corresponding to the more polar product, judged to be approximately twice that of the other.

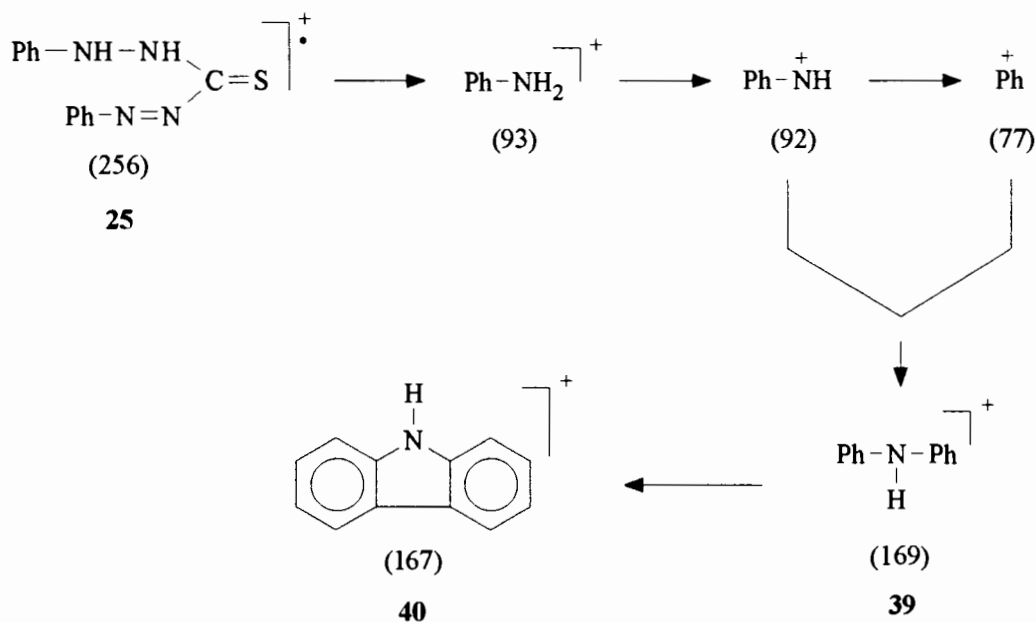
Separation of these two reaction products was achieved by column chromatography on silica using toluene as the eluent. The first few fractions of the first compound to elute from the column were observed to change from a pale yellow colour to a light blue merely on standing in daylight in the laboratory. This blue colour persisted indefinitely and the colour change was fully reversible on alternate exposure to light and dark. These observations record the classic response of the mercury(II) dithizonate system to light; similar observations were responsible for the first recognition of the

photochromism of these complexes.⁵² The blue colour was not evident in the more concentrated fractions, which were collected as the bulk of the material eluted, but these solutions did darken in the light from yellow-orange to green-red; the colour here is presumed to correspond to a state of only partial photoisomerization due to the low level of activating light intensity. A degree of darkening of the fractions containing the second component was also noticed but the effect seemed less pronounced and the blue colour was not observed in any of these solutions.

The identity of the two reaction products was investigated by ¹H NMR spectroscopy and the less polar compound, which eluted first from the column, was established to be the required 4-(4'-alkoxybiphenyl)mercury(II) dithizonate **23**. The second product was either the mercury(II) bis(dithizonate), Hg(HDz)₂, or the mono-substituted compound, HgBr(HDz), obviously formed from unreacted mercury(II) bromide present in the starting material. The degree of substitution could not be determined from the NMR spectrum since the two dithizonate moieties in the bis-substituted compound are chemically equivalent and give rise to signals of identical shift. However, determination of the melting point (220–223 °C) identified this product as the mercury(II) bis(dithizonate) (lit.,⁷⁴ m.p. 223–224 °C). The yield of this material was always some 20–30% that of the organomercury(II) dithizonate **23**: evidently the observed intensities of the two compounds when spotted on TLC plates was not a concentration effect but rather due to the fact that in one of the compounds there are two identical absorbing chromophores compared to only one such in the other product.

The mass spectra of three of the organomercury(II) dithizonates **23c**, **d** and **f** were recorded. A molecular ion was observed only in the case of compound **23c**. Most of the peaks corresponding to the successive loss of methylene units from the alkoxy chains, were detected in the mass spectra. A strong peak at $m/z = 422$ was observed in the spectrum of **23f**, corresponding to the loss of the dithizonate moiety from the molecular ion; a peak at 508 may represent the recombination of the dithizonate with a

phenyl radical. An interesting feature present in the spectra of all three compounds is the existence of relatively strong peaks at $m/z = 167$, 168 and 169. These peaks are also observed in the mass spectrum of dithizone⁸⁷ **25** and have been attributed to the formation of diphenylamine **39** and its rearrangement to carbazole **40** as shown in Scheme 8,⁸⁷ where m/z values are given in parentheses.

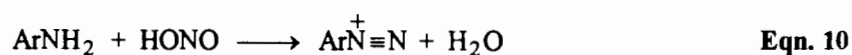


Scheme 8

For the compounds **23d** and **f** the peak at 169 is further reinforced by the fragment $\text{C}_{12}\text{H}_{25}^+$.

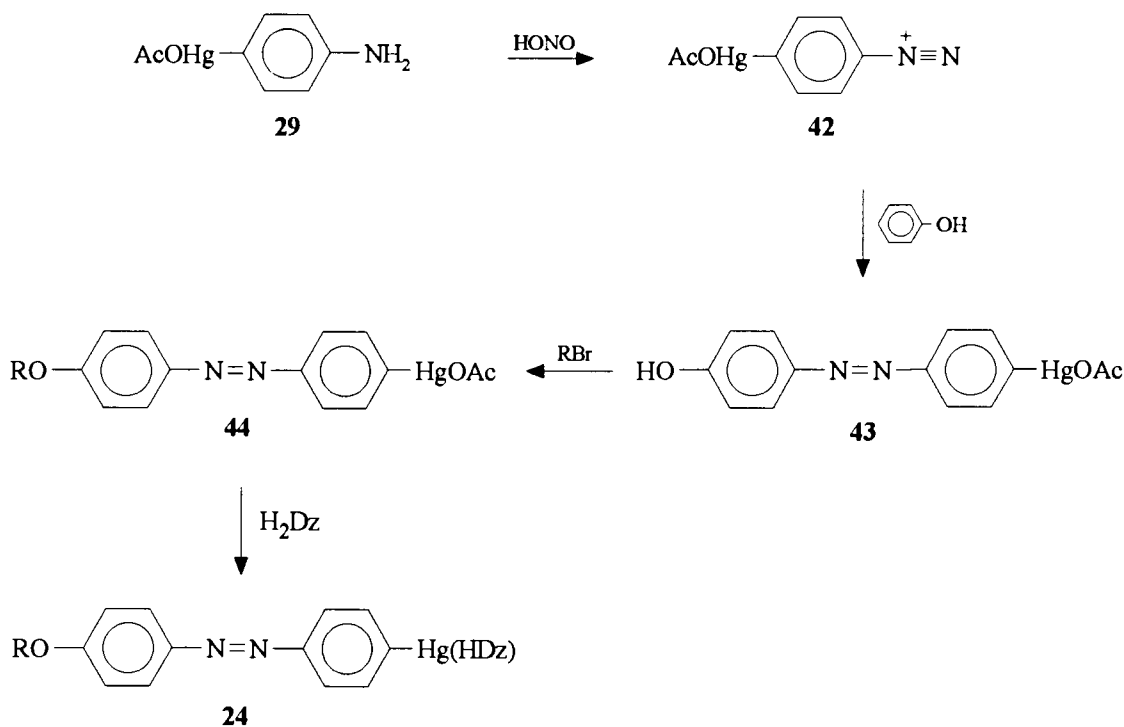
Preparation of the azobenzene series

The diazonium cations **41**, formed by reaction of primary aromatic amines with nitrous acid (Eqn. 10), are versatile synthetic reagents.⁸⁸



41

It was anticipated that diazotization of 4-aminophenylmercury(II) acetate **29** followed by coupling of the diazonium product **42** with phenol to give the azo compound **43** and subsequent reaction of this with an n-alkyl bromide would yield the potential organomercury mesogens **44**, which could then be complexed with dithizone to incorporate the photochromic moiety, as **24** (Scheme 9).



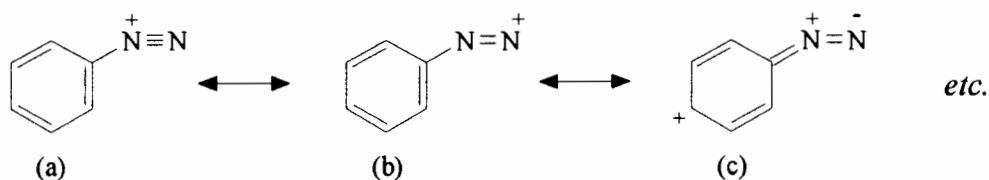
Scheme 9

However, preparation of the 4-acetoxymercurio-4'-hydroxyazobenzene **43** proved less than straightforward; the attempted synthesis is discussed below with reference to the mechanisms of diazotization and coupling.

Diazotization

Diazonium cations are usually prepared as the salts in aqueous acid media.⁸⁸ In the method chosen here,⁸⁹ the nitrous acid was generated *in situ* by reaction of hydrochloric acid and sodium nitrite (Eqn. 11).

Aromatic diazonium cations are stabilized by resonance interaction of the nitrogen atoms and the ring as shown in Scheme 11.



Scheme 11

The contribution of structures of type (c) increases the order of the C–N bond and thus stabilizes the diazonium ion against decomposition by loss of nitrogen; such deamination products are commonly obtained in the reactions of primary aliphatic amines for which resonance stabilization is not possible.⁹³

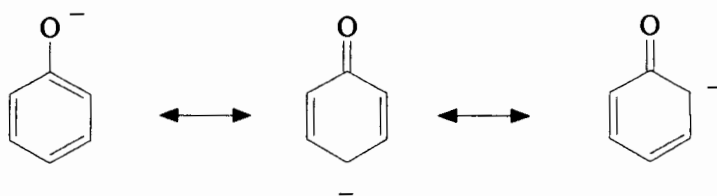
However, even aromatic diazonium ions are stable only at low temperature. For example, virtually all diazonium salts react with water, exchanging the diazo group for a hydroxyl group; at temperatures below about 5 °C this reaction usually proceeds only slowly,⁸⁸ but for diazonium salts obtained from weakly basic amines it may seriously interfere with other required reactions.⁹² Although pK_a values for 4-aminophenylmercury(II) acetate are not available in the literature, the basicity of this compound would be expected to be reduced from that of the parent molecule, aniline, since the electron withdrawing effect of the $-\text{HgOAc}$ substituent acts to decrease the electron density at the nitrogen atom. In the experiments conducted here the reaction temperature was maintained at or below 3 °C, where necessary by the addition of ice to the mixture.

In addition to their sensitivity to temperature, diazotization reactions are strongly pH dependent. Increasing the solvent acidity promotes the formation of more powerful nitrosating agents such as the nitrosonium ion, NO^+ , but at the same time increases the concentration of the unreactive, protonated form of the amine (Eqn. 12).⁹⁰ Diazo

coupling reactions involve nucleophilic attack of π -electron systems on the β -nitrogen of the diazonium species: in mildly acidic or neutral solutions the already-formed diazonium cation faces attack from unchanged amine, and the products of self-coupling may be the aryl triazenes Ar-N=N-NHAr , or the diazoamino compounds ArN=N-Ar-NH_2 .⁸⁹ In the usual experimental procedure for the preparation of diazonium salts, the amine is dissolved in a suitable volume of water containing 2.5–3 equivalents of mineral acid; the excess of the acid maintains the proper conditions of acidity necessary to stabilize the diazonium salt during formation and hence minimizes such secondary reactions as self-coupling.⁸⁹

Azo-coupling

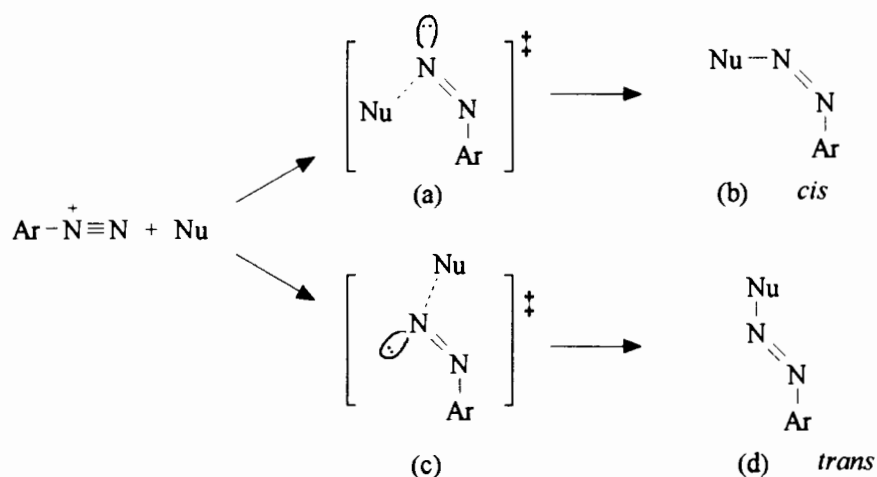
In this work, the required coupling reaction is that between the diazonium species and phenol. Because the diazonium cation is a relatively weak electrophile powerful electron donating groups must be present in the aromatic system of the other coupling component if reaction is to occur. Phenols are not reactive enough and must be coupled in slightly alkaline solution, where they are converted to the more reactive phenoxide ion.⁹⁴ Again the pH is important because in acid media the phenol is protonated and loses its reactivity, whereas in moderately alkaline solution the diazonium ion is converted to the unreactive diazotate anion, Ar-N=N-O^- .⁹⁴ Reaction with the phenoxide ion occurs at sites of increased electron density, *viz.* *ortho* or *para* to the activating group, as shown in Scheme 12 (coupling does not occur at the O atom because of the relatively weak O–N bond that would result compared with the C–N bond).⁹⁵



Scheme 12

Because of the bulk of the attacking nucleophile, substitution at the *para*-carbon atom is favoured.⁹⁴ This is exactly the geometry required to generate an elongated linear molecule of the kind required in this work.

Another requirement for construction of a mesogen is the formation of *trans* isomer. Two types of transition state may be envisaged for nucleophilic attack at the β -nitrogen of a diazonium cation: these are depicted in Scheme 13.⁹⁶



Scheme 13

The repulsion between the lone pair on the β -nitrogen and the aryl group of the diazonium species favours a *trans* configuration of these two groups as in structure (a). This is the dominant interaction in the system when the repulsion between the attacking nucleophile and the aryl diazonium group is small: a situation which pertains when the distance $\text{Nu}-\text{N}_\beta$ is large. In such a case the transition state is said to be 'reactant-like', structure (a) is on a lower energy level than (c) and the nucleophile attacks N_β in a *cis* configuration.

If, however, the transition state is 'product-like', the $\text{Nu}-\text{N}_\beta$ distance is short, repulsion between Nu and Ar is stronger than that between the N_β lone pair and Ar , and the transition state (c) leading to the *trans* azo compound (d) is favoured.

It has been established⁹⁶ that the transition states of diazo coupling reactions are more 'product-like' than for diazonium ion interaction with anions such as OH^- , CN^- or N_3^- , a result which is consistent with general expectation since the interaction of a cation with a small anion having a localized negative charge is likely to proceed through a more 'reactant-like' transition state than the reaction of the cation with a molecule or anion such as the phenoxide ion, in which the negative charge is more highly delocalized.⁹⁶

Thus, while *cis* compounds are formed in reactions with hydroxide and cyanide ions, the *trans* isomers are the products in reactions with diazo coupling components such as phenols.

Attempted synthesis of 4-acetoxymercuro-4'-hydroxyazobenzene 43

Details of the diazotizations and coupling reactions attempted are given in Chapter 3 (Experimental) and are discussed here more generally. The initial diazotizations were performed in both hydrochloric and acetic acids; in the latter medium the nitrosating agent is expected to be the nitrosyl acylate, AcONO .⁹²

The 4-aminophenylmercury(II) acetate **29** dissolved in aqueous acetic acid with heating; on subsequent cooling to 0 °C a precipitate was observed which may have been the starting material but was quite possibly the protonated amine salt $\text{ArNH}_3^+\text{AcO}^-$. Dissolution of **29** in aqueous hydrochloric acid was not achieved; however, in both instances, the dropwise addition of a chilled solution of sodium nitrite to the suspension of **29** in acid at 0 °C was accompanied by the immediate formation of an intense yellow colour. Since this colour was also observed in the successful diazotization of aniline (see below) it was taken to indicate formation of the diazonium cation. However, in contrast to the reaction with aniline, the colour of the diazotized

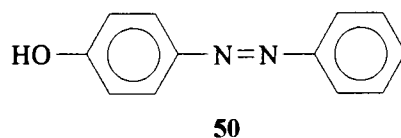
solution of **29** rapidly darkened, becoming orange-brown even before addition of the sodium nitrite was complete.

The diazonium salts are usually reacted further without isolation: dropwise addition of the cold diazonium solution to a chilled solution of phenol in 10% aqueous sodium hydroxide gave a dark brown mixture which on filtration yielded a small amount of a brown solid. Analysis of this material by TLC revealed a single main component, although traces of other products were observed. The material was of limited solubility in most organic solvents but sufficiently soluble in DMSO to obtain a ^1H NMR spectrum which showed two broad multiplets in the phenyl region; however, no signal attributable to the methyl protons of the $-\text{HgOAc}$ group was detected, indicating that this was not the required product **43**. The extraction of the filtrate with ethyl acetate yielded a black, tarry material smelling strongly of phenol.

Various experiments were performed in an attempt to prepare the azo-coupled product **43** successfully. Considering simply the colour differences observed in the diazotizations of aniline and of the acetate **29**, it is possible that the diazonium salt underwent side-reactions before the phenol was even introduced. Diazotization was therefore attempted in a solution in which the concentration of hydrochloric acid was doubled in order to limit the possibility of self-coupling before addition to an alkaline solution of phenol. A second experiment was performed at $-5\text{ }^\circ\text{C}$ to guard against partial hydrolysis of the diazonium salt to the phenol.

In both instances only a small quantity of brown solid was obtained, with the greater amount of material extracted as a black tar from the filtrate.

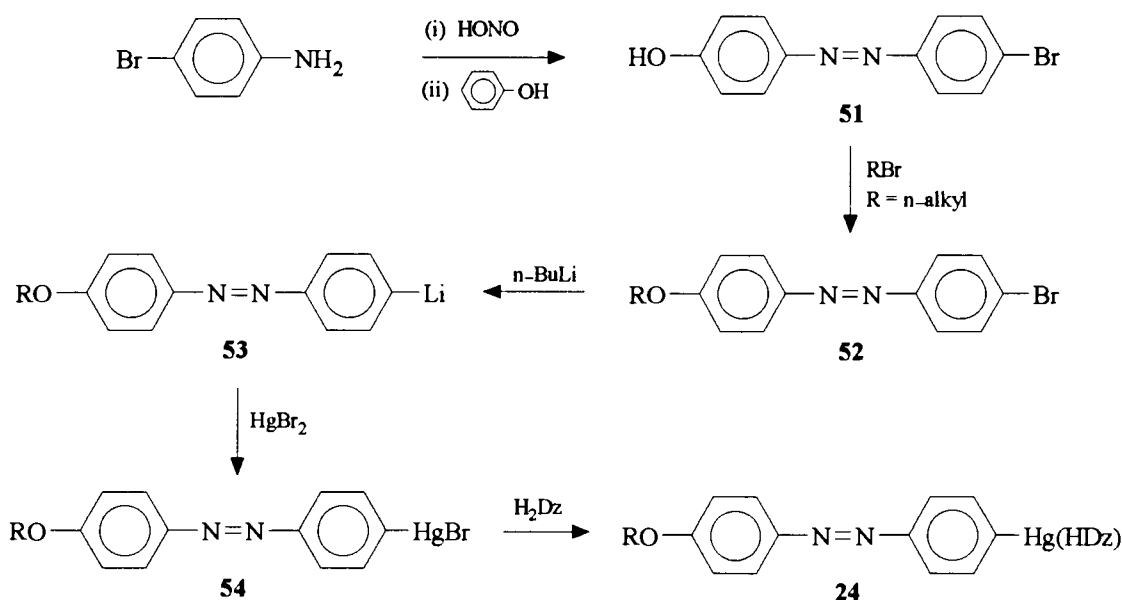
In an experiment performed under the standard experimental conditions,⁸⁹ aniline was diazotized in hydrochloric acid and successfully coupled with a solution of phenol in 10% aqueous sodium hydroxide, to give 4-hydroxyazobenzene **50**.



The difficulties encountered in the preparation of the azo-compounds **43** must therefore arise from the presence of the $-\text{HgOAc}$ group and its unknown effect on, or response to, the conditions employed in the diazotization and coupling reactions. For example, nitrosyl chloride is known to cleave diorganomercury(II) compounds to give the nitroso derivative (Eqn. 15) and nitrogen oxides such as N_2O_3 react with diarylmercurials to give nitroso compounds or diazonium salts or both (Eqn. 16)⁶¹ and it is possible that similar mechanisms are operating in the reactions attempted here.



Because of the many possible side-reactions and uncertainties involved in the diazotization and coupling of 4-aminophenylmercury(II) acetate, a revised synthetic route was drawn up (Scheme 14) starting from 4-bromoaniline and proceeding to the required organomercury(II) dithizonates **24** by the same method developed for the biphenyl compounds **23**.

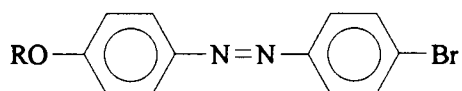


Synthesis of 4-bromo-4'-hydroxyazobenzene 51

The diazotization of 4-bromoaniline and the azo-coupling to phenol to give 4-bromo-4'-hydroxyazobenzene **51** were readily achieved according to standard procedure for this type of reaction.⁸⁹ The product was assumed to be the *trans* (*E*) isomer although there is no direct evidence for this configuration. However, the argument already presented concerning the transition states through which the reaction proceeds indicates that the *trans* isomer is the expected product. No signals indicating a mixture of isomers were observed in the ¹H NMR spectrum.

Synthesis of the 4-n-alkoxy-4'-bromoazobenzenes 52

The ethers **52a–d** were prepared in the usual way, *i.e.* by reaction of **51** with the appropriate n-alkyl bromide in the presence of sodium hydride in DMF at elevated temperature. Again the product was taken to be the *trans* isomer, an assumption consistent with the fact that the isomerization of the *cis* (*Z*) form of azobenzene to the sterically less crowded and thermodynamically more stable *trans* isomer is effected by heat.⁹⁷



R

52 a	C ₅ H ₁₁
b	C ₈ H ₁₇
c	C ₁₀ H ₂₁
d	C ₁₄ H ₂₉

Attempted synthesis of 4-(4'-n-octyloxyazobenzene)mercury(II) bromide 54
(R = C₈H₁₇)

Because of the presence of the –N=N– group and its potential sensitivity towards organolithium reagents, the reaction of the brominated azobenzene derivatives **52** with n-butyllithium was performed below room temperature. A solution of the azobenzene **52b** was chilled to 0 °C in diethyl ether: addition of a slight excess of n-butyllithium was immediately accompanied by a colour change from golden-yellow to black; however, this faded after a few minutes stirring to give a murky, brown solution. When this mixture was transferred to a solution of mercury(II) bromide similarly maintained at 0 °C, a fluffy brown precipitate was instantly formed and analysis by TLC failed to detect any unreacted mercury(II) bromide. The mixture was concentrated to dryness and the residue proved to be moderately soluble in aromatic hydrocarbons such as toluene; however, the purification of this material was not attempted since, from experience with the biphenyls, the separation and identification of the reaction products was most easily achieved after complexation with the dithizonate ligand.

Reaction with dithizone was conducted as described for the biphenyls **36**: addition of triethylamine to a suspension in dichloromethane of dithizone and the brown product obtained above, gave a bright red solution. A small amount of undissolved black material was filtered off and analysis of the filtrate by TLC indicated three main components which appeared, in order of decreasing R_F value, as yellow, intense red and bright pink spots on the TLC plate. This last spot was recognized as unreacted dithizone. The other two products were cleanly separated by chromatography on silica gel using toluene as the eluent. They were identified as the unreacted starting material **52b** and mercury(II) bis(dithizonate).

An exactly similar result was obtained when the reaction between **52b** and n-butyllithium was performed at a temperature below $-70\text{ }^{\circ}\text{C}$; in this instance the addition of the n-butyllithium was not accompanied by the initial black colour observed previously, but the solution did darken to brown. Since the unreacted starting materials were recovered, the above colour changes remain unexplained. The addition of the mixture of **52b** and n-butyllithium to the solution of mercury(II) bromide must induce co-precipitation of the mercury(II) bromide, so that when an aliquot of the reaction mixture was withdrawn and spotted on the TLC plate the dissolved mercury salt was not detected and the reaction was incorrectly deemed successful.

These investigations could not be pursued because of time limitations but it is probable that careful attention to the conditions of the reaction, as was necessary for the preparation of the mercurated biphenyls **36**, would result in the successful preparation of the 4-(4'-n-alkoxyazobenzene)mercury(II) dithizonates **24**.

Thermal studies

Optical microscopy

The detection of liquid crystalline behaviour and the identification of the type of mesophase relies in the first instance on polarized optical microscopy. The technique is based on the birefringence of the liquid crystalline state: at the melting point a solid exhibiting a mesophase transforms to a turbid liquid and plane polarized light incident on this sample (as illustrated in Fig. 14) gives rise to two refracted rays which result in characteristic interference patterns when viewed through a second polarizer, called the analyser and set at right angles to the first. On heating to the clearing point the turbid liquid becomes isotropic and consequently optically clear: the field of vision appears black through crossed polarizers.

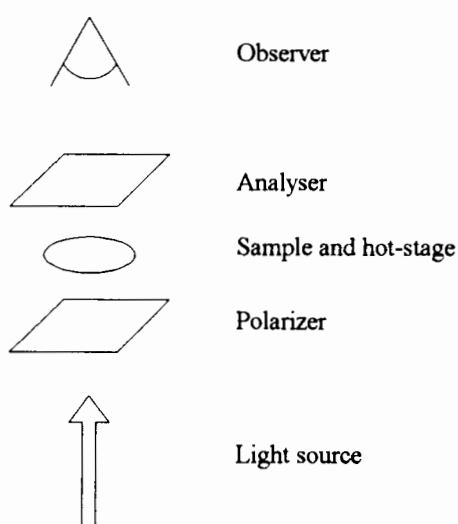


Fig 14 Schematic view of a polarized, hot-stage microscope.¹⁰

The parameter \mathbf{n} , the 'director' (introduced in Chapter 1), defines the direction of the preferred axis of alignment in a liquid crystal. In an actual sample the orientation of \mathbf{n} is imposed by the boundary conditions and by external fields; without special preparation of the support and cover slide (by chemical treatment or mechanical

manipulation) the boundary conditions will vary over the substrate, resulting in variations in the director throughout the sample and thus in differences in birefringence.⁹⁸ This is seen as a characteristic pattern or 'texture' when the mesophase is viewed through crossed polarizers.

The texture is thus defined as 'the sum of the topological elements which are large enough to be observed under the polarizing microscope'.³³ It has also been described as the liquid crystal analogue to 'morphology' in solid crystals because the texture arises from the typical molecular short range order which in turn depends on the molecular structure.³³

Liquid crystal texture is critically dependent on external influences such as boundary surfaces, sample thickness and purity, external electric and magnetic fields and also the thermal and temporal history of the sample.³³ Depending on these conditions, a given mesophase can display different microscopic textures, so that a change in texture does not necessarily imply a change in liquid crystal phase. The characteristic textures of a mesophase may be distorted by adverse environmental conditions. Impurities can induce the appearance of a mesophase where none exists in the pure sample or can suppress formation of a mesophase which would otherwise be present. Impurities can also act to broaden the liquid crystal range by shifting the phase transitions to lower temperatures by several degrees.⁹⁹

It will be obvious that the unambiguous identification of a mesophase by optical microscopy is a skill attained only by the experience of repeated observations and comparison with a great many standards. Nevertheless, certain so-called 'type-textures' are diagnostic of a given mesophase and the main features of these are briefly described below for the nematic and some of the more commonly encountered smectic phases.³³

Liquid crystal type-textures

The textures are best developed and most characteristic when obtained as part of a cooling sequence.¹⁰ For example, on cooling an isotropic melt the nematic phase is often observed to separate at the clearing point in the form of free-standing droplets which exhibit the characteristic 'four-leaf clover' pattern visible in both the large and small droplets in the upper right corner of Fig. 15. These droplets are a type-texture of the nematic phase since they are not observed elsewhere.

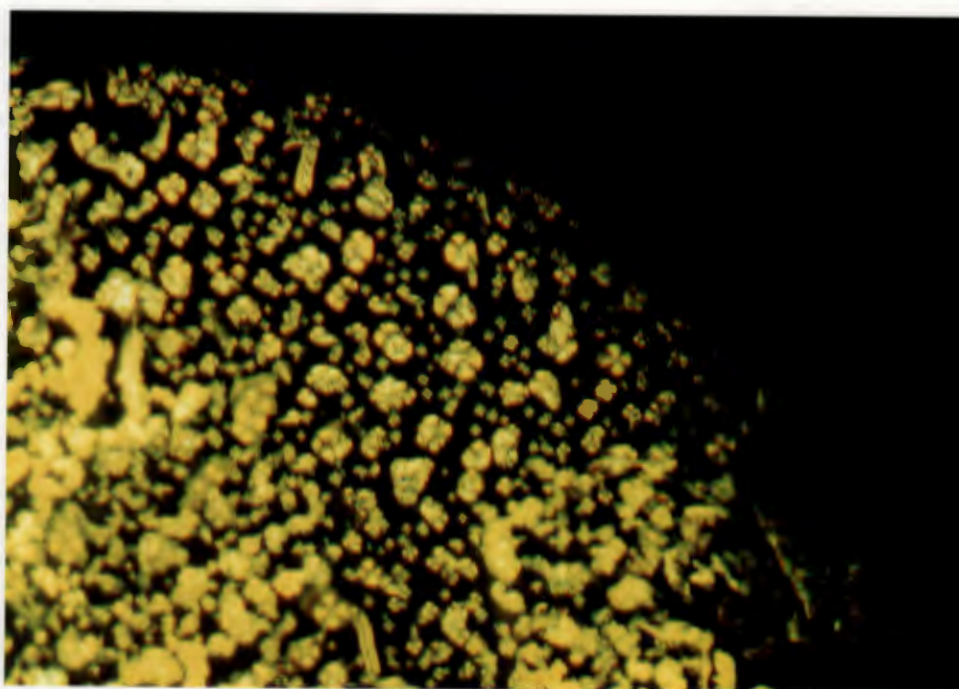


Fig 15 Nematic droplets (top right corner) of compound 52a at 88 °C.

The term 'nematic', from the Greek word for 'thread', reflects the thread-like disclination lines which are often observed in the textures of this mesophase and which arise from discontinuities in the director pattern. The schlieren pattern is a variation of the thread-like texture in which the director is oriented perpendicular to the surfaces of the glass slides between which the sample is sandwiched. This texture appears in both the smectic B and C phases as well as in the nematic phase and is easily recognized by the characteristic double (Fig. 16a) or quadruple (Fig. 16b) singularities. These black

bands are regions of extinction called, respectively, two- and four-schlieren brushes, with only the latter appearing in S_C phases.

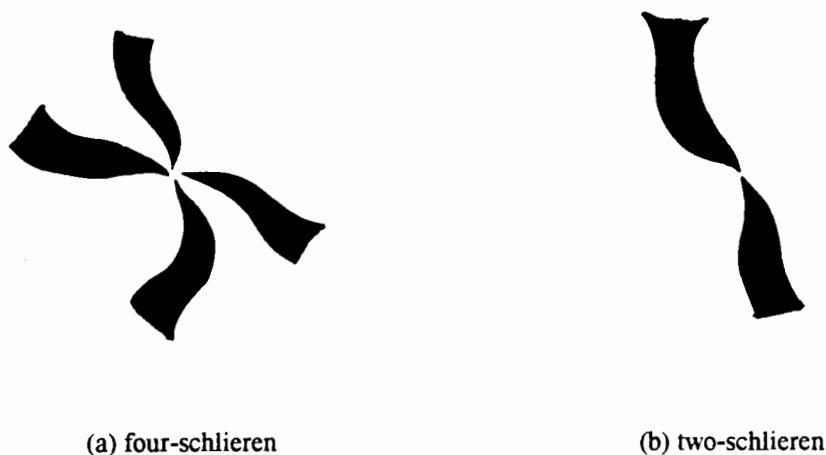


Fig 16 Schematic representation of the singularities observed in schlieren liquid crystal textures.

The mosaic and marbled textures are sub-forms of the so-called homogeneous texture which describes a situation in which the director is oriented parallel to the boundary surfaces. The mosaic texture is typically observed in the smectic B mesophases and is distinguished by its striking interference colours and surfaces with curved grain boundaries. In the nematic marbled texture, on the other hand, surfaces with different orientations nonetheless exhibit a regular direction of extinction and give rise to areas with sharp, straight borders.

The smectic A and C phases are the most commonly encountered of the smectic phases and are recognized by the typical fan shaped or focal-conic texture. The latter term refers to the occurrence of elliptical or hyperbolic structures possessing a common focus: both shapes are visible in Fig. 17. This fan structure is less distinct in smectic C mesophases which are therefore described as exhibiting a 'broken focal-conic' texture.

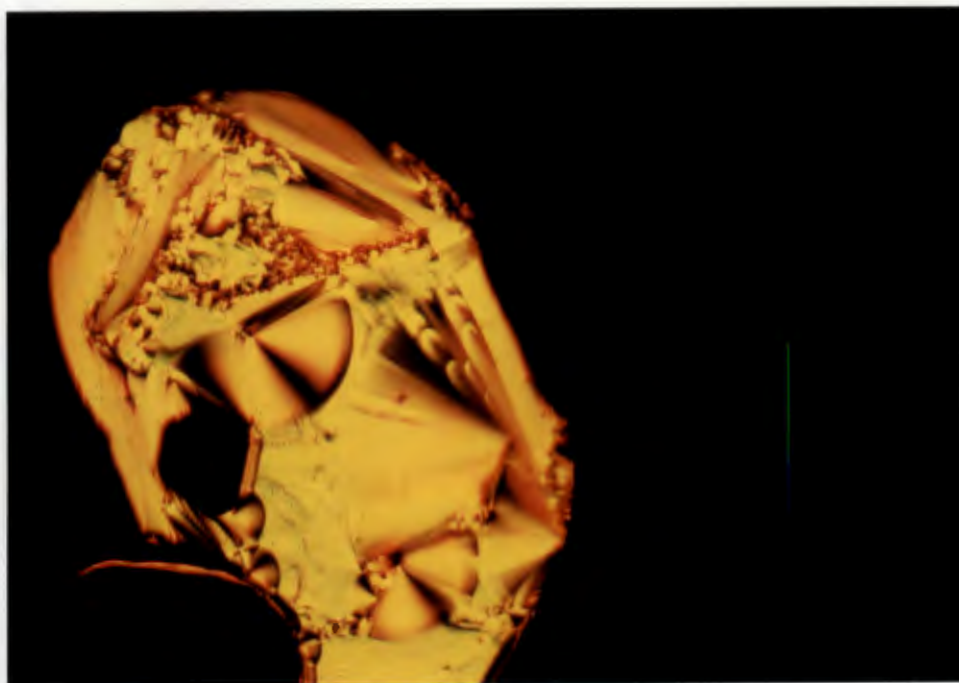


Fig 17 Focal-conic texture of compound **52b** at 95 °C.

The formation of the so-called bâtonnets on cooling the isotropic melt indicates the existence of a smectic phase. Bâtonnets are rod-shaped structures with cylindrically symmetrical protrusions and are analogous to nematic droplets with regard to the conditions of their formation. On further cooling the bâtonnets coalesce to form larger structures from which the compact focal-conic texture is ultimately derived.

Thermal analysis

Mesophase transitions involve energy changes and these thermal events may therefore be detected by the techniques of thermal analysis. In the differential scanning calorimetry (DSC) experiment the sample and a reference material are separately maintained at identical temperatures throughout a controlled heating and cooling program; any difference in the independent energy supplies to the sample and reference is then recorded as a function of temperature.¹⁰⁰ Thermal events in the sample therefore appear as either endo- or exothermic deviations from the DSC baseline,

where the convention is to represent the endothermic response as positive, *i.e.* above the baseline.

The investigation of liquid crystalline behaviour by DSC is a necessary complement to a study of the optical textures because, as already mentioned, all changes in texture do not necessarily correspond to a change in mesophase type and, conversely, all phase changes do not always lead to an easily identifiable change in texture.¹⁰

Thermal behaviour of the Schiff-base mercury(II) acetates 31 and dithizonates 22

The mesomorphism of 4-(4'-methoxybenzylideneanilino)mercury(II) acetate was first reported by Vorländer⁴² who recorded a liquid crystalline phase bounded by a clearing point of 176 or 177 °C and a melting point of 180 °C. Although a weakly birefringent structure of indeterminate texture was observed optically in this temperature range for the same compound prepared in this work, separate peaks corresponding to crystal → mesophase and mesophase → isotropic liquid transitions were not detected in the DSC thermogram.

Similar results were obtained for the compounds **31b–e**. However, it is often difficult to distinguish between real and apparent birefringence³³ and in the case of the compounds **31c–e** an apparently birefringent texture proved on closer examination to be simply unmelted crystallites in an otherwise isotropic environment. The thermal behaviour of 4-(4'-butoxybenzylideneanilino)mercury(II) acetate **31b** is discussed below with reference to Fig. 18 in which the DSC thermogram obtained at a heating rate of 10 °C min⁻¹ is reproduced. Both peaks (a) and (b) were also observed in the reverse cooling run.

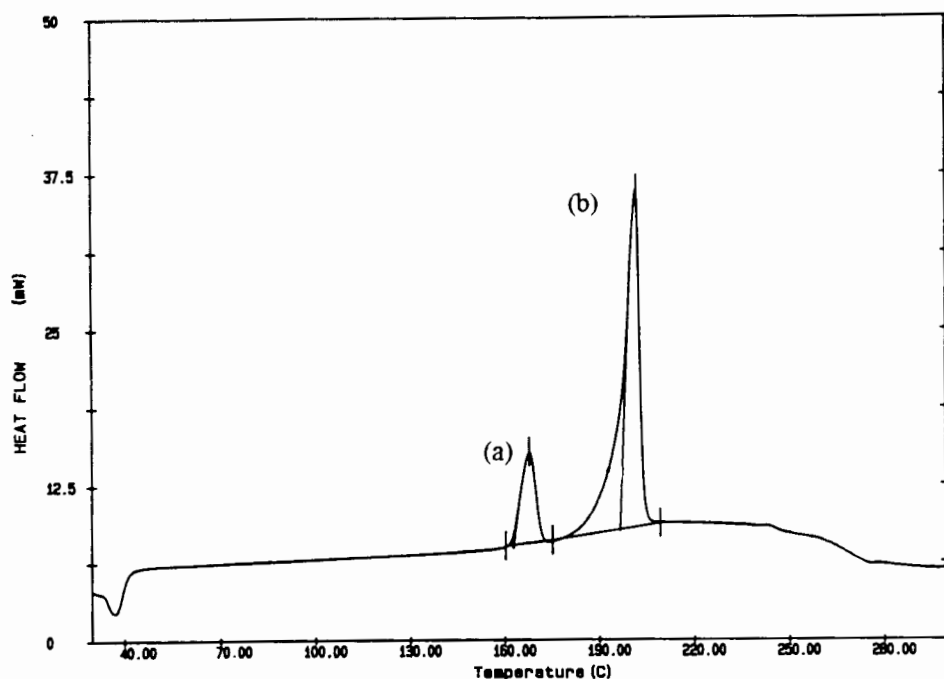


Fig. 18 DSC thermogram obtained at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ for the compound **31b**.

The large peak (b) occurring at an onset temperature of $196\text{ }^{\circ}\text{C}$, as determined by linear extrapolation of the leading edge of the endotherm to the baseline of the DSC thermogram, is an ordinary fusion peak corresponding to the transition from the solid crystal to the isotropic melt. The smaller peak (a) was attributed to a reversible solid–solid transformation: such transitions are often not detected by optical microscopy and no thermal event was observed to occur at this temperature when the sample was studied under the polarizing microscope.

That the two peaks (a) and (b) do not represent, respectively, solid \rightarrow mesophase and mesophase \rightarrow liquid transitions was further substantiated by their relative magnitudes: the latter transition is always characteristically weak relative to the major transformation from the solid to the mesophase and hence both are readily identified in the DSC trace.⁹⁹

As in the case of compound **31a**, a weak birefringence was observed optically on both heating and cooling through a temperature range of 176–181 °C although no evidence of a mesophase transition was detected in the DSC thermogram (Fig. 18). The type of optical texture could not be identified although the observed viscosity of the sample would suggest the presence of a smectic rather than a nematic mesophase. Attempts at recording the texture on film were unsuccessful because of a low level of light intensity.

The azomethine linkage, $-\text{CH}=\text{N}-$, present in the Schiff base compounds, is subject to attack by atmospheric water; this has always presented a serious drawback in the application to liquid crystal display devices of mesogens containing this group.² When the thermal behaviour of **31b** was reinvestigated by DSC after 2–3 months' storage, extremely broad and poorly defined transition peaks were obtained.

In contrast to the above organomercury(II) acetates, the thermal behaviour of the corresponding dithizonate complexes **22a–e** was straightforward. However, no evidence of liquid crystalline behaviour was observed in any of these compounds.

Single, and generally sharp, peaks corresponding to the direct transition from the solid crystal to the isotropic melt were obtained in the DSC thermograms, and this behaviour was reproducible on repeated heating and cooling. The melting points, given by the onset temperature of the endotherm in the DSC trace, are collected in Table 3 and agree to within *ca.* 2 °C of those obtained optically.

Table 3 Melting point temperatures for the compounds **22a–e** as determined by DSC.

Compound	Temp / °C
22a	189
b	176
c	151
d	129
e	123

The expected trend of decreasing melting point with increasing length of the alkoxy chain was observed, reflecting the greater disorder in the crystal packing of the longer chain homologues such as **22d** and **e**.

*Thermal behaviour of the 4-n-alkoxy-4'-bromobiphenyls **34** and the 4-(4'-n-alkoxybiphenyl)mercury(II) dithizonates **23***

The 4-alkoxy-4'-bromobiphenyls **34a–j** were prepared as intermediates in the synthesis of the 4-(4'-alkoxybiphenyl)mercury(II) dithizonates **23**.

Investigations by optical microscopy and DSC showed that the biphenyls **34** exhibited a well-defined mesomorphic behaviour and although these compounds are not new, their mesogenic properties do not appear to have been reported and are therefore described here in some detail.

The optical, thermal and thermodynamic data for the compounds **34a–j** are presented in Table 4 and Fig. 19 shows a representative DSC trace. The thermal stability of the compounds was studied by thermogravimetry and none exhibited any weight loss through even partial decomposition over the temperature range studied, viz., from 0 °C to some 10 or 15 °C above the clearing point.

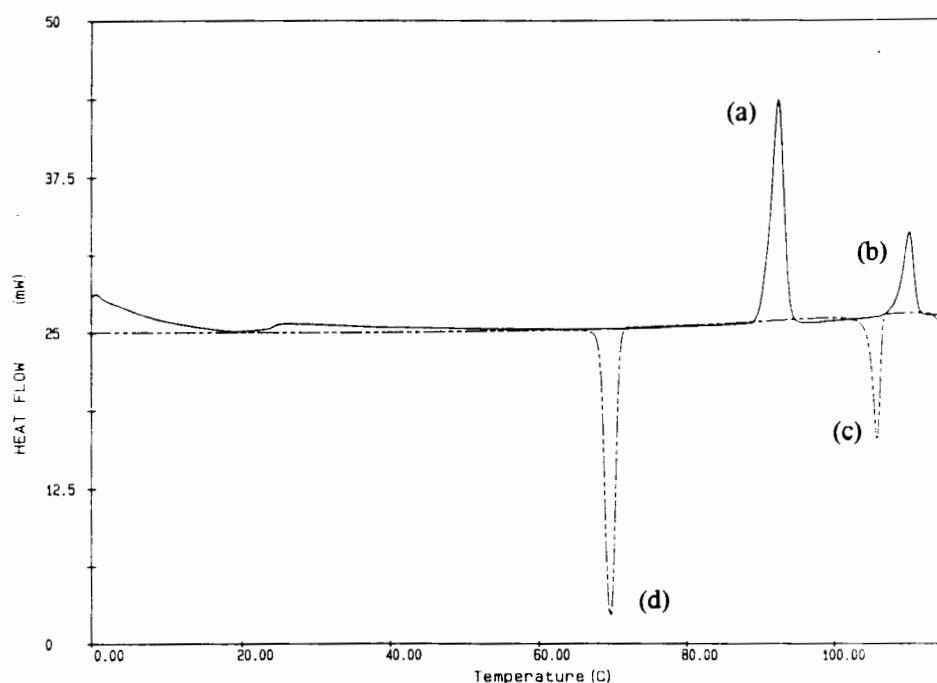


Fig 19 DSC thermogram obtained at a scan rate of $10\text{ }^{\circ}\text{C min}^{-1}$ for compound **34h**
(solid line represents heating scan; dashed line represents cooling scan)

The thermal behaviour of the homologues **34a–c** was interesting, although these compounds were not mesogenic. Instead they exhibited a crystalline polymorphism which was detected by DSC (see Fig. 20) as an irreversible solid–solid ($K_1 \rightarrow K_2$) transition prior to melting to the isotropic liquid. That this behaviour was not observed for the homologous compounds having $n \geq 10$ (compare Fig. 19) may be attributed to the different solvents employed in recrystallization. For the purposes of investigation by DSC and optical microscopy the longer chain homologues **34d–j** were recrystallized from chloroform from which they were obtained as large, semi-translucent, white plates; the compounds **34a–c** were extremely soluble in chloroform and were therefore purified by recrystallization from methanol to give a fine, white powder. Solvent recrystallization can give a kinetically stable crystal K_1 that transforms on heating to a thermodynamically stable form K_2 , which can then persist on subsequent cooling.¹⁰¹ In the case of **34a–c** K_1 is present only in the heating process of virgin samples, indicating that on cooling from the isotropic melt, the solid phase K_2 is stable down to $0\text{ }^{\circ}\text{C}$.

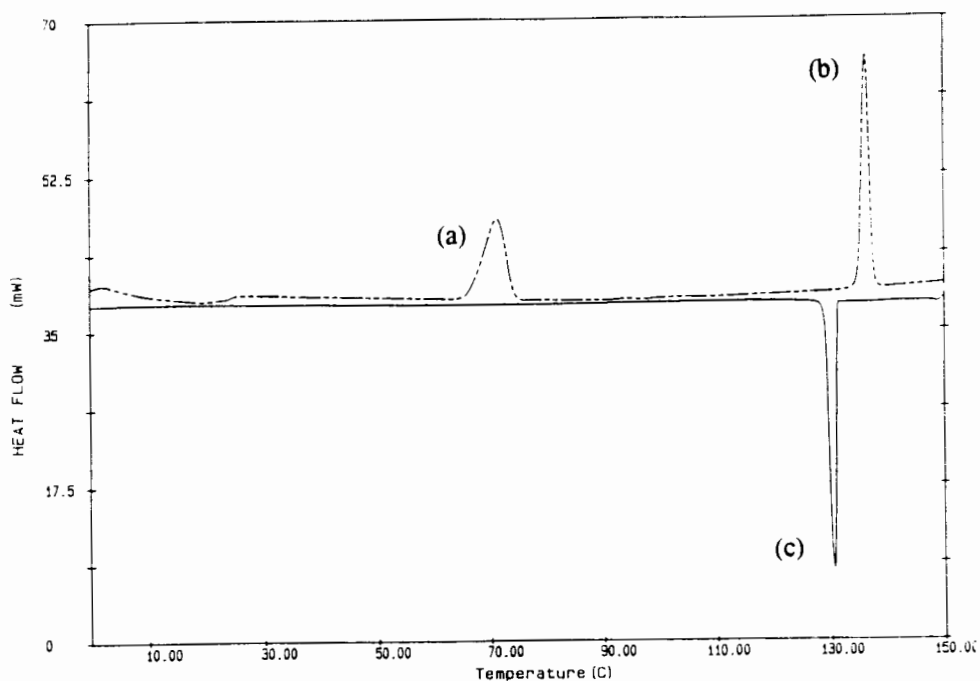


Fig 20 DSC thermogram obtained at a scan rate of $10\text{ }^{\circ}\text{C min}^{-1}$ for compound **34c**

(dashed line represents heating scan; solid line represents cooling scan)

For the data reported in Table 4 the onset point of each endotherm was recorded as the transition temperature. The enthalpy changes, ΔH , were evaluated by electronic integration of the area under the peaks and comparison with the known enthalpies of the standards used for calibration. The enthalpy values were obtained in units of J g^{-1} but are reported here in kJ mol^{-1} to allow comparison with values reported in the literature. Because the peaks obtained were always sharper and better-resolved in the second heating and cooling cycle the transition temperatures and enthalpies given in Table 4 are those determined from the second heating scan.

The transition from the normal crystalline state to the mesophase gives the melting point; this transition corresponds to the first endothermic peak (a) observed in Fig. 19. The second peak (b) represents the mesophase \rightarrow isotropic liquid transformation which occurs at the clearing point.

Table 4 Optical, thermal and thermodynamic data for the compounds **34a–j**: $C_nH_{2n+1}OC_6H_4C_6H_4Br$

Compound	<i>n</i>	Transition ^a	Temp. / °C	$\Delta H / \text{kJ mol}^{-1}$
34a	3	$K_1 \rightarrow K_2$	– ^b	– ^b
		$K_2 \rightarrow I$	141	17.0
34b	4	$K_1 \rightarrow K_2$	63	6.1
		$K_2 \rightarrow I$	133	11.8
34c	5	$K_1 \rightarrow K_2$	66	16.5
		$K_2 \rightarrow I$	135	16.6
34d	10	$K \rightarrow S$	73	26.8
		$S \rightarrow I$	121	15.8
34e	11	$K \rightarrow S$	92	38.9
		$S \rightarrow I$	118	16.6
34f	12	$K \rightarrow S_1$	79	– ^c
		$S_1 \rightarrow S_2$	84	– ^c
		$S_2 \rightarrow I$	117	16.7
34g	14	$K \rightarrow S$	91	45.4
		$S \rightarrow I$	109	15.3
34h	15	$K \rightarrow S$	102	49.2
		$S \rightarrow I$	107	10.0
34i	16	$K \rightarrow S$	96	50.7
		$S \rightarrow I$	105	15.2
34j	18	$I \rightarrow S^d$	97	- 13.3
		$S \rightarrow K^d$	86	- 58.3

^a K = crystal, S = smectic mesophase, I = isotropic liquid. ^b DSC peak broad and ill defined.

^c DSC peaks insufficiently resolved to allow determination of enthalpy values

^d Monotropic transition.

The transition from the normal crystalline state to the mesophase gives the melting point; this transition corresponds to the first endothermic peak (a) observed in Fig. 19. The second peak (b) represents the mesophase \rightarrow isotropic liquid transformation which occurs at the clearing point. The cooling scan in Fig. 19 illustrates a feature which is typical of almost all liquid crystal transitions and which was observed in the DSC thermograms of all the compounds **34a–j**. Liquid crystal transitions are easily nucleated and hence rarely supercool: the transition from the isotropic liquid to the mesophase, represented by peak (c), occurs at very nearly the same temperature as in the heating mode compared to the major transition to the solid crystal, given by peak (d), which behaves like a normal melt \rightarrow crystal transformation and can supercool by as much as 30 °C ⁹⁹(20 °C in Fig. 19).

All the mesophase transitions recorded in Table 4 were enantiotropic with an exception in the case of compound **34j** for which a monotropic liquid crystal phase was observed; the enthalpy values for this entry in Table 4 are therefore negative. The DSC trace for **34j** is reproduced in Fig. 21a. A single endothermic event (a) corresponding to the direct K \rightarrow I transition is obtained and the liquid crystal phase change is only detected on cooling. However, this transition to the mesophase may be observed on both heating and cooling scans by reversing the cooling programme to the heating mode before the final supercooled transition is reached.⁹⁹ Fig. 21b shows such a run performed at a heating rate of only 1 °C min⁻¹ so as to achieve a clear resolution of the peaks. The data indicate a small but definite mesophase range bounded by the melting point at 96 °C ($\Delta H = 13.8$ kJ mol⁻¹) and clearing point of 100 °C ($\Delta H = 0.6$ kJ mol⁻¹). Under ordinary heating conditions this liquid crystal phase is thermodynamically unstable and goes undetected. It is noted here that the magnitudes of the transition enthalpies obtained from Fig. 21b are very different to those recorded in Table 4 for the corresponding monotropic transitions. This difference must somehow arise from the special nature of the DSC experiment performed in Fig. 21b

because more closely comparable values for the transition enthalpies on heating and cooling are usually observed.

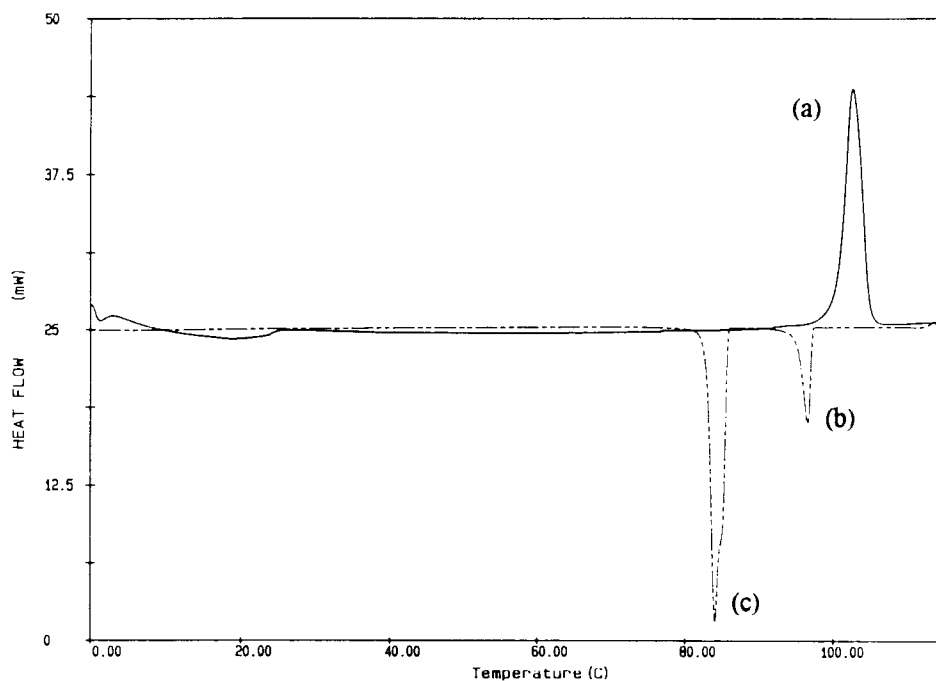


Fig 21a DSC thermogram obtained at a scan rate of 10 °C min⁻¹ for compound 34j
(solid line represents heating scan; dashed line represents cooling scan)

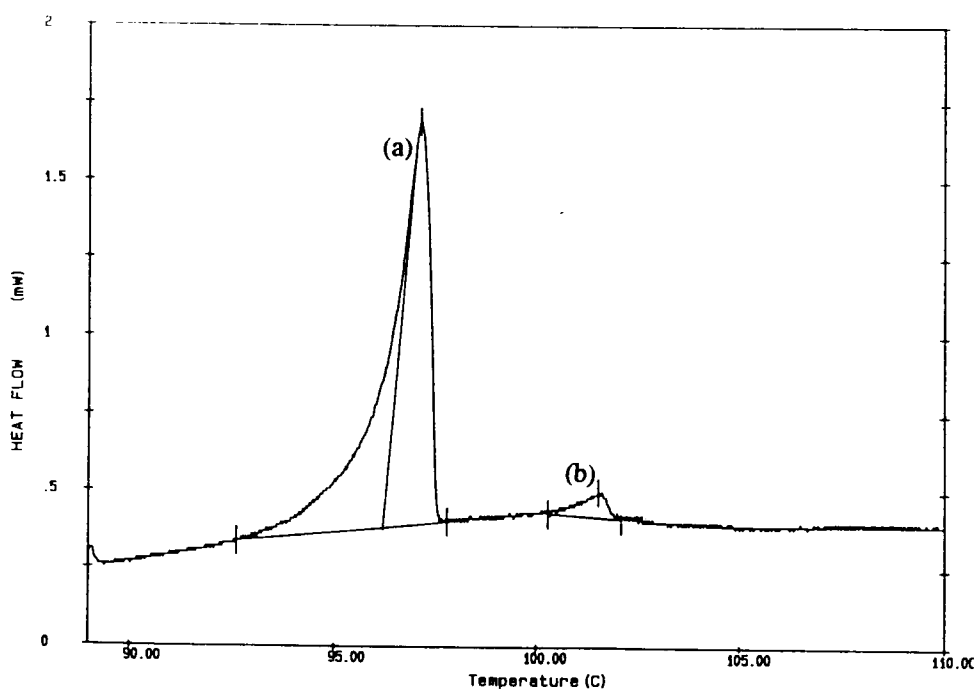


Fig 21b DSC thermogram obtained at a scan rate of 1 °C min⁻¹ for compound 34j

Although the type of mesophase cannot be determined from the DSC trace and must be assigned on the basis of the optical texture, some information about the phase changes may be derived from the relative magnitudes of the transition enthalpies.¹⁰ As already mentioned in Chapter 1 (Introduction) the enthalpy change, ΔH_{NI} , associated with the nematic \rightarrow isotropic liquid transition is typically only 2% of the value ΔH_{KN} observed at the clearing point.

For the compounds **34d–j** the enthalpy changes observed for the mesophase \rightarrow isotropic liquid transitions varied between 20 and 60% of the values for the solid \rightarrow mesophase transitions. This is in line with the range of values encountered in the literature for smectic mesophase transitions (see for example ref. 102). On these grounds a smectic phase was suspected and this was supported by the extreme viscosities of the samples: whereas nematic phases have low viscosities approaching that of water, smectic phases can appear so viscous that it is difficult to recognise them as fluid.³³

Fig. 22 shows the typical liquid crystal texture which was observed for all the compounds **34d–j**: on cooling from the isotropic melt, large grey and white domains formed and the overall appearance of the texture was identical to the mosaic structure observed in a published photograph of the smectic G (S_G) mesophase.¹⁰⁴ The smectic G mesophases are variations of the tilted phases in which the molecules exhibit a pseudo-hexagonal packing within the layers as well as considerable inter-layer correlations.¹⁰⁵



Fig. 22 Liquid crystal texture of the compound 34i obtained on cooling through 104 °C

However, on further cooling, a second texture was often observed to overlay the grey and white mosaic pattern. This is illustrated in Fig. 23 where the small, interlocking yellow structures describe the so-called fan texture which is characteristic of the S_A or S_C phase. This is probably best seen in the lower right corner of Fig.23 although the pattern here is not particularly compact and therefore less distinctive.

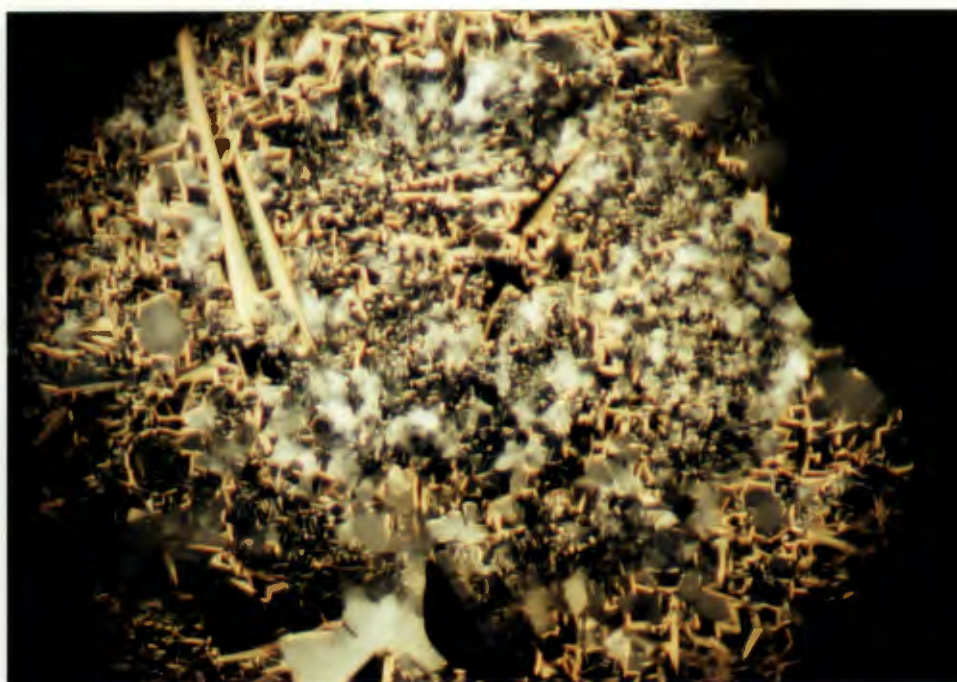


Fig 23 Liquid crystal texture of the compound 34j obtained on cooling through 98 °C

The fan texture was observed to replace the mosaic texture assigned as the S_G mesophase on cooling the sample; however the S_G phase, since it is the more ordered of either the S_A or S_C phases, is expected to be the lower temperature modification.

Considering simply the normal thermodynamic ordering of the mesophases the only reasonable assignment of the textures observed is to ascribe the mosaic structure to the smectic D mesophase, since this is the only mesophase type which exhibits both a mosaic texture and which is less ordered than a mesophase exhibiting the characteristic fan texture, *viz.* the S_C phase.³³ This latter assignment is not unreasonable since the terminal ether function is known to promote the formation of the tilted S_C rather than orthogonal S_A phases; due to the interaction of the oxygen atom dipole moments.³³

Although the failure to prepare samples of the intermediate 4-(4'-alkoxybiphenyl)-mercury(II) bromides **36** ($X = Br$) of sufficient purity for the purposes of thermal study was disappointing, the real interest lay in the dithizonate derivatives of these compounds. However, the thermal behaviour of the complexes **23a–e** proved unexceptional: DSC and microscopic studies were carried out on these products but none exhibited any signs of mesomorphic behaviour, on either heating or cooling. Melting points some 30 to 70 °C higher than those for the corresponding 4-alkoxy-4'-bromobiphenyls were observed; the results of the DSC studies are shown in Table 5.

Table 5 Melting point temperatures for the compounds **23a–e** as determined by DSC.

Compound	Temp / °C
23a	178 (dec.)
b	171
c	166
d	155
e	114

Thermal behaviour of the 4-n-alkoxy-4'-bromoazobenzenes 52

The azobenzene derivatives **52a–b** exhibited a complex thermal behaviour with the appearance of irreversible crystalline polymorphism as well as monotropic and enantiotropic nematic and smectic phases.

Well-defined liquid crystalline textures were observed. The characteristic nematic drops were obtained in the case of compounds **52a** and **b** on cooling of the isotropic melt (Fig. 15). The nematic phase was extremely fluid and the so-called nematic 'sparking' was observed in which a bright flash appeared across the field of vision when a point pressure was applied to the mesophase. The phenomenon arises from the fluidity of the nematic mesophase which allows for a rapid change in birefringence. Further cooling gave rise to the texture shown in Fig. 24.

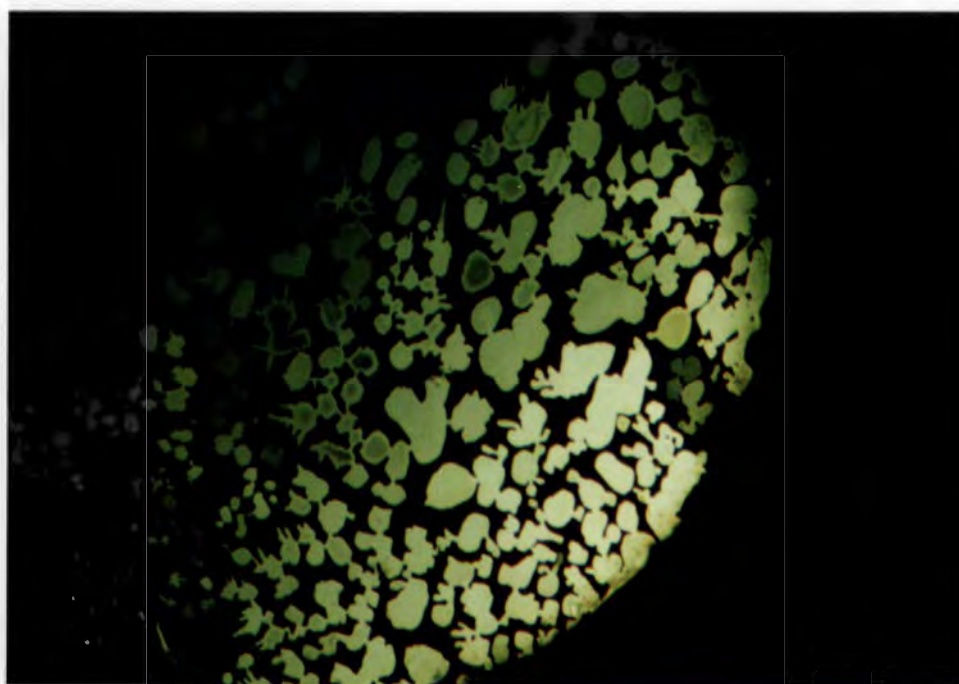


Fig. 24 Liquid crystal texture of compound **52a** obtained on cooling through 84 °C.

The elongated protrusions observed from some of the large flat areas were identified as poorly developed bâtonnets which indicate a smectic phase. The smectic phases of the compounds **52a - b** were identified as S_A on the basis of their focal-conic textures (Fig. 17).

The thermal behaviour of the compounds **52a–b** is summarized in Table 6 below.

Table 6 Optical, thermal and thermodynamic data for the compounds **52a–d**:



Compound	n	Transition ^a	Temp. / °C	$\Delta H / \text{kJ mol}^{-1}$
52a	5	I→N	90	- 2.9
		N→S	85	- 1.8
		S→K	71	- 7.1
b	8	I→N	100	- 2.1
		N→S	90	- 1.6
		S→K	78	- 8.8
c	10	I→S	95	6.4
		S→K	75	37.6
d	14	$K_1 \rightarrow K_2$	76	4.2
		$K_2 \rightarrow S$	86	37.6
		S→I	100	8.2

^a K = crystal, N = nematic mesophase, S = smectic mesophase, I = isotropic liquid

Photochromic studies

The organomercury(II) dithizonates **22** and **23** exhibited similar photochromism to that observed for mercury(II) bis(dithizonate),^{51,52} *i.e.* a reversible colour change from yellow to blue on irradiation with visible light of solutions of these compounds in organic solvents.

The visible absorption spectra of these solutions were recorded in chloroform in the range 400–700 nm; the spectra of the activated blue forms were obtained by irradiating the sample in the quartz optical cell and then rapidly scanning the region of interest. Periodic repeat scans then allowed the return reaction to be monitored. The results of this study are collected in Table 7 and typical spectra are reproduced in Fig. 25.

Table 7 Visible absorption wavelength maxima for the normal yellow and (in parentheses) activated blue forms of solutions of the compounds **22** and **23** in chloroform.

Compound	$\lambda_{\text{max}} / \text{nm}$	Compound	$\lambda_{\text{max}} / \text{nm}$
22a	475 (586)	23a	476 (588)
b	474 (586)	b	476 (589)
c	477 (587)	c	476 (589)
d	476 (587)	d	477 (589)
e	477 (587)	e	478 (589)

The existence of the isobestic point in Fig. 25 indicates the absence of any side-reactions and that there are only two species involved in the equilibrium.

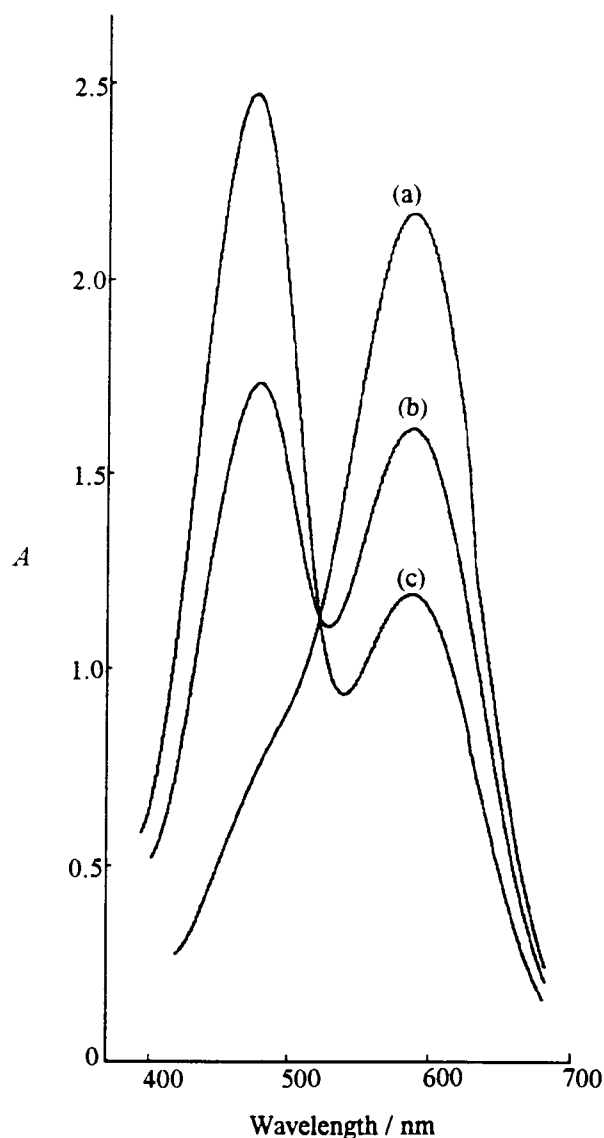


Fig. 25 Spectra showing the blue \rightarrow yellow thermal return reaction after irradiation of the photochromic organomercury(II) dithizonates **22c** (10^{-5} mol dm $^{-3}$ in CHCl $_3$): (a) photo-excited blue form (some yellow isomer present as a shoulder); (b) after 2 min in dark; and (c) after 4 min in dark, predominantly yellow form present.

The absorption maxima of both the yellow and blue forms appeared to be essentially independent of the nature of the long-chain organic ligand, a result consistent with the observation already made that the transitions involved are primarily associated with the delocalized electronic system of the dithizonate ligand and that the replacement of one of the two dithizonate moieties in the mercury(II) bis(dithizonate) by an alkyl or aryl group does not significantly alter the behaviour of the remaining one.⁷⁴ On the other hand, while the half-life of the labile blue form of mercury(II) bis(dithizonate) is of the

order of a minute the same parameter for all the compounds **22** and **23** was consistently increased.

Although difficulty was encountered in obtaining reproducible thermal return rates for these compounds, a qualitative study indicated that the half-lives increased with increasing chain length of the alkoxyaryl substituent: a maximum value of *ca.* 9 minutes was recorded for the compound **23e**.

The usual solvent sensitivity of the photochromic dithizonate system was observed for the compounds in this study: unless scrupulously pre-dried solvents were used, the return reaction was too rapid to obtain the spectrum of the activated blue form. Contamination of the solvent by atmospheric water or some other substances during handling and transfer to the optical cells will account for the irreproducibility of the thermal return rates described above.

Two of the compounds, **22c** and **23c**, were investigated for photochromism in the solid state: the samples were separately smeared onto glass slides and irradiated through an IR-absorbing filter to limit heat absorption. The materials appeared to deteriorate on continued exposure: a degree of darkening was observed after 1 hour and this increased with time but no red → violet colour change was observed as was reported for the mercury(II) bis(dithizonate)⁵¹ and this experiment was discontinued after 6 hours. It would appear that the photoisomerization does not proceed at a measurable rate in the absence of a solvent.

Conclusion

The objective of this study was to synthesize a photochromic liquid crystal: although the photochromism of the mercury(II) bis(dithizonates) was retained in the 4-(4'-n-alkoxybenzylideneanilino)- and 4-(4'-n-alkoxybiphenyl)mercury(II) dithizonates and the half-lives of the activated blue forms of these complexes increased relative the bis-dithizonates, none of the organomercury(II) dithizonates investigated exhibited any liquid crystalline behaviour.

The Schiff base, biphenyl and azobenzene series of compounds prepared in this study for subsequent coordination with dithizone conform closely to the model described for a calamitic mesogen (see Fig. 6 in Chapter 1, Introduction) but exhibit distinctly different molecular geometries. The energetically preferred conformations of the Schiff bases are non-planar (Fig. 23): the nitrogen aryl substituent is usually twisted along the C–N axis by an angle which depends on the sum of the steric and electronic effects in the molecule while the other aromatic ring is practically co-planar with the azomethine group.¹⁰⁵ On the other hand, both the 4, 4'-disubstituted biphenyl and azobenzene groups are essentially planar.³³

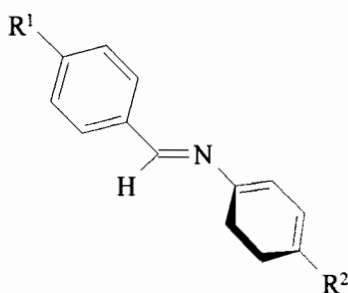


Fig. 23 Preferred molecular conformation of the *trans* Schiff bases

Although the mesomorphism of many non-planar Schiff bases has been confirmed, this difference in molecular geometry may be an important factor when comparing the well-

defined mesomorphic behaviour of the 4-n-alkoxy-4'-bromobiphenyls **34** with that of the 4-(4'-n-alkoxybenzylideneanilino)mercury(II) acetates **31**, although too close a comparison of these compounds is not appropriate because of the presence in the latter of the metal centre which, as described in Chapter 1 (Introduction), can have a profound effect on the mesomorphism. In this regard, availability of data for the more closely analogous 4-(4'-n-alkoxybiphenyl)mercury(II) bromides **36** (X = Br) would have been an advantage.

The lack of any mesomorphic behaviour of the organomercury(II) dithizonates is probably best attributed to the geometry of the dithizonate ligand, the shape and bulk of which might well be sufficient to overcome any tendency exhibited by the long-chain organic ligands towards the parallel arrangement of molecules which exists in and defines the calamitic liquid crystalline state. It is tempting to speculate whether the dithizonate moiety is inherently unsuited to the formation of mesophases or whether the further extension of the rigid, long-chain organic group by the introduction of additional substituted benzene rings might yet result in the successful preparation of a photochromic liquid-crystalline mercury(II) dithizonate.

Chapter Three

Experimental

CHAPTER 3

EXPERIMENTAL

General

All reagents used in the preparative work were analytically pure and mostly supplied by Aldrich. Except where otherwise indicated, all solvents used were laboratory reagent grade. Thin-layer chromatography was performed on Merck silica gel 60 F₂₅₄ plates and Merck silica gel 60 was used for column chromatography.

¹H NMR spectra were obtained on Varian VXR 200 or Varian Unity 400 spectrometers by Ms M. M. Nair and Mr N. W. Hendricks, Department of Chemistry, University of Cape Town. The ¹³C NMR spectra were similarly obtained on the Varian Unity 400 instrument. Chemical shifts are quoted relative to tetramethylsilane and coupling constants *J* are given in Hertz. The aromatic atom numbering used throughout in the NMR assignments is defined in Figures 12 and 13 in Chapter 2.

Elemental analyses are not reported for most of the compounds prepared in this work: for substantial periods of time the instrument available in the Department was not functional and even when operating, gave results that were suspect. Satisfactory analyses were not obtained even for twice-recrystallized products which appeared pure from consideration of the melting points and ¹H NMR spectra. Some samples were dispatched for analysis by Mrs M. Maksa on a Carlo-Erba Model 1106 instrument at the Institute of Energy Technology, CSIR, Pretoria, and these data are reported. Mass spectra (electron impact ionization) were recorded on a modified Kratos MS 80RF spectrometer by Dr P. R. Boshoff at the Cape Technikon Mass Spectrometry Unit, Cape Town.

The thermal behaviour of the compounds prepared in this work was studied using a Nikon SMZ-10 optical microscope equipped with a Linkam CO-600 hot-stage. Photographs were taken with a Nikon AFX-II camera at 40 × magnification. In the experimental data for the preparative work that follows, where a single figure is quoted for a melting point this is the onset temperature determined from the DSC thermogram; otherwise, where a range is given this is the melting point as determined on a Reichert-Jung Thermovar hot-stage.

Thermal analyses were performed by Ms R. Mohammed, Department of Chemistry, University of Cape Town. The DSC thermograms were recorded on a Perkin-Elmer DSC-7 instrument at heating and cooling rates of 10 °C min⁻¹ unless otherwise indicated, and with a nitrogen flow rate of 40 cm³ min⁻¹. The instrument was calibrated with indium (156.6 °C, 28.45 J g⁻¹) and zinc (419.47 °C, 108.37 J g⁻¹). Thermogravimetric (TG) analyses were performed on a Perkin-Elmer TGA-7 instrument calibrated with alumel and perkalloy (magnetic transition temperatures 163 and 596 °C, respectively), and with a nitrogen flow rate of 50 cm³ min⁻¹.

Visible absorption spectra were recorded on a Phillips PU-8700 UV/visible spectrophotometer using a quartz cuvette of path length 1.00 cm. Solvents used were dried according to established methods. Samples were irradiated using an Osram 'Power Star' 400 W HQI-T metal halide lamp.

Preparative Work

Preparation of the azomethines

Synthesis of 4-aminophenylmercury(II) acetate 29

Freshly distilled aniline (5.84 g, 62.7 mmol) was added to a solution of mercury(II) acetate (10.0 g, 31.4 mmol) in water (50 cm³) and the reaction mixture allowed to stir at room temperature for a total of 3 h, during which time a white precipitate formed. This product was filtered off and air-dried to give **29** (9.21 g, 83.4%), m.p. 158–160 °C; δ_{H} (200 MHz; CDCl₃) 2.08 (3H, s, CH₃OCO–), 3.74 (2H, br. s, NH₂), 6.69 (2H, d, *J* 8.5, aromatic) and 7.06 (2H, d, *J* 8.5, aromatic).

Preparation of the 4-n-alkoxybenzaldehydes **30**

Synthesis of 4-dodecyloxybenzaldehyde 30c (using K₂CO₃)

4-Hydroxybenzaldehyde (1.0 g, 8.19 mmol) was added to a mixture of cyclohexanone (7 cm³) and anhydrous potassium carbonate (4.53 g, 32.8 mmol) giving an orange solution to which was added iododecane (3.88 g, 13.1 mmol). The reaction mixture was refluxed vigorously at an oil-bath temperature of 175 °C for a total of 1.5 h, during which time it became a light yellow colour, and was monitored by TLC (7 : 3 EtOAc : toluene) for the complete disappearance of the 4-hydroxybenzaldehyde. The solution was then decanted from the potassium carbonate and the latter washed with diethyl ether (4 x 10 cm³). The washings were added to the cyclohexanone extract and both solvents removed under reduced pressure. Short-path vacuum distillation of the residual material yielded **30c** as a pale yellow fraction obtained at 176–180 °C / 4 mmHg. A considerable quantity of orange-coloured residue remained which began to char on further heating. The product **30c** partially solidified on standing in the cold

(0.61 g, 25.6%); b.p. 176–180 °C / 4 mmHg (lit.,⁶⁶ 194 °C / 8 mmHg); δ_{H} (200 MHz; CDCl_3) 0.88 (3H, t, CH_3 -), 1.26 (18H, m, $-(\text{CH}_2)_9$ -), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2$ -), 4.04 (2H, t, $-\text{OCH}_2$ -), 6.99 (2H, d, J_{ab} 8.7, H_{a}), 7.82 (2H, d, J_{ba} 8.8, H_{b}) and 9.87 (1H, s, $-\text{CHO}$).

Synthesis of 4-n-alkoxybenzaldehydes 30a–c (using NaH)

In a typical procedure, sodium hydride (0.18 g, 6.14 mmol; an 80% dispersion in mineral oil) was added to a solution of 4-hydroxybenzaldehyde (0.50 g, 4.09 mmol) in freshly distilled DMF (10 cm^3). The addition was accompanied by vigorous effervescence and the evolution of H_2 ; this exothermic reaction was allowed to subside slightly before addition of the appropriate alkyl bromide (4.91 mmol) in a single portion. The reaction flask was immediately placed in an oil-bath preheated to 110–115 °C and allowed to reflux gently, whereupon the reaction mixture soon lightened in colour from dark orange to pale yellow. The reaction was monitored by TLC (70 : 30 EtOAc : toluene) for the complete disappearance of the 4-hydroxybenzaldehyde; reaction was complete after 2½–3 hours. The mixture was allowed to cool slightly and the product was precipitated from solution by the addition of hexane. This solid material was filtered, washed with hexane and air-dried to yield the products **30a–c**. The experimental data obtained for the compounds **30a–c** are as follows:

4-Dodecyloxybenzaldehyde 30a

0.98 g, 82.4%; m.p. 20–23 °C (lit.,⁶⁶ 24 °C); δ_{H} (200 MHz; CDCl_3) 0.88 (3H, t, CH_3 -), 1.27 (18H, m, $-(\text{CH}_2)_9$ -), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2$ -), 4.04 (2H, t, $-\text{OCH}_2$ -), 6.99 (2H, d, J_{ab} 8.7, H_{a}), 7.82 (2H, d, J_{ba} 8.8, H_{b}) and 9.87 (1H, s, $-\text{CHO}$); δ_{C} (100 MHz; CDCl_3) 14.01 (CH_3 -), 22.67 (CH_3CH_2 -), 25.99 ($\text{CH}_3\text{CH}_2\text{CH}_2$ -), 29.07–29.66 ($-(\text{CH}_2)_7$ -), 31.94 ($-\text{OCH}_2\text{CH}_2$ -), 68.39 ($-\text{OCH}_2$ -), 114.77 (C_2), 129.73 (C_4), 131.95 (C_3), 164.30 (C_1) and 190.78 ($-\text{CHO}$).

4-Tetradecyloxybenzaldehyde 30b

1.16 g, 89.2%; m.p. 33–34 °C (lit.,⁶⁶ 34 °C); δ_{H} (200 MHz; CDCl_3) 0.88 (3H, t, CH_3 -), 1.26 (22H, m, $-(\text{CH}_2)_{11}$ -), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2-$), 4.04 (2H, t, $-\text{OCH}_2-$), 6.98 (2H, d, J_{ab} 8.8, H_{a}), 7.82 (2H, d, J_{ba} 8.8, H_{b}) and 9.87 (1H, s, $-\text{CHO}$); δ_{C} (100 MHz; CDCl_3) 14.07 (CH_3 -), 22.66 (CH_3CH_2 -), 25.93 ($\text{CH}_3\text{CH}_2\text{CH}_2$ -), 29.03–29.62 ($-(\text{CH}_2)_9$ -), 31.89 ($-\text{OCH}_2\text{CH}_2-$), 68.41 ($-\text{OCH}_2-$), 114.73 (C_2), 129.73 (C_4), 131.94 (C_3), 164.26 (C_1) and 190.74 ($-\text{CHO}$).

4-Octadecyloxybenzaldehyde 30c

1.36 g, 88.9%; m.p. 45–48 °C (lit.,⁶⁶ 49 °C); δ_{H} (200 MHz; CDCl_3) 0.88 (3H, t, CH_3 -), 1.26 (30H, m, $-(\text{CH}_2)_{15}$ -), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2-$), 4.04 (2H, t, $-\text{OCH}_2-$), 6.99 (2H, d, J_{ab} 8.7, H_{a}), 7.82 (2H, d, J_{ba} 8.8, H_{b}) and 9.87 (1H, s, $-\text{CHO}$); δ_{C} (100 MHz; CDCl_3) 13.98 (CH_3 -), 22.57 (CH_3CH_2 -), 25.84 ($\text{CH}_3\text{CH}_2\text{CH}_2$ -), 29.23–29.57 ($-(\text{CH}_2)_{13}$ -), 31.81 ($-\text{OCH}_2\text{CH}_2-$), 68.33 ($-\text{OCH}_2-$), 114.65 (C_2), 129.64 (C_4), 131.85 (C_3), 164.18 (C_1) and 190.68 ($-\text{CHO}$).

Preparation of the Schiff-base mercury(II) acetates 31 and dithizonates 22***Attempted synthesis of 4-(4'-methoxybenzylideneanilino)mercury(II) acetate 31a (in toluene)***

Freshly distilled 4-methoxybenzaldehyde (0.23 g, 1.69 mmol) was added to a suspension of 4-aminophenylmercury(II) acetate (0.50 g, 1.42 mmol) in toluene (15 cm^3) and the resulting mixture was vigorously boiled under reflux. No visible reaction was observed, the amine remained undissolved and analysis of the reaction mixture by TLC (7 : 3 EtOAc : toluene) did not detect the formation of any products. The reaction was discontinued after 8 h at reflux.

Attempted synthesis of 4-(4'-methoxybenzylideneanilino)mercury(II) acetate 31a (in benzene)

Freshly distilled 4-methoxybenzaldehyde (0.23 g, 1.69 mmol) was added to a suspension of 4-aminophenylmercury(II) acetate (0.50 g, 1.42 mmol) in benzene (20 cm³). The reaction flask was fitted with a Dean and Stark trap for the azeotropic removal of water and the reaction mixture was heated to reflux temperature. Heating was discontinued after 12 h at which time the amine remained undissolved and no water was observed to have collected in the trap.

Synthesis of 4-(4'-alkoxybenzylideneanilino)mercury(II) acetates 31a–e (solid state)

In a typical procedure, a finely powdered sample of 4-aminophenylmercury(II) acetate (1.00 g, 2.84 mmol) was placed in a small round-bottomed flask and the appropriate 4-alkoxybenzaldehyde (2.84 mmol) added. The two reagents were closely mixed and the open reaction flask then placed in an oil-bath preheated to 150–155 °C. A yellow colour was immediately obvious as the mixture began to liquefy, a vapour was observed to escape the flask and a few fine droplets of a liquid, which was assumed to be water, condensed at the mouth of the flask. After less than 2–3 min heating at an oil-bath temperature of 150–155 °C the mixture abruptly solidified; the flask was then removed from the heat and the condensate removed from the mouth of the flask by touching a small piece of tissue to the droplets. The solid material was recrystallized from dichloromethane to give the product as a microcrystalline powder. The experimental data obtained for the compounds **31a–e** are as follows:

4-(4'-Methoxybenzylideneanilino)mercury(II) acetate 31a

1.18 g, 88.1%; m.p. 176 °C; δ_{H} (200 MHz; CDCl₃) 2.02 (3H, s, CH₃OCO–), 3.80 (3H, s, CH₃O–), 6.91 (2H, d, J_{ab} 8.8, H_{a}), 7.12 (2H, d, J 8.6, H_{c} or H_{d}), 7.24 (2H, d,

J 8.6, H_c or H_d), 7.77 (2H, d, J_{ba} 8.8, H_b), 8.26 (1H, s, $-CH=N-$, *trans* isomer) and 8.37 (s, $-CH=N-$, *cis* isomer).

4-(4'-Butoxybenzylideneanilino)mercury(II) acetate 31b

1.25 g, 85.6%; m.p. 186 °C; (Found: C, 43.9; H, 3.8; N, 2.7. Calc. for $C_{19}H_{21}HgNO_3$: C, 44.6; H, 4.1; N, 2.7%); δ_H (200 MHz; $CDCl_3$) 0.92 (3H, t, CH_3-), 1.44 (2H, sextet, CH_3CH_2-), 1.74 (2H, quintet, $CH_3CH_2CH_2-$), 2.03 (3H, s, CH_3OCO-), 3.96 (2H, t, $-OCH_2-$), 6.90 (2H, d, J_{ab} 8.8, H_a), 7.12 (2H, d, J 8.5, H_c or H_d), 7.25 (2H, d, J 8.5, H_c or H_d), 7.76 (2H, d, J_{ba} 8.8, H_b), 8.26 (1H, s, $-CH=N-$, *trans* isomer) and 8.37 (s, $-CH=N-$, *cis* isomer).

4-(4'-Dodecyloxybenzylideneanilino)mercury(II) acetate 31c

1.50 g, 84.7%; m.p. 183 °C; δ_H (200 MHz; $CDCl_3$) 0.88 (3H, t, CH_3-), 1.27 (18H, m, $-(CH_2)_9-$), 1.81 (2H, quintet, $-OCH_2CH_2-$), 2.10 (3H, s, CH_3OCO-), 4.02 (2H, t, $-OCH_2-$), 6.97 (2H, d, J_{ab} 8.8, H_a), 7.19 (2H, d, J 8.5, H_c or H_d), 7.32 (2H, d, J 8.5, H_c or H_d), 7.83 (2H, d, J_{ba} 8.7, H_b) and 8.33 (1H, s, $-CH=N-$); δ_C (100 MHz; $CDCl_3$) 14.09 (CH_3-), 22.67 (CH_3CH_2-), 23.18 ($CH_3CH_2CH_2-$), 25.99 (CH_3OCO-), 29.15–29.62 ($-(CH_2)_7-$), 31.90 ($-OCH_2CH_2-$), 68.24 ($-OCH_2-$), 114.73 (C_2), 121.54 (C_6 or C_7), 128.76 (C_4), 130.65 (C_3), 136.77 (C_6 or C_7), 153.45 (C_5 or C_8), 160.49 ($-CH=N-$), 162.12 (C_1) and 177.58 (C_5 or C_8).

4-(4'-Tetradecyloxybenzylideneanilino)mercury(II) acetate 31d

1.54 g, 83.2%; m.p. 151 °C; δ_H (200 MHz; $CDCl_3$) 0.86 (3H, t, CH_3-), 1.24 (22H, m, $-(CH_2)_{11}-$), 1.79 (2H, quintet, $-OCH_2CH_2-$), 2.10 (3H, s, CH_3OCO-), 4.00 (2H, t, $-OCH_2-$), 6.95 (2H, d, J_{ab} 8.8, H_a), 7.18 (2H, d, J 8.5, H_c or H_d), 7.30 (2H, d, J 8.5, H_c or H_d), 7.81 (2H, d, J_{ba} 8.8, H_b) and 8.32 (1H, s, $-CH=N-$).

4-(4'-Octadecyloxybenzylideneanilino)mercury(II) acetate 31e

1.34 g, 66.7%; m.p. 119 °C; δ_{H} (200 MHz; CDCl_3) 0.87 (3H, t, CH_3 -), 1.26 (30H, m, $-(\text{CH}_2)_{15}$ -), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2-$), 2.10 (3H, s, CH_3OCO -), 4.02 (2H, t, $-\text{OCH}_2-$), 6.97 (2H, d, J_{ab} 8.8, H_{a}), 7.20 (2H, d, J 8.5, H_{c} or H_{d}), 7.32 (2H, d, J 8.5, H_{c} or H_{d}), 7.83 (2H, d, J_{ba} 8.8, H_{b}) and 8.34 (1H, s, $-\text{CH}=\text{N}-$); δ_{C} (100 MHz; CDCl_3) 14.10 (CH_3 -), 22.68 (CH_3CH_2 -), 23.13 ($\text{CH}_3\text{CH}_2\text{CH}_2$ -), 26.00 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ -), 29.16–29.68 ($-(\text{CH}_2)_{13}$ -), 31.91 (CH_3OCO -), 68.24 ($-\text{OCH}_2-$), 114.73 (C_2), 121.55 (C_6 or C_7), 128.76 (C_4), 130.66 (C_3), 136.76 (C_6 or C_7), 153.45 (C_5 or C_8), 160.52 ($-\text{CH}=\text{N}-$), 162.10 (C_1) and 177.60 (C_5 or C_8).

Synthesis of 4-(4'-n-alkoxybenzylideneanilino)mercury(II) dithizonates 22a–e

In a typical procedure, the 4-(4'-n-alkoxybenzylideneanilino)mercury(II) acetate **31** (1.1 g) and dithizone **25** (1 molar equiv.) were separately dissolved in dichloromethane (50 cm^3 each) and then shaken together for 15 min with a 1 M aqueous ammonia solution (100 cm^3). A bright red colour was immediately obtained in the organic phase. The two phases were separated and the organic layer was washed first with water (100 cm^3), then with 1 M aqueous sodium hydroxide (100 cm^3) and finally again with water (100 cm^3). The aqueous washings were a pale yellow colour and were discarded. The combined organic phases were dried over magnesium sulfate, filtered and evaporated to dryness. The residue was recrystallized from benzene–hexane to yield **22** as a deep-red microcrystalline powder. The experimental data obtained for the compounds **22a–e** are as follows:

4-(4'-Methoxybenzylideneanilino)mercury(II) dithizonate 22a

0.97 g, 62.2%; m.p. 189 °C; δ_{H} (200 MHz; CDCl_3) 3.89 (3H, s, CH_3O -), 7.00 (2H, d, J_{ab} 8.9, H_{a}), 7.28 (obscured by residual CHCl_3 , H_{c} or H_{d}), 7.44 (7H, m, H_{f} , H_{g} , H_{h} , H_{i} and H_{c} or H_{d}), 7.88 (2H, d, J_{ba} 8.8, H_{b}), 7.96 (2H, m, H_{e}), 8.43 (1H, s, $-\text{CH}=\text{N}-$) and 9.23 (1H, br. s, $-\text{NH}-$); δ_{C} (100 MHz; CDCl_3) 55.45 (CH_3O -), 114.25 (C_2),

115.18 (C_{14} or C_{15}), 121.43 (C_6 or C_7), 123.03 (C_{10} or C_{16}), 123.34 (C_{10} or C_{16}), 129.37 (C_{14} or C_{15} or C_{11}), 129.44 (C_{14} or C_{15} or C_{11}), 130.60 (C_3 or C_{12}), 130.76 (C_3 or C_{12}), 137.39 (C_6 or C_7), 142.18 (C_{13} or C_9), 151.41 (C_{13} or C_9), 152.39 (C_5 or C_8) and 159.79 ($-\text{CH}=\text{N}-$).

4-(4'-Butoxybenzylideneanilino)mercury(II) dithizonate 22b

0.90 g, 59.2%; m.p. 176 °C; (Found: C, 50.5; H, 3.8; N, 9.7. Calc. for $\text{C}_{30}\text{H}_{29}\text{HgN}_5\text{OS}$: C, 50.9; H, 4.1; N, 9.9%); δ_{H} (200 MHz; CDCl_3) 1.00 (3H, t, CH_3-), 1.54 (2H, sextet, CH_3CH_2-), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2-$), 4.04 (2H, t, $-\text{OCH}_2-$), 6.98 (2H, d, J_{ab} 8.8, H_{a}), 7.07 (1H, m, H_{j}), 7.26 (2H, d, J 8.4, H_{c} or H_{d}), 7.40 (7H, m, H_{f} , H_{g} , H_{h} , and H_{i}), 7.47 (2H, d, J 8.4, H_{c} or H_{d}), 7.85 (2H, d, J_{ba} 8.8, H_{b}), 7.94 (2H, m, H_{e}), 8.39 (1H, s, $-\text{CH}=\text{N}-$) and 9.20 (1H, s, $-\text{NH}-$); δ_{C} (100 MHz; CDCl_3) 13.83 (CH_3-), 19.22 (CH_3CH_2-), 31.21 ($-\text{OCH}_2\text{CH}_2-$), 67.90 ($-\text{OCH}_2-$), 114.71 (C_2), 115.16 (C_{14} or C_{15}), 121.43 (C_6 or C_7), 123.02 (C_{10} or C_{16}), 123.31 (C_{10} or C_{16}), 128.95 (C_4), 129.34 (C_{14} or C_{15} or C_{16}), 129.42 (C_{14} or C_{15} or C_{16}), 130.57 (C_3 or C_{12}), 130.73 (C_3 or C_{12}), 137.41 (C_6 or C_7), 142.14 (C_{13} or C_9), 151.45 (C_{13} or C_9), 152.39 (C_5 or C_8) 160.01 ($-\text{CH}=\text{N}-$), 162.01 (C_1) and 177.60 (C_5 or C_8).

4-(4'-Dodecyloxybenzylideneanilino)mercury(II) dithizonate 22c

0.98 g, 67.6%; m.p. 151 °C; (Found: C, 54.7; H, 5.2; N, 8.1. Calc. for $\text{C}_{38}\text{H}_{45}\text{HgN}_5\text{OS}$: C, 55.6; H, 5.5; N, 8.5); δ_{H} (400 MHz; CDCl_3) 0.89 (3H, t, CH_3-), 1.28 (16H, m, $-(\text{CH}_2)_8-$), 1.48 (2H, m, $-\text{OCH}_2\text{CH}_2\text{CH}_2-$), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2-$), 4.03 (2H, t, $-\text{OCH}_2-$), 6.99 (2H, d, J_{ab} 8.8, H_{a}), 7.07 (1H, m, H_{j}), 7.26 (2H, d, J 8.0, H_{c} or H_{d}), 7.39 (7H, m, H_{f} , H_{g} , H_{h} , and H_{i}), 7.48 (2H, d, J 8.0, H_{c} or H_{d}), 7.85 (2H, d, J_{ba} 8.8, H_{b}), 7.96 (2H, m, H_{e}), 8.41 (1H, s, $-\text{CH}=\text{N}-$) and 9.21 (1H, s, $-\text{NH}-$); δ_{C} (100 MHz; CDCl_3) 14.11 (CH_3-), 22.68 (CH_3CH_2-), 26.01 ($\text{CH}_3\text{CH}_2\text{CH}_2-$), 29.18–29.64 ($-(\text{CH}_2)_7-$), 31.91 ($-\text{OCH}_2\text{CH}_2-$), 68.25 ($-\text{OCH}_2-$), 114.75 (C_2), 115.16 (C_{14} or C_{15}); 121.44 (C_6 or C_7), 123.04 (C_{10} or C_{16}), 123.33

(C_{10} or C_{16}), 128.96 (C_4), 129.37 (C_{14} or C_{15} or C_{16}), 129.44 (C_{14} or C_{15} or C_{16}), 130.59 (C_3 or C_{12}), 130.76 (C_3 or C_{12}), 137.39 (C_6 or C_7), 142.18 (C_{13} or C_9), 151.40 (C_{13} or C_9), 152.43 (C_5 or C_8), 160.05 ($-\text{CH}=\text{N}-$), 162.03 (C_1) and 177.60 (C_5 or C_8).

4-(4'-Tetradecyloxybenzylideneanilino)mercury(II) dithizonate 22d

0.80 g, 55.9%; m.p. 129 °C; δ_{H} (200 MHz; CDCl_3) 0.89 (3H, t, CH_3-), 1.27 (22H, m, $-(\text{CH}_2)_{11}-$), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2-$), 4.03 (2H, t, $-\text{OCH}_2-$), 6.99 (2H, d, J_{ab} 8.8, H_{a}), 7.07 (1H, m, H_{j}), 7.28 (obscured by residual CHCl_3 , H_{c} or H_{d}), 7.44 (9H, m, H_{f} , H_{g} , H_{h} , H_{i} and H_{c} or H_{d}), 7.86 (2H, d, J_{ba} 8.8, H_{b}), 7.95 (2H, m, H_{e}), 8.42 (1H, s, $-\text{CH}=\text{N}-$) and 9.22 (1H, br. s, $-\text{NH}-$).

4-(4'-Octadecyloxybenzylideneanilino)mercury(II) dithizonate 22e

0.70 g, 50.0%; m.p. 123 °C; δ_{H} (200 MHz; CDCl_3) 0.87 (3H, t, CH_3-), 1.26 (30H, m, $-(\text{CH}_2)_{15}-$), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2-$), 4.02 (2H, t, $-\text{OCH}_2-$), 6.98 (2H, d, J_{ab} 8.8, H_{a}), 7.10 (1H, m, H_{j}), 7.28 (obscured by residual CHCl_3 , H_{c} or H_{d}), 7.44 (9H, m, H_{f} , H_{g} , H_{h} , H_{i} and H_{c} or H_{d}), 7.86 (2H, d, J_{ba} 8.8, H_{b}), 7.94 (2H, m, H_{e}), 8.48 (1H, s, $-\text{CH}=\text{N}-$) and 9.21 (1H, br. s, $-\text{NH}-$).

Synthesis of ethylmercury(II) dithizonate

Solutions of ethylmercury(II) chloride (Johnson Matthey Alfa Products; 0.50 g, 1.89 mmol) and dithizone **25** (0.48 g, 1.89 mmol) in dichloromethane (50 cm^3 each) were shaken together for 15 min with a 1 M aqueous ammonia solution (100 cm^3). The product was isolated from the organic phase following the procedure described above for the compounds **22** and was recrystallized from benzene-hexane to yield ethylmercury(II) dithizonate as a deep-red microcrystalline powder (0.66 g, 72.5%); δ_{H} (400 MHz; CDCl_3) 1.45 (3H, t, CH_3-), 1.93 (2H, q, CH_3CH_2-), 7.03 (1H, m, H_{j}), 7.36 (4H, m, H_{h} and H_{i}), 7.43 (1H, m, H_{g}), 7.48 (2H, m, H_{f}), 7.89 (2H, m, H_{e}), and

9.17 (1H, s, NH); δ_C (100 MHz; $CDCl_3$) 14.64 (CH_3-), 25.20 (CH_3CH_2-), 115.09 (C_{14} or C_{15}), 122.82 (C_{10}), 123.04 (C_{16}), 129.39 (C_{14} or C_{15} or C_{11}), 129.40 (C_{14} or C_{15} or C_{11}), 130.59 (C_{12}), 142.29 (C_{13} or C_9), 151.54 (C_{13} or C_9) and 155.58 ($-C(S)-$).

Preparation of the biphenyls

Synthesis of 4-bromo-4'-hydroxybiphenyls 34a-j

In a typical procedure, sodium hydride (0.90 g, 3.0 mmol; an 80% dispersion in mineral oil) was added to a solution of 4-bromo-4'-hydroxybiphenyl **34** (0.50 g, 2.0 mmol) in freshly distilled DMF (10 cm³). The addition was accompanied by vigorous effervescence and the evolution of H₂ gas; this exothermic reaction was allowed to subside slightly before addition of the appropriate alkyl bromide (2.4 mmol) in a single portion. Traces of a creamy white precipitate were observed in the reaction flask which was then placed in an oil-bath preheated to 110–115 °C. The mixture was gently refluxed and monitored by TLC (7 : 3 EtOAc : toluene) for the disappearance of the 4-hydroxy-4'-bromobiphenyl. Reaction was complete after 1.5 h and the reaction mixture was then poured onto crushed ice (20 g), whereupon the product precipitated as a white solid. This material was filtered, washed thoroughly with cold water and allowed to air-dry. The crude product was recrystallized from methanol (**34a-c**) to give a fine white powder or from chloroform (**34d-j**) to give large, white, semi-translucent plates. The experimental data obtained for the compounds **34a-j** are as follows:

4-Bromo-4'-n-propoxybiphenyl 34a

0.47 g, 81.0%; m.p. 141 °C; δ_H (200 MHz; $CDCl_3$) 1.06 (3H, t, CH_3-), 1.84 (2H, sextet, CH_3CH_2-), 3.97 (2H, t, $-OCH_2-$), 6.96 (2H, d, J_{ab} 8.9, H_a), 7.41 (2H, d, J_{cd} 8.7, H_c), 7.48 (2H, d, J_{ba} 8.9, H_b) and 7.53 (2H, d, J_{dc} 8.6, H_d); δ_C (100 MHz;

CDCl₃) 10.52 (CH₃-), 22.59 (CH₃CH₂-), 69.63 (-OCH₂-), 114.91 (C₂), 120.70 (C₅), 127.92 (C₆ or C₇), 128.26 (C₆ or C₇), 131.76 (C₃), 132.25 (C₄), 139.81 (C₈) and 159.00 (C₁).

4-Bromo-4'-n-butoxybiphenyl 34b

0.50 g, 82.1%; m.p. 133 °C; δ_H (200 MHz; CDCl₃) 0.96 (3H, t, CH₃-), 1.44 (2H, sextet, CH₃CH₂-), 1.81 (2H, quintet, -OCH₂CH₂-), 3.99 (2H, t, -OCH₂-), 6.96 (2H, d, *J*_{ab} 8.8, *H*_a), 7.41 (2H, d, *J*_{cd} 8.7, *H*_c), 7.48 (2H, d, *J*_{ba} 8.9, *H*_b) and 7.53 (2H, d, *J*_{dc} 8.6, *H*_d); δ_C (100 MHz; CDCl₃) 14.04 (CH₃-), 22.68 (CH₃CH₂-), 28.97 (-OCH₂CH₂-), 68.16 (-OCH₂-), 114.93 (C₂), 120.70 (C₅), 127.92 (C₆ or C₇), 128.26 (C₆ or C₇), 131.76 (C₃), 132.25 (C₄), 139.83 (C₈) and 159.03 (C₁).

4-Bromo-4'-n-pentyloxybiphenyl 34c

0.52 g, 81.3%; m.p. 135 °C; δ_H (200 MHz; CDCl₃) 0.95 (3H, t, CH₃-), 1.42 (4H, m, -(CH₂)₂-), 1.81 (2H, quintet, -OCH₂CH₂-), 3.99 (2H, t, -OCH₂-), 6.96 (2H, d, *J*_{ab} 8.8, *H*_a), 7.41 (2H, d, *J*_{cd} 8.4, *H*_c), 7.47 (2H, d, *J*_{ba} 8.7, *H*_b) and 7.52 (2H, d, *J*_{dc} 8.6, *H*_d); δ_C (100 MHz; CDCl₃) 14.05 (CH₃-), 22.49 (CH₃CH₂-), 28.23 (CH₃CH₂CH₂-), 28.99 (-OCH₂CH₂-), 68.14 (-OCH₂-), 114.92 (C₂), 120.71 (C₅), 127.94 (C₆ or C₇), 128.28 (C₆ or C₇), 131.77 (C₃), 132.25 (C₄), 139.82 (C₈) and 159.02 (C₁).

4-Bromo-4'-n-decyloxybiphenyl 34d

0.67 g, 85.9%; c.p. 73, m.p. 121 °C; δ_H (200 MHz; CDCl₃) 0.90 (3H, t, CH₃-), 1.29 (14H, m, -(CH₂)₇-), 1.80 (2H, quintet, -OCH₂CH₂-), 4.00 (2H, t, -OCH₂-), 6.97 (2H, d, *J*_{ab} 8.9, *H*_a), 7.41 (2H, d, *J*_{cd} 8.7, *H*_c), 7.49 (2H, d, *J*_{ba} 8.9, *H*_b) and 7.54 (2H, d, *J*_{dc} 8.7, *H*_d); δ_C (100 MHz; CDCl₃) 14.10 (CH₃-), 22.68 (CH₃CH₂-), 26.05 (CH₃CH₂CH₂-), 29.28-29.60 (-(CH₂)₅-), 31.90 (-OCH₂CH₂-), 68.14 (-OCH₂-), 114.92 (C₂), 120.70 (C₅), 127.90 (C₆ or C₇), 128.25 (C₆ or C₇), 131.75 (C₃), 132.23 (C₄), 139.82 (C₈) and 159.02 (C₁).

4-Bromo-4'-n-undecyloxybiphenyl 34e

0.70 g, 86.4%; c.p. 92, m.p. 118 °C; δ_{H} (200 MHz; CDCl_3) 0.90 (3H, t, CH_3 -), 1.29 (14H, m, $-(\text{CH}_2)_8$ -), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2$ -), 4.00 (2H, t, $-\text{OCH}_2$ -), 6.97 (2H, d, J_{ab} 8.9, H_{a}), 7.41 (2H, d, J_{cd} 8.7, H_{c}), 7.48 (2H, d, J_{ba} 8.8, H_{b}) and 7.54 (2H, d, J_{dc} 8.7, H_{d}); δ_{C} (100 MHz; CDCl_3) 14.10 (CH_3 -), 22.68 (CH_3CH_2 -), 26.05 ($\text{CH}_3\text{CH}_2\text{CH}_2$ -), 29.28–29.60 ($-(\text{CH}_2)_6$ -), 31.90 ($-\text{OCH}_2\text{CH}_2$ -), 68.14 ($-\text{OCH}_2$ -), 114.92 (C_2), 120.70 (C_5), 127.90 (C_6 or C_7), 128.25 (C_6 or C_7), 131.75 (C_3), 132.23 (C_4), 139.82 (C_8) and 159.02 (C_1).

4-Bromo-4'-n-dodecyloxybiphenyl 34f

0.76 g, 90.5%; c.p. 88, m.p. 117 °C; δ_{H} (200 MHz; CDCl_3) 0.89 (3H, t, CH_3 -), 1.28 (18H, m, $-(\text{CH}_2)_9$ -), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2$ -), 4.00 (2H, t, $-\text{OCH}_2$ -), 6.97 (2H, d, J_{ab} 8.8, H_{a}), 7.41 (2H, d, J_{cd} 8.7, H_{c}), 7.48 (2H, d, J_{ba} 8.8, H_{b}) and 7.54 (2H, d, J_{dc} 8.7, H_{d}); δ_{C} (100 MHz; CDCl_3) 14.10 (CH_3 -), 22.67 (CH_3CH_2 -), 26.05 ($\text{CH}_3\text{CH}_2\text{CH}_2$ -), 29.27–29.59 ($-(\text{CH}_2)_7$ -), 31.93 ($-\text{OCH}_2\text{CH}_2$ -), 68.14 ($-\text{OCH}_2$ -), 114.91 (C_2), 120.70 (C_5), 127.90 (C_6 or C_7), 128.25 (C_6 or C_7), 131.75 (C_3), 132.23 (C_4), 139.81 (C_8) and 159.02 (C_1).

4-Bromo-4'-n-tetradecyloxybiphenyl 34g

0.88 g, 87.6%; c.p. 91, m.p. 109 °C; δ_{H} (200 MHz; CDCl_3) 0.88 (3H, t, CH_3 -), 1.26 (22H, m, $-(\text{CH}_2)_{11}$ -), 1.80 (2H, quintet, $-\text{OCH}_2\text{CH}_2$ -), 3.99 (2H, t, $-\text{OCH}_2$ -), 6.96 (2H, d, J_{ab} 8.8, H_{a}), 7.40 (2H, d, J_{cd} 8.8, H_{c}), 7.47 (2H, d, J_{ba} 8.9, H_{b}) and 7.53 (2H, d, J_{dc} 8.7, H_{d}); δ_{C} (100 MHz; CDCl_3) 14.10 (CH_3 -), 22.68 (CH_3CH_2 -), 26.05 ($\text{CH}_3\text{CH}_2\text{CH}_2$ -), 29.27–29.66 ($-(\text{CH}_2)_9$ -), 31.92 ($-\text{OCH}_2\text{CH}_2$ -), 68.15 ($-\text{OCH}_2$ -), 114.91 (C_2), 120.69 (C_5), 127.91 (C_6 or C_7), 128.25 (C_6 or C_7), 131.75 (C_3), 132.24 (C_4), 139.82 (C_8) and 159.02 (C_1).

4-Bromo-4'-n-pentadecyloxybiphenyl 34h

0.81 g, 88.0%; c.p. 103, m.p. 107 °C; δ_{H} (200 MHz; CDCl_3) 0.89 (3H, t, CH_3 -), 1.27 (24H, m, $-(\text{CH}_2)_{12}$ -), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2$ -), 3.99 (2H, t, $-\text{OCH}_2$ -), 6.96 (2H, d, J_{ab} 8.8, H_{a}), 7.42 (2H, d, J_{cd} 8.7, H_{c}), 7.48 (2H, d, J_{ba} 8.8, H_{b}) and 7.53 (2H, d, J_{dc} 8.7, H_{d}); δ_{C} (100 MHz; CDCl_3) 14.11 (CH_3 -), 22.69 (CH_3CH_2 -), 26.05 ($\text{CH}_3\text{CH}_2\text{CH}_2$ -), 29.27–29.69 ($-(\text{CH}_2)_{10}$ -), 31.93 ($-\text{OCH}_2\text{CH}_2$ -), 68.16 ($-\text{OCH}_2$ -), 114.92 (C_2), 120.69 (C_5), 127.91 (C_6 or C_7), 128.26 (C_6 or C_7), 131.76 (C_3), 132.25 (C_4), 139.83 (C_8) and 159.02 (C_1).

4-Bromo-4'-n-hexadecyloxybiphenyl 34i

0.85 g, 89.5%; c.p. 96, m.p. 105 °C; δ_{H} (200 MHz; CDCl_3) 0.88 (3H, t, CH_3 -), 1.27 (26H, m, $-(\text{CH}_2)_{13}$ -), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2$ -), 3.99 (2H, t, $-\text{OCH}_2$ -), 6.96 (2H, d, J_{ab} 8.8, H_{a}), 7.41 (2H, d, J_{cd} 8.7, H_{c}), 7.48 (2H, d, J_{ba} 8.9, H_{b}) and 7.53 (2H, d, J_{dc} 8.6, H_{d}); δ_{C} (100 MHz; CDCl_3) 14.10 (CH_3 -), 22.68 (CH_3CH_2 -), 26.05 ($\text{CH}_3\text{CH}_2\text{CH}_2$ -), 29.28–29.68 ($-(\text{CH}_2)$ -), 31.92 ($-\text{OCH}_2\text{CH}_2$ -), 68.16 ($-\text{OCH}_2$ -), 114.92 (C_2), 120.70 (C_5), 127.92 (C_6 or C_7), 128.26 (C_6 or C_7), 131.76 (C_3), 132.25 (C_4), 139.83 (C_8) and 159.03 (C_1).

4-Bromo-4'-n-octadecyloxybiphenyl 34j

0.86 g, 85.1%; m.p. 101 °C; δ_{H} (200 MHz; CDCl_3) 0.89 (3H, t, CH_3 -), 1.27 (30H, m, $-(\text{CH}_2)_{15}$ -), 1.81 (2H, quintet, $-\text{OCH}_2\text{CH}_2$ -), 3.98 (2H, t, $-\text{OCH}_2$ -), 6.97 (2H, d, J_{ab} 8.8, H_{a}), 7.42 (2H, d, J_{cd} 8.6, H_{c}), 7.48 (2H, d, J_{ba} 8.8, H_{b}) and 7.54 (2H, d, J_{dc} 8.5, H_{d}); δ_{C} (100 MHz; CDCl_3) 14.10 (CH_3 -), 22.69 (CH_3CH_2 -), 26.06 ($\text{CH}_3\text{CH}_2\text{CH}_2$ -), 29.28–29.70 ($-(\text{CH}_2)_{13}$ -), 31.93 ($-\text{OCH}_2\text{CH}_2$ -), 68.16 ($-\text{OCH}_2$ -), 114.93 (C_2), 120.70 (C_5), 127.92 (C_6 or C_7), 128.26 (C_6 or C_7), 131.76 (C_3), 132.25 (C_4), 139.84 (C_8) and 159.03 (C_1).

Preparation of the 4-(4'-alkoxybiphenyl)mercury(II) halides 36 and dithizonates 23

In the preparations described below all glassware was oven-dried and, in the case of reactions involving n-butyllithium, flamed before use; the reaction flask was flushed with nitrogen before and during reagent addition and the subsequent reaction was conducted under a nitrogen atmosphere. Diethyl ether and THF were pre-dried over sodium wire.

(a) Reactions involving Grignard reagents***Attempted synthesis of 4-(4'-dodecyloxybiphenyl)magnesium bromide 35 (R = C₁₂H₂₅)***

Magnesium turnings (0.017 g, 0.719 mmol) and diethyl ether (2 cm³) were placed in a round-bottomed flask which was then fitted with a reflux condenser and dropping funnel. The mixture was stirred and a solution of the 4-bromo-4'-dodecyloxybiphenyl **34f** (0.30 g, 0.719 mmol) in diethyl ether (4 cm³) was added dropwise from the funnel. No immediate reaction was observed and the mixture was therefore gently heated for 30 min but without apparent effect. Stirring was then discontinued and a few crystals of iodine added to the warm mixture, again without result. The mixture was then heated to reflux and maintained at this temperature for 12 h. However, at the end of this period, the magnesium turnings still appeared bright and unaffected. This reaction was not pursued further.

Attempted synthesis of 4-(4'-propoxybiphenyl)magnesium bromide 35 (R = C₃H₇)***(i) Reaction in diethyl ether***

Reaction of 4-bromo-4'-propoxybiphenyl **34a** (0.3 g, 1.03 mmol) and magnesium (0.025 g, 1.03 mmol) in diethyl ether (5 cm³) was attempted according to the same method as for 4-bromo-4'-dodecyloxybiphenyl but using a much more finely divided grade of magnesium metal. Again, however, no reaction was observed even after addition of iodine and subsequent reflux for 18 h; the magnesium was recovered quantitatively by filtration, confirming the absence of any reaction.

(ii) Reaction in THF

The above reaction of the biphenyl **34a** and magnesium was repeated using THF as solvent instead of diethyl ether. No reaction was detected by visual inspection after 18 h reflux.

(b) Reactions involving n-butyllithium***Attempted synthesis of 4-(4'-propoxybiphenyl)mercury(II) bromide 36 (X = Br)******(i) Reaction in THF with addition of solid HgCl₂***

A solution of the biphenyl **34a** (0.30 g, 1.03 mmol) in THF (5 cm³) was cooled to below -70 °C using a dry ice-acetone bath. n-Butyllithium (0.77 cm³, 1.24 mmol; a 1.6 M solution in hexane) was then introduced *via* a rubber septum and the mixture was allowed to stir at below -70 °C for 30 min before addition of solid mercury(II) chloride (0.28 g, 1.03 mmol) in a single portion. The reaction mixture was kept in the cooling bath and the whole allowed to warm slowly to room temperature over a period of about 4 h. Some 30 min after addition of the mercury salt, traces of metallic mercury were observed in the solution. The quantity of mercury increased with time and the mixture assumed a greyish colour. This experiment was not pursued further.

The following variations on this procedure were attempted:

(ii) Reaction in diethyl ether

The above reaction was repeated on the same scale and according to the same method changing only the solvent to diethyl ether. Once again, metallic mercury was observed to form in the reaction mixture after *ca.* 30 min stirring and this experiment was therefore abandoned.

(iii) Reaction in THF with addition of dissolved HgCl₂

The procedure of reaction (i) was repeated except that the mercury(II) chloride was added as a solution in THF (5 cm³) and over a period of a few minutes. Reaction was discontinued when metallic mercury was observed to deposit from solution as before.

(iv) Reaction in diethyl ether with addition of dissolved HgCl₂

A solution of mercury(II) chloride in diethyl ether (5 cm³) was added to a solution of the biphenyl **34a** and n-butyllithium in diethyl ether (5 cm³) prepared as in (i). Metallic mercury was again detected on allowing the reaction mixture to warm slowly to room temperature and the experiment was discontinued.

(v) Reaction at room temperature

n-Butyllithium (0.77 cm³, 1.03 mmol; a 1.6 M solution in hexane) was added to a solution of the biphenyl **34a** (0.30 g, 1.03 mmol) in THF (5 cm³) at room temperature and the resulting mixture was stirred for 30 min before slow addition of a solution of mercury(II) chloride (0.28 g, 1.03 mmol) in THF (5 cm³). The mixture was left to stir at room temperature; a pronounced green colour was soon observed as well as a considerable deposit of mercury. Analysis by TLC (7 : 3 EtOAc : toluene) revealed a complex mixture of products, separation of which was not attempted.

(vi) Reaction at room temperature with reverse order of reagent addition

n-Butyllithium (0.39 cm³, 0.62 mmol; a 1.6 M solution on hexane) was added to a solution of the biphenyl **34a** (0.15 g, 0.52 mmol) in diethyl ether (5 cm³) at room temperature and the resulting mixture was allowed to stir for 30 min. It was then transferred *via* a metal cannula under a positive pressure of nitrogen to a solution of mercury(II) chloride (0.14 g, 0.52 mmol) in diethyl ether (5 cm³) at room temperature. A fluffy white precipitate formed immediately and this was stirred for 4 h at room temperature without the appearance of metallic mercury. Isolation of the solid by filtration was attempted but most of the solid material was not retained by the filter paper; filtration was repeated using a finer grade of filter paper but even then some of the material was not retained. On exposure to the air the solid appeared to decompose as portions of the material rapidly turned yellow and then darkened to a brown-orange colour. This product was not analysed.

Synthesis of 4-n-propoxybiphenyl 38

n-Butyllithium (1.0 cm³, 1.65 mmol) was added to a solution of the biphenyl **34a** (0.40g, 1.37 mmol) in diethyl ether (5 cm³) at room temperature and the mixture was allowed to stir for 30 min. Subsequent addition of water (0.02 cm³, 1.37 mmol) was accompanied by immediate formation of a white precipitate. The volume of the solvent was reduced by evaporation of the ether in a stream of nitrogen gas and the mixture was then filtered to yield the product **38** (0.20 g, 68.6%) as a white solid. δ_{H} (200 MHz; CDCl₃) 1.06 (3H, t, -CH₃), 1.84 (2H, sextet, CH₃CH₂-), 3.97 (2H, t, -OCH₂-), 6.98 (2H, d, *J* 8.8, *H_a*) and 7.24–7.59 (7H, m, *H_b* and remaining ArH).

Synthesis of 4-(4'-alkoxybiphenyl)mercury(II) dithizonates 23a–e

In a typical procedure, described here in detail for the preparation of the dithizonate **23d**, n-butyllithium (0.67 cm³, 1.08 mmol; a 1.6 M solution in hexane) was added to a

solution of 4-tetradecyloxy-4'-bromobiphenyl **34g** (0.40 g, 0.90 mmol) in diethyl ether (5 cm³) at room temperature. A slightly murky solution was obtained and this was allowed to stir at room temperature for 30 min. It was then transferred *via* a metal cannula under a positive pressure of nitrogen to a solution of mercury(II) bromide (0.32 g, 0.90 mmol) in diethyl ether (5 cm³) at room temperature. A fluffy white precipitate was immediately formed on addition and the resulting mixture was left to stir at room temperature for 1 h. The volume of the solvent was then reduced to approximately half by evaporation in a stream of nitrogen gas and the solid was isolated by filtration through a fine grade of filter paper. After drying overnight *in vacuo* over silica gel, 0.55 g of the intermediate product was obtained. This was suspended in dichloromethane (50 cm³), to which solid dithizone **25** (0.22 g, 0.86 mmol; calculated by assuming a 100% yield of the intermediate) was added in a single portion; a turbid, red mixture was immediately obtained. Addition of a few drops of triethylamine gave a clear, red solution; this was allowed to stir for 15 min and a small quantity of undissolved black material was then filtered off. The filtrate was concentrated to dryness under reduced pressure and the residue was chromatographed on silica gel using toluene as the eluant to give the product **23d** (0.32 g, 42.7% calc. from **34g**) and mercury(II) bis(dithizonate) (85 mg). Experimental data obtained for the latter compound were: m.p. 220–223 °C (lit⁷⁴ 223–224 °C); δ_{H} (400 MHz; CDCl₃) 7.10 (1H, m, *H_j*), 7.31 (3H, m, *H_g* and *H_h* or *H_i*), 7.42 (4H, m, *H_f* and *H_h* or *H_i*), 7.74 (2H, m, *H_e*), and 9.33 (1H, br. s, *NH*); δ_{C} (100 MHz; CDCl₃) 115.09 (*C₁₄* or *C₁₅*), 122.85 (*C₁₀*), 123.74 (*C₁₆*), 129.39 (*C₁₄* or *C₁₅* or *C₁₁*), 129.54 (*C₁₄* or *C₁₅* or *C₁₁*), 130.90 (*C₁₂*), 142.07 (*C₁₃* or *C₉*), 150.43 (*C₁₃* or *C₉*) and 152.89 (–*C(S)*–); *m/z* 711 (*M*⁺), 618, 255, 226, 169, 168, 167, 105, 93, 77.

The experimental data obtained for the compounds **23a–e** are as follows:

4-(4'-butoxybiphenyl)mercury(II) dithizonate 23a

0.33 g, 49.3%; m.p. 178 (dec.) °C; δ_{H} (400 MHz; CDCl₃) 1.00 (3H, t, *CH*₃–), 1.53 (2H, sextet, *CH*₃*CH*₂–), 1.81 (2H, quintet, –*OCH*₂*CH*₂–), 4.02 (2H, t, –*OCH*₂–), 6.99

(2H, d, J_{ab} 8.4, H_a), 7.08 (1H, m, H_j), 7.40 (7H, m, H_f , H_g , H_h and H_i), 7.48 (2H, d, J_{cd} 7.6, H_c), 7.55 (2H, d, J_{ba} 8.0, H_b) and 7.61 (2H, d, J_{dc} 7.2, H_d), 7.95 (2H, m, H_e) and 9.21 (1H, br. s, $-NH-$).

4-(4'-pentyloxybiphenyl)mercury(II) dithizonate 23b

0.21 g, 32.3%; m.p. 171 °C; δ_H (400 MHz; $CDCl_3$) 0.95 (3H, t, CH_3-), 1.44 (4H, m, $CH_3(CH_2)_2-$), 1.82 (2H, quintet, $-OCH_2CH_2-$), 4.01 (2H, t, $-OCH_2-$), 6.99 (2H, d, J_{ab} 8.8, H_a), 7.08 (1H, m, H_j), 7.40 (7H, m, H_f , H_g , H_h and H_i), 7.49 (2H, d, J_{cd} 8.4, H_c), 7.55 (2H, d, J_{ba} 9.0, H_b), 7.62 (2H, d, J_{dc} 8.0, H_d), 7.96 (2H, m, H_e) and 9.21 (1H, br. s, $-NH-$).

4-(4'-decyloxybiphenyl)mercury(II) dithizonate 23c

0.19 g, 31.7%; m.p. 166 °C; δ_H (400 MHz; $CDCl_3$) 0.89 (3H, t, CH_3-), 1.29 (12H, m, $-(CH_2)_6-$), 1.48 (2H, m, $-OCH_2CH_2CH_2-$), 1.80 (2H, quintet, $-OCH_2CH_2-$), 4.01 (2H, t, $-OCH_2-$), 6.99 (2H, d, J_{ab} 8.8, H_a), 7.08 (1H, m, H_j), 7.40 (7H, m, H_f , H_g , H_h and H_i), 7.49 (2H, d, J_{cd} 8.4, H_c), 7.55 (2H, d, J_{ba} 8.8, H_b), 7.62 (2H, d, J_{dc} 8.4, H_d), 7.95 (2H, m, H_e) and 9.21 (1H, br. s, $-NH-$); δ_C (100 MHz; $CDCl_3$) 14.13 (CH_3-), 22.69 (CH_3CH_2-), 26.08 ($CH_3CH_2CH_2-$), 29.32–29.59 ($-(CH_2)_5-$), 31.91 ($-OCH_2CH_2-$), 68.15 ($-OCH_2-$), 114.88 (C_2), 115.18 (C_{14} or C_{15}), 123.05 (C_{10} or C_{16}), 123.33 (C_{10} or C_{16}), 127.10 (C_6 or C_7), 128.07 (C_6 or C_7), 129.44 (C_{14} or C_{15} or C_{11}), 130.75 (C_{12}), 137.12, 140.93, 142.15 (C_{13} or C_9), 150.43 (C_{13} or C_9), 152.89 ($-C(S)-$) and 158.95; m/z 170, 169, 168, 167, 155, 141, 85, 71, 57, 43.

4-(4'-tetradecyloxybiphenyl)mercury(II) dithizonate 23d

0.32 g, 42.7%; m.p. 155 °C; δ_H (400 MHz; $CDCl_3$) 0.88 (3H, t, CH_3-), 1.27 (22H, m, $-(CH_2)_{11}-$), 1.48 (2H, quintet, $-OCH_2CH_2-$), 4.01 (2H, t, $-OCH_2-$), 6.99 (2H, d, J_{ab} 9.2, H_a), 7.08 (1H, m, H_j), 7.41 (7H, m, H_f , H_g , H_h and H_i), 7.49 (2H, d, J_{cd} 8.0, H_c), 7.55 (2H, d, J_{ba} 8.8, H_b), 7.62 (2H, d, J_{dc} 8.0, H_d), 7.96 (2H, m, H_e) and 9.23 (1H, br. s, $-NH-$); δ_C (100 MHz; $CDCl_3$) 14.13 (CH_3-), 22.70 (CH_3CH_2-), 29.07

(CH₃CH₂CH₂-), 29.31–29.68 (-(CH₂)₉-), 31.93 (-OCH₂CH₂-), 68.15 (-OCH₂-), 114.88 (C₂), 115.18 (C₁₄ or C₁₅), 123.05 (C₁₀ or C₁₆), 123.33 (C₁₀ or C₁₆), 127.10 (C₆ or C₇), 128.07 (C₆ or C₇), 129.34 (C₁₄ or C₁₅ or C₁₁), 129.45, 130.75 (C₁₂), 132.88, (C₄), 137.13, (C₈), 140.93, 142.15 (C₁₃ or C₉), 150.43 (C₁₃ or C₉), 154.49 (-C(S)-) and 158.95(C₅); *m/z* 837 (M⁺), 169, 168, 167, 155, 141, 113, 99, 85, 71, 57, 43.

4-(4'-octadecyloxybiphenyl)mercury(II) dithizonate 23e

0.15 g, 28.3%; 114 °C; δ_H (400 MHz; CDCl₃) 0.88 (3H, t, CH₃-), 1.26 (30H, m, -(CH₂)₁₅-), 1.47 (2H, m, -OCH₂CH₂CH₂-), 1.80 (2H, quintet, -OCH₂CH₂-), 4.01 (2H, t, -OCH₂-), 6.99 (2H, d, *J*_{ab} 9.2, H_a), 7.08 (1H, m, H_j), 7.41 (7H, m, H_f, H_g, H_h and H_i), 7.49 (2H, d, *J*_{cd} 8.0, H_c), 7.54 (2H, d, *J*_{ba} 8.8, H_b), 7.62 (2H, d, *J*_{dc} 8.0, H_d), 7.96 (2H, m, H_e) and 9.22 (1H, br. s, -NH-) *m/z* 508, 422, 169, 168, 167, 155, 141, 85, 71, 57, 43.

Preparation of the azobenzenes

Attempted synthesis of 4-acetoxymercurio-4'-hydroxyazobenzene 43

(i) Reaction in HCl (3 equivs.)

Partial dissolution of 4-aminophenylmercury(II) acetate **29** (0.50 g, 1.42 mmol) in a mixture of concentrated hydrochloric acid (0.4 cm³, 4.65 mmol) and water (10 cm³) was achieved by heating; this hot mixture was then cooled to 0 °C in an ice bath with vigorous stirring so as to maintain the amine in a state of fine division while in suspension. A chilled solution of sodium nitrite (0.12 g, 1.74 mmol) in water (2 cm³) was added dropwise to the above mixture, maintaining the reaction temperature below 3 °C by the addition of crushed ice when necessary. The first few drops of sodium nitrite produced an intense yellow colour but this darkened to orange-brown before the addition was complete. A small quantity of precipitated material was observed. The

cold diazonium solution was then added to a chilled solution of phenol (0.13 g, 1.42 mmol) in 10% aqueous sodium hydroxide (8 cm³), again maintaining the temperature below 3 °C by the addition of ice. A very dark brown mixture was obtained and this was stirred for 1 h in ice before the solid was collected by filtration and washed thoroughly with water. After drying overnight *in vacuo* over silica gel, 0.32 g of product was obtained. The material was of limited solubility in most organic solvents; analysis by TLC (70 : 30 EtOAc : toluene) revealed one main component and traces of other products. δ_{H} (200 MHz; DMSO) 7.16 (m), 7.37 (d, *J* 8.5), 7.41 (m) and 7.49 (d, *J* 8.6); assignment of these broad resonances was not possible. The filtrate from the above separation was extracted with ethyl acetate and the organic phase concentrated to give a black tar smelling strongly of phenol.

(ii) Reaction in aqueous acetic acid

4-Aminophenylmercury(II) acetate **29** (0.53 g, 1.51 mmol) was dissolved with heating in a mixture of glacial acetic acid (3 cm³) and water (6 cm³). The resulting solution was then cooled to 0 °C in an ice-bath and diazotization with sodium nitrite (0.12 g, 1.74 mmol) in water (4 cm³) was performed as described above. An intense yellow colour was observed on addition of the first few drops of sodium nitrite solution but the reaction mixture quickly darkened and a fine suspension was observed in solution. The slow addition of the cold diazonium solution to a chilled solution of phenol (0.14 g, 1.51 mmol) in 10% aqueous sodium hydroxide (8 cm³), at a rate so as to maintain the temperature below 3 °C, gave a dark brown mixture. This was left to stir overnight. A small quantity of brown solid was obtained which gave the same NMR spectrum as that of the product obtained in (i) above. However, the greater quantity of material was obtained as a black tar on extraction of the filtrate with ethyl acetate.

(iii) Reaction in HCl (6 equivs.)

Reaction (i) was repeated except that the diazotization was performed in a mixture containing twice the volume of concentrated acid (0.8 cm³, 9.30 mmol). Again, a

brown solution was obtained and addition of this to a solution of phenol in 40% aqueous sodium hydroxide gave an even darker mixture from which a small amount of a black solid was obtained.

(iv) *Diazotization at $-5\text{ }^{\circ}\text{C}$*

Reaction (i) was repeated except that the temperature of the reaction mixture during addition of the sodium nitrite was maintained at $-5\text{ }^{\circ}\text{C}$ by cooling in an ice-salt bath. The same material as obtained in the reaction (i) above was isolated.

Synthesis of 4-hydroxyazobenzene 50

Freshly distilled aniline (0.60 g, 6.44 mmol) was added to a mixture of concentrated hydrochloric acid (1.5 cm^3 , 17.4 mmol) and water (10 cm^3) and the resultant solution cooled to $0\text{ }^{\circ}\text{C}$ whereupon the amine hydrochloride salt was observed to separate as a white precipitate. A chilled solution of sodium nitrite (0.53 g, 7.68 mmol) in water (4 cm^3) was added dropwise, with vigorous stirring, to the above mixture, maintaining the reaction temperature below $3\text{ }^{\circ}\text{C}$ by the addition of crushed ice when necessary. The precipitated hydrochloride salt dissolved during the addition and a clear yellow solution was obtained. The cold diazonium solution was then added dropwise to a chilled solution of phenol (0.61 g, 6.44 mmol) in 10% aqueous sodium hydroxide (10 cm^3), again maintaining the temperature below $3\text{ }^{\circ}\text{C}$ by the addition of ice. The required product **50** immediately separated as a deep red precipitate. Once addition was complete the mixture was stirred for 1 h at $0\text{ }^{\circ}\text{C}$ and the solid then collected by filtration and washed with copious quantities of water. This product was dried *in vacuo* over silica gel. Recrystallization from ethanol yielded **50** as orange needles (0.82 g, 64.1%); m.p. $153\text{--}155\text{ }^{\circ}\text{C}$ (lit.,⁸⁵ $153\text{--}155\text{ }^{\circ}\text{C}$); δ_{H} (200 MHz) 1.71 (1H, br. s, $-\text{OH}$), 6.94 (2H, d, J_{ab} 8.9, H_{a}), 7.49 (3H, m, H_{d} and H_{e}) and 7.88 (4H, m, H_{b} and H_{c}).

Synthesis of 4-bromo-4'-hydroxyazobenzene 51

4-Bromoaniline (0.8 g, 4.65 mmol) was dissolved with heating in a mixture of concentrated hydrochloric acid (1.2 cm³, 14.0 mmol) and water (10 cm³) and the solution was then chilled to 0 °C in an ice bath. On cooling, a white precipitate of the amine hydrochloride salt appeared. This mixture was diazotized with a solution of sodium nitrite (0.39 g, 5.65 mmol) in water (4 cm³) according to the procedure (i) described for **43** (above) and then added dropwise to a solution of (0.44 g, 4.65 mmol) in 10% aqueous sodium hydroxide (10 cm³) at 0 °C. An orange-red colour was observed on addition and a precipitate was slowly formed. The reaction mixture was allowed to stir overnight at room temperature to effect complete precipitation, and the resulting solid was then filtered, washed thoroughly with water and dried *in vacuo* over silica gel before recrystallization from ethanol to yield **51** as a brick-red microcrystalline powder (0.88 g, 68.2%); δ_{H} (200 MHz) 1.73 (1H, br. s, -OH), 6.96 (2H, d, J_{ab} 8.9, H_{a}), 7.62 (2H, d, J_{cd} 8.8, H_{c}), 7.75 (2H, d, J_{dc} 8.8, H_{d}) and 7.86 (2H, d, J_{ba} 8.9, H_{b}).

Synthesis of 4-n-alkoxy-4'-bromoazobenzenes 52a-d

In a typical procedure, sodium hydride (0.05 g, 1.62 mmol; an 80% dispersion in mineral oil) was added to a solution of 4-bromo-4'-hydroxyazobenzene **51** (0.30 g, 1.08 mmol) in freshly distilled DMF (8 cm³). The addition was accompanied by vigorous effervescence and the evolution of H₂ gas. Once this exothermic reaction had subsided the appropriate alkyl bromide (1.30 mmol) was added and the resulting mixture was then placed in an oil-bath preheated to 110–115 °C. The mixture was maintained at this temperature with gentle reflux for 1½–2 h after which time analysis by TLC did not detect the starting material. The reaction mixture was allowed to cool slightly and then poured onto crushed ice, whereupon the product precipitated as an

orange-yellow solid. Recrystallization was effected from hexane. The experimental data for the compounds **52a–d** are as follows:

4-Bromo-4'-pentyloxyazobenzene 52a

0.30 g, 78.9%; m.p. 93 °C; δ_{H} (200 MHz; CDCl_3) 0.89 (3H, t, CH_3 -), 1.39 (4H, m, $-(\text{CH}_2)_2$ -), 1.77 (2H, quintet, $-\text{OCH}_2\text{CH}_2$ -), 3.98 (2H, t, $-\text{OCH}_2$ -), 6.94 (2H, d, J_{ab} 9.0, H_{a}), 7.56 (2H, d, J_{cd} 8.8, H_{c}), 7.70 (2H, d, J_{dc} 8.9, H_{d}) and 7.84 (2H, d, J_{ba} 9.0, H_{b}); δ_{C} (100 MHz; CDCl_3) 28.19 ($-\text{CH}_3$), 28.86, 68.40 ($-\text{OCH}_2$ -), 114.76 (C_2), 124.28, 124.37, 132.32, 146.67, and 151.51.

4-Bromo-4'-octyloxyazobenzene 52b

0.36 g, 85.7%; m.p. 87 °C; δ_{H} (200 MHz; CDCl_3) 0.82 (3H, t, CH_3 -), 1.25 (10H, m, $-(\text{CH}_2)_5$ -), 1.75 (2H, quintet, $-\text{OCH}_2\text{CH}_2$ -), 3.97 (2H, t, $-\text{OCH}_2$ -), 6.93 (2H, d, J_{ab} 9.1, H_{a}), 7.55 (2H, d, J_{cd} 8.8, H_{c}), 7.69 (2H, d, J_{dc} 8.9, H_{d}) and 7.83 (2H, d, J_{ba} 9.0, H_{b}); δ_{C} (100 MHz; CDCl_3) 14.06 ($-\text{CH}_3$), 22.64 (CH_3CH_2 -), 26.01 ($\text{CH}_3\text{CH}_2\text{CH}_2$ -), 29.20–29.33 ($-(\text{CH}_2)_3$ -), 31.80 ($-\text{OCH}_2\text{CH}_2$ -), 68.43 ($-\text{OCH}_2$ -), 114.79 (C_2), 124.05, 124.43, 132.21, 146.73, 151.56 and 162.02 (C_1).

4-Bromo-4'-tetradecyloxyazobenzene 52c

0.38 g, 79.1%; m.p. 83 °C; δ_{H} (200 MHz; CDCl_3) 0.89 (3H, t, CH_3 -), 1.28 (14H, br. s, $-(\text{CH}_2)_7$ -), 1.82 (2H, quintet, $-\text{OCH}_2\text{CH}_2$ -), 4.04 (2H, t, $-\text{OCH}_2$ -), 7.00 (2H, d, J_{ab} 9.1, H_{a}), 7.62 (2H, d, J_{cd} 8.9, H_{c}), 7.76 (2H, d, J_{dc} 8.8, H_{d}) and 7.90 (2H, d, J_{ba} 9.0, H_{b}); δ_{C} (100 MHz; CDCl_3) 14.09 ($-\text{CH}_3$), 22.67 (CH_3CH_2 -), 26.01 ($\text{CH}_3\text{CH}_2\text{CH}_2$ -), 29.19–29.56 ($-(\text{CH}_2)_7$ -), 31.89 ($-\text{OCH}_2\text{CH}_2$ -), 68.43 ($-\text{OCH}_2$ -), 114.79 (C_2), 124.05, 124.89, 132.22 and 162.02.

4-Bromo-4'-tetradecyloxyazobenzene 52d

0.41 g, 80.4%; c.p. 86, m.p. 100 °C; δ_{H} (200 MHz; CDCl_3) 0.88 (3H, t, CH_3 -), 1.27 (22H, m, $-(\text{CH}_2)_{11}$ -), 1.82 (2H, quintet, $-\text{OCH}_2\text{CH}_2$ -), 4.04 (2H, t, $-\text{OCH}_2$ -), 7.00

(2H, d, J_{ab} 9.1, H_a), 7.62 (2H, d, J_{cd} 8.9, H_c), 7.76 (2H, d, J_{dc} 8.9, H_d) and 7.90 (2H, d, J_{ba} 9.0, H_b); δ_C (100 MHz; $CDCl_3$) 14.09 ($-CH_3$), 22.68 (CH_3CH_2-), 26.01 ($CH_3CH_2CH_2-$), 29.19–29.65 ($-(CH_2)_9-$), 31.92 ($-OCH_2CH_2-$), 68.44 ($-OCH_2-$), 114.79 (C_2), 124.05, 124.88, 132.22, 151.56 and 162.02.

Attempted synthesis of 4-bromo-4'-octyloxyazobenzenemercury(II) dithizonate 24a

In the attempted preparations described below the same precautions for the strict exclusion of air and water from the reaction mixtures were observed as were described for the reactions of the biphenyls **34** with n-butyllithium.

(i) Reaction at 0 °C

n-Butyllithium (0.29 cm³, 0.47 mmol) was added to a solution of 4-bromo-4'-octyloxyazobenzene **52b** (0.15 g, 0.39 mmol) in diethyl ether (5 cm³) maintained at 0 °C in an ice bath. Immediately on addition the colour of the solution changed from golden-yellow to black, but this colour faded after a few minutes stirring and a brown, murky solution was obtained. This mixture was allowed to stir at 0 °C for 30 min and then transferred *via* a metal cannula under a positive pressure of nitrogen to a solution of mercury(II) bromide (0.14 g, 0.39 mmol) in diethyl ether (5 cm³), similarly maintained at 0 °C. A fluffy brown precipitate was immediately formed and the mixture was stirred at 0 °C for 1 h. The volume of the solvent was then reduced to approximately half by evaporation in a stream of nitrogen gas and the solid product was isolated from the remaining solvent by filtration. A slight cloudiness was observed in the filtrate as not all of the solid was retained by the filter paper during filtration. This product was dried overnight *in vacuo* over silica gel to give a dark brown material (0.26 g). This was suspended in dichloromethane (50 cm³) and solid dithizone **25** (0.12 g, 0.47 mmol) added to give a dark-red, turbid mixture. Addition of a few drops of triethylamine resulted in a bright red solution which was stirred at room temperature for 15 min. A small amount of undissolved black material was then filtered off, the

filtrate was concentrated to dryness and chromatographed on silica gel using toluene as eluant to give the starting material **52b** as an orange-yellow solid (0.10 g) and mercury(II) bis(dithizonate) as a bright red solid (0.21 g).

(ii) Reaction at below $-70\text{ }^{\circ}\text{C}$

The reaction described above was repeated on the same scale and according to the same method except that the solution of the azobenzene **52b** in diethyl ether was cooled to below $-70\text{ }^{\circ}\text{C}$ in a dry ice-acetone bath. At this temperature the azobenzene crystallized and addition of the n-butyllithium gave a brown, murky solution. Addition of this mixture to a solution of mercury(II) bromide, reaction with dithizone and subsequent work-up as described in (i) resulted in the recovery of the unreacted starting material **52b** (0.13 g) and mercury(II) bis(dithizonate) (0.25 g).

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