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Desorption kinetics of a xanthenol–dioxane clathrate

Ayesha Jacobs,[a]* Luigi R. Nassimbeni[a] and Benjamin Taljaard[b]

[a]Faculty of Applied Sciences, Cape Technikon, PO Box 652, Cape Town 8000, South Africa, and [b]Department of Chemistry, University of Port Elizabeth, Port Elizabeth 6000, South Africa
Correspondence e-mail: jacobsa@ctech.ac.za

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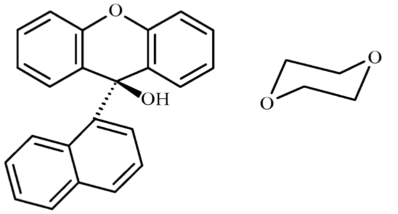
The host xanthenol compound forms a 1:1 clathrate with dioxane, namely 9-(1-naphthyl)-9*H*-xanthen-9-ol–1,4-dioxane, $C_{23}H_{16}O_2 \cdot C_4H_8O_2$. The structure of this clathrate is reported, along with a study of the kinetics of desolvation and the determination of an activation energy. The guest molecules are stabilized by $O_{host}—H\cdots O_{guest}$ hydrogen bonds [O—H = 0.968 (2) Å, O···O = 2.7532 (13) Å and O—H···O = 151.9 (4)°].

Comment

The conformations of the two components of 9-(1-naphthyl)-9*H*-xanthen-9-ol–dioxane, (I), are shown in Fig. 1. A search of the Cambridge Structural Database (CSD, Version 5.25; Allen, 2002) revealed that no structures of this host molecule have been published to date. We present here the crystal structure of the title clathrate, (I).



(I)

Bond lengths and angles for the host and guest in (I) generally fall in the expected ranges. The xanthene ring of the host is slightly non-planar, with the dihedral angle between the least-squares planes of the two phenyl rings being 5.17 (4)°. The host naphthalene moiety and the xanthene ring are nearly orthogonal, the dihedral angle between their least-squares planes being 88.21 (2)°. This is comparable with the conformation found in similar structures, such as bis(9-phenyl-9-hydroxy)xanthene tris(dioxane) clathrate (Csöregh *et al.*, 1993). In other structures, such as 9-(cyclohepta-2,4,6-trien-1-yl)xanthen-9-ol (Badejo *et al.*, 1991), the dihedral angle is substantially different, at 21.9 (2)°. The 1,4-dioxane guest molecule is in the expected chair conformation (Fig. 1).

Dioxane is an interesting guest molecule, since it has two O atoms which are capable of being hydrogen-bond acceptors. A series of similar hosts have been observed to include dioxane, with host–guest stoichiometries varying from 2:1 to 2:3 (Csöregh *et al.*, 1993), with the guests situated in channels or cages. In this study, each host molecule is hydrogen bonded *via*

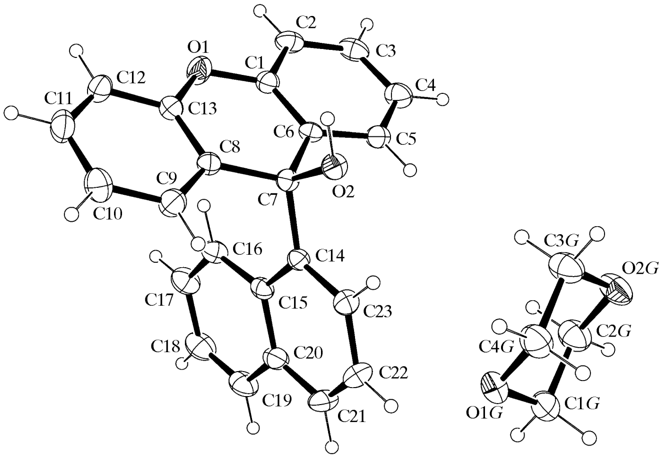


Figure 1
A view of the two components of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

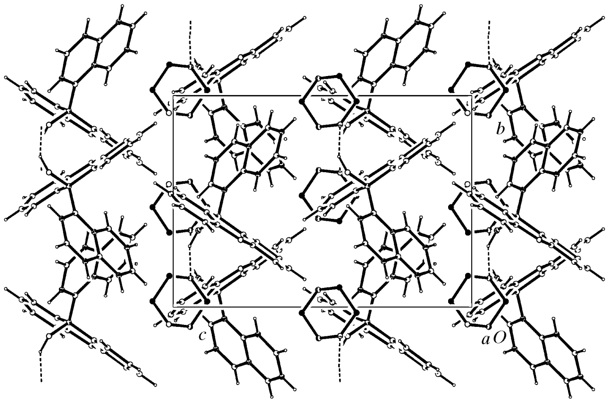


Figure 2
The structure of (I), viewed down [100]. The hydrogen bond is shown as a dashed line.

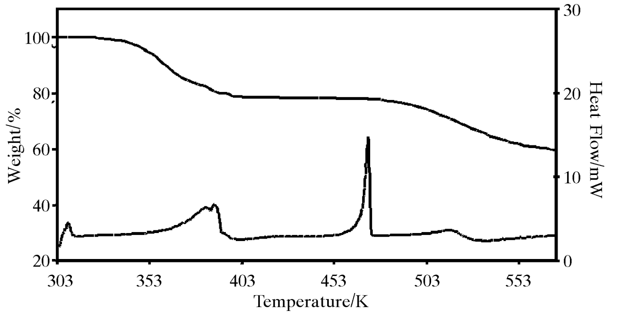


Figure 3
TGA and DSC curves for (I).

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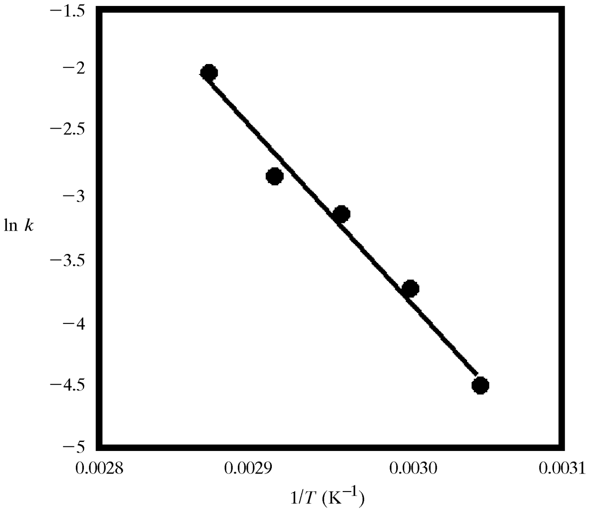

Figure 4
Arrhenius plot for the desolvation of (I).

its hydroxyl moiety to one dioxane molecule (Table 1). This is consistent with Csöregh's study, which suggested that the more bulky the substituent attached to the xanthene ring, the greater the tendency for a single host–guest interaction.

In the crystal structure of (I), the host molecules pack in zigzag layers parallel to [100] and the dioxane guests lie in cages created by the host framework (Fig. 2). The hydrogen-bonded host–guest units form spirals which extend along [010]. The spiral shape is largely due to the torsion angle between the xanthenol and naphthalene moieties of the host [C8—C7—C14—C15 = 61.56 (14)°]. We used the program *SECTION*(Barbour,1999*a*) to map the cavities and found that the approximate size of these cages is 7.6 × 6.5 × 7.4 Å. This compares favourably with other structures, such as the 9-[4-(*tert*-butyl)phenyl]fluoren-9-ol–dioxane clathrate (Csöregh *et al.*, 1993), where the cages have approximate dimensions 5.7 × 7.1 × 9.7 Å.

Thermogravimetric analysis (TGA) of (I) shows a single mass-loss step (calculated mass loss = 21.4% and observed mass loss = 21.3%), which is consistent with a host–guest ratio of 1:1. Two endotherms were observed in the differential scanning calorimetry (DSC) profile. The first of these ($T_{\rm on}$ = 380.4 K) corresponds to the loss of guest and the second ($T_{\rm on}$ = 468.0 K) represents the host melt. Both TGA and DSC curves are shown in Fig. 3.

The kinetics of desolvation for (I) were determined by performing a series of isothermal TG experiments between 328 and 348 K. The resultant mass–time curves were sigmoidal and fitted the Avrami–Erofeev rate law (*A*4), $[-\ln(1-\alpha)]^{1/4} = kt$, where α is the extent of the reaction and k is the rate constant (Brown, 1988). The corresponding Arrhenius plot is shown in Fig. 4. An activation energy of 111 (2) kJ mol^{-1} was obtained.

Experimental

The host compound was synthesized using the method of Dilthey *et al.* (1939). IR spectra of the host alone showed $\nu_{\rm max}$ values ($CHCl_3$) of 3584.1 (*s*, free OH) and 3370.1 cm^{-1} (*br*, bonded OH). IR spectra were recorded on a Perkin–Elmer 1600 Series FT spectrometer. Suitable crystals of (I) were obtained by slow evaporation of dilute solutions of the host in liquid dioxane at room temperature. The crystals were crushed for thermal analysis. TGA was performed on a Mettler–Toledo Star$^{\rm e}$ system and DSC was carried out on a Perkin–Elmer PC7 Series system.

Crystal data

$C_{23}H_{16}O_2 \cdot C_4H_8O_2$
M_r = 412.46
Orthorhombic, $Pna2_1$
a = 13.597 (3) Å
b = 10.404 (2) Å
c = 14.735 (3) Å
V = 2084.5 (7) Å^3
Z = 4
D_x = 1.314 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 703 reflections
θ = 4.5–26.6°
μ = 0.09 mm^{-1}
T = 173 (2) K
Rectangular, colourless
0.36 × 0.30 × 0.27 mm

Data collection

Nonius KappaCCD area-detector diffractometer
1° φ scans and ω scans
14 703 measured reflections
2202 independent reflections
2095 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.027
$\theta_{\rm max}$ = 26.6°
$h = -15 \rightarrow 16$
$k = -13 \rightarrow 13$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.076
S = 1.07
2202 reflections
284 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 0.3201P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.004
$\Delta\rho_{\rm max}$ = 0.27 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.27 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1···O2$G^{\rm i}$	0.968 (3)	1.861 (2)	2.7532 (13)	151.9 (4)

Symmetry code: (i) $x-\frac{1}{2}, \frac{3}{2}-y, z$.

The aromatic H atoms of the host and the CH_2 H atoms of the dioxane guest were located in difference electron-density maps, but they were geometrically constrained with C—H distances fixed at 0.95 and 0.99 Å, respectively. The hydroxyl H atom was located in a difference electron-density map, and was initially refined isotropically. Thereafter, it was placed in a geometrically calculated position based on the relationship between O—H and O···O distances (Olovsson & Jönsson, 1975), and its position was refined under distance restraints, starting with O2—H1 = 0.919 (15) Å and H1···O2G = 1.837 (1) Å. Friedel pairs were merged for the final refinement.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 1999*b*); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1455). Services for accessing these data are described at the back of the journal.

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