Enclathration of Diethyl Ether

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The host 9,9′-dihydroxy-9,9′-di(4-*tert*-butylphenyl)-9,9′-dihydroanthracene enclathrates diethyl ether from the vapour and forms a stable inclusion compound. The enthalpy of the guest-release reaction has been measured and reconciled with the crystal structure.

Inclusion compounds of highly volatile guests are often unstable at room temperature and atmospheric pressure, and organic host compounds which enclathrate volatile guests from the vapour phase are rare. We have investigated the structure–stability relationships of diol host compounds with a variety of volatile guest molecules,[1-3] and we now report on a diol host which forms a highly stable inclusion compound with diethyl ether. The host compound 9,9′-dihydroxy-9,9′-di(4-*tert*-butylphenyl)-9,9′-dihydroanthracene was synthesized by reacting the Grignard derivative of 4-*tert*-butylbromobenzene with anthraquinone. Crystals of the inclusion compound were obtained by slow evaporation of a solution of the host in diethyl ether. The crystals are colourless tabular plates and remain stable for several days at room temperature. This remarkable stability is shown by the thermal analysis results given in Fig. 1.

The differential scanning calorimetry (DSC) curve gives an onset temperature T_{on} = 64.2 °C for the guest release reaction, 29.8 °C above its normal boiling point, while thermal gravimetry (TG) confirms the host : guest ratio of 1:2 which was employed in the crystal structure analysis (weight loss found = 23.5%, required = 23.7%). In a previous publication[4] we suggested that the function $T_{on} - T_b$ (T_{on} = onset temperature and T_b = normal boiling point of the guest) may be a useful parameter of compound stability. For most inclusion compounds of volatile guests $T_{on} < T_b$, but there are some notable exceptions. In particular, Weber has characterized a large number of inclusion compounds of 1,1′-binaphthyl-2,2′-dicarboxylic acid,[5] and the 1:2 methanol inclusion compound has $T_{on} - T_b = +82$ °C.

The equilibrium constant of the thermal decomposition reaction was investigated by measuring the vapour pressure of the diethyl ether at various temperatures. This was carried out

$$\mathrm{H{\cdot}2G(s)} \rightleftharpoons \mathrm{H(s) + 2G(g)}$$

$$\mathrm{H = diol\ host,\ G = diethyl\ ether}$$

by placing freshly prepared crystals of the inclusion compound in a small flask connected to a pressure transducer. The apparatus, evacuated at 0 °C to remove surface ether and air, was placed in an insulated air chamber whose temperature could be controlled to 0.1 °C. The compound was heated at 0.5 °C min^{-1} from 25 °C to 60 °C and the pressure recorded. The results are shown in Fig. 2(*a*). Curve (i) was obtained by heating large single crystals with dimensions varying typically from 0.5 to 2 mm, and the vapour pressure can be seen to rise slowly to 50 °C and sharply thereafter, reaching 1 atm* at 56 °C. At this point the crystals have decomposed to a fine powder, but the reaction is reversible, and upon cooling the vapour pressure decreases and the inclusion compound reforms. A second run on the now powdered sample yields curve (ii), a smooth variation of pressure with temperature. Fig. 2(*b*) shows plots of 2 ln *P versus* T^{-1}, the slopes of which yield the enthalpy changes, ΔH, of the reaction.

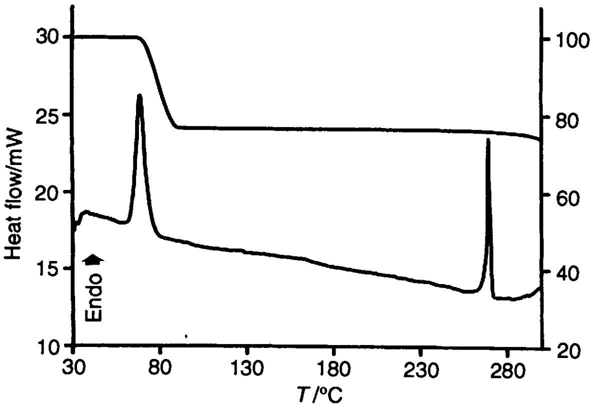

Fig. 1 TG and DSC curves for the diethyl ether inclusion complex

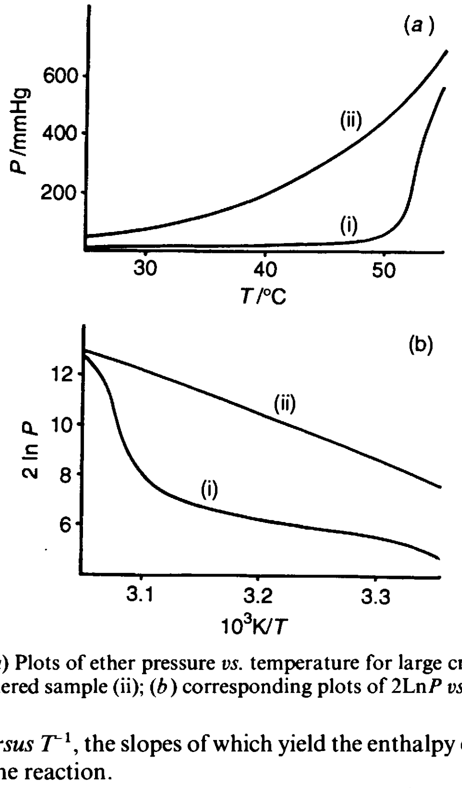

Fig. 2 (*a*) Plots of ether pressure *vs.* temperature for large crystals, (i) and powdered sample (ii); (*b*) corresponding plots of 2Ln*P vs.* T^{-1}

Curve (ii) yields a value of ΔH = 147 kJ mol^{-1} representing the enthalpy change of the guest-release reaction from finely powdered crystals. The initial part of curve (i), from 25 to 45 °C yields a much lower value of 59 kJ mol^{-1}, which we interpret as a diffusion-inhibited desorption from the large crystals. Beyond 50 °C however, the fast release of the volatile diethyl ether, probably due to fracturing of the large crystals, has a much higher apparent ΔH of 1436 kJ mol^{-1}.

The structure of the diol–ether inclusion compound is shown

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* 1 atm = 1.01 × 10^5 Pa.

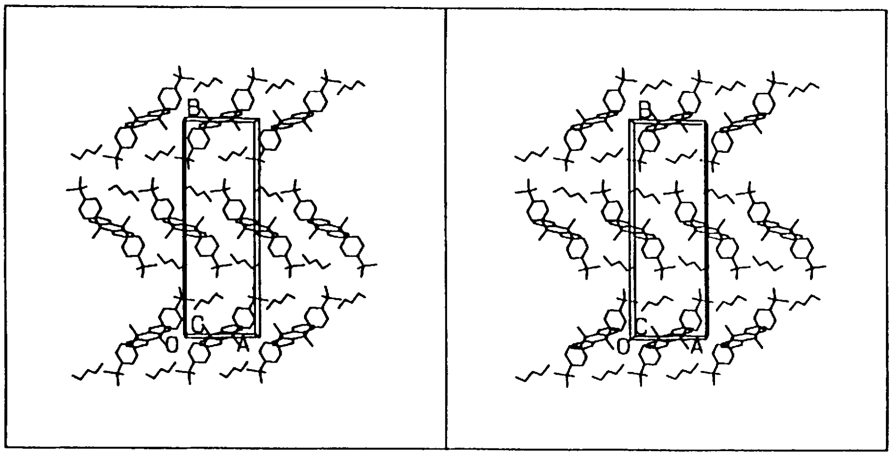

Fig. 3 Stereographic projection of the structure along [001]

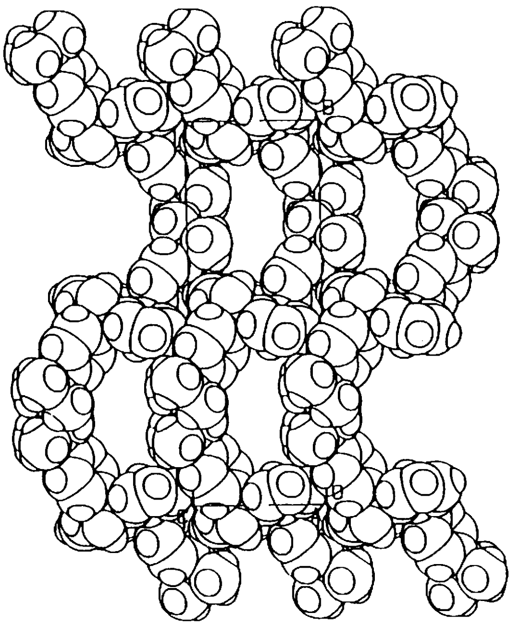

Fig. 4 Projection along [100]—host drawn with van der Waals radii and guest omitted.

as a stereographic projection in Fig. 3, viewed along [001]. There is a weak hydrogen bond between host and guest, with O···O distance of 2.948(6) Å. The guest molecules lie in undulating channels running parallel to [100]. These can be clearly seen in Fig. 4 which is a van der Waals representation of the structure with the guest molecules omitted. The high thermal stability of this compound cannot be justified by the relatively weak hydrogen bond alone, but can be rationalized by the tight fit of the guest molecules in the channels.

Interestingly, the host compound absorbs diethyl ether directly from the vapour, and we have measured the kinetics of enclathration using an especially constructed vacuum balance linked to a microcomputer, details of which have been published.[6] The mass gain *versus* time curve follows first order kinetics and has a half-life of 18 min when the host compound is exposed to a vapour pressure of pure diethyl ether at 290 mmHg* at 10 °C. The resultant inclusion compound is that reported in the crystal structure, and this has been confirmed by comparing the powder diffraction pattern of this, the beta-phase, with that generated from the coordinates derived from the single crystal structure.[7] When the beta-phase is heated to about 70 °C in a vacuum, the guest is released and the ensuing host compound reverts to the alpha-phase as confirmed by the resulting powder diffraction pattern, distinctly different from that of the beta-phase. The new host also enclathrates acetone. The question of selectivity towards different solvents has yet to be investigated.

Crystal data for $C_{34}H_{36}O_2{\cdot}2C_4H_{10}O$, $M_r = 624.87$, monoclinic, space group $P2_1/a$, $a = 8.771(2)$, $b = 25.132(5)$, $c = 9.042(3)$ Å, $\beta = 104.75(3)°$, $Z = 2$, $D_c = 1.08$ g cm^{-3}, crystal size = 0.34 × 0.38 × 0.44 mm. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using Mo-Kα ($\lambda = 0.7107$ Å) radiation to $\theta_{max} = 25°$; 3716 unique reflections were collected. The least squares refinement converged to a final $R = 0.070$ for 1830 reflections with $I > 2\sigma(I)$; $R_w = 0.070$ with $w = (\sigma^2F + 1.84 \times 10^{-4}F^2)^{-1}$. Residual electron density (max, min) = 0.29, -0.27 e Å^{-3}. All heavy atoms were treated anisotropically and hydrogen atoms were refined with geometrical constraints. The hydroxy hydrogen was located unambiguously in a difference electron density map and refined with a constrained bond length. The location of the guest atoms were found routinely, and they refined uneventfully, yielding acceptable bond lengths and angles.

References

1 M. H. Moore, L. R. Nassimbeni and M. L. Niven, *Inorg. Chim. Acta*, 1987, **131**, 45.
2 M. H. Moore, L. R. Nassimbeni and M. L. Niven, *Inorg. Chim. Acta*, 1987, **132**, 61.
3 D. R. Bond, L. Johnson, L. R. Nassimbeni and F. Toda, *J. Solid State Chem.*, 1991, **92**, 68.
4 M. R. Caira, L. R. Nassimbeni, M. L. Niven, W.-D. Schubert, E. Weber and N. Dörpinghaus, *J. Chem. Soc., Perkin Trans. 2*, 1990, 2129.
5 E. Weber and M. Czugler, *Top. Curr. Chem.*, 1988, **149**, 45.
6 L. J. Barbour, K. Achleitner and J. R. Greene, *Thermochim. Acta*, 1992, **205**, 171.
7 K. Yvon, W. Jeitschko and E. Parthe, *J. Appl. Cryst.*, 1977, **10**, 73.

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* 1 mmHg ≈ 133 Pa.