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Complexation with diol host compounds.
Part 9. Structures and thermal analyses of inclusion compounds of *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene with acetonitrile and 3-hydroxypropionitrile

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Abstract

The host compound (**H**), *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene forms inclusion compounds with acetonitrile (compound **1**) and 3-hydroxypropionitrile (compound **2**) both with host : guest ratio of 1 : 2.

Crystal data: (**1**) $C_{26}H_{20}O_2 \cdot 2C_2H_3N$, $M_r = 446.54$, $a = 8.530(2)$, $b = 16.995(6)$, $c = 9.034(1)$ Å, $\beta = 109.15(2)°$, space group $P2_1/c$, $D_m = 1.18$ g cm^{-3}, $D_c = 1.20$ g cm^{-3} for $Z = 2$, $R = 0.096$ for 1363 reflections; (**2**) $C_{26}H_{20}O_2 \cdot 2C_3H_5NO$, $M_r = 506.60$, $a = 8.444(1)$, $b = 9.7931(7)$, $c = 16.558(2)$ Å, $\beta = 104.32(1)°$, space group $P2_1/n$, $D_m = 1.28$ g cm^{-3}, $D_c = 1.27$ g cm^{-3} for $Z = 2$, $R = 0.066$ for 1567 reflections.

The thermal decomposition of (**1**) shows that the guest release reaction occurs in a single step, but that the activation energy varies with the extent of decomposition, from 83 to 114 kJ mol^{-1}. DSC of (**2**) shows that decomposition is more complex, with possible phase changes of the host structure.

INTRODUCTION

Inclusion compounds have become of primary importance in recent years, not only because of their intrinsic chemical interest, but also because they have considerable industrial application in molecular separation processes. Recently their use in the separation of enantiomers has been reviewed [1] while the optical resolution of racemates and the control of reactions of guest compounds by using host–guest compounds have been discussed [2,3]. The classification of these compounds is difficult, but a

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system of nomenclature has been proposed which takes into account both the topology and the interactions occurring in these compounds. In particular when hydrogen bonds bind host to guests, the resulting compound may be named a coordinato-clathrate [4].

We have studied a number of hydroxy and diol host compounds which form inclusion compounds with a variety of guest molecules, sometimes with concomitant hydrogen bonding. The host compound *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene (**H**) forms inclusion compounds with 1,4-butanediol [5], methanol [6], ethanol [7], acetophenone, 2-methylcyclopentanone [8], 2-methylcyclohexanone and 4-methylcyclohexanone [9].

Recently the structures of inclusion compounds of (**H**) with 4-vinylpyridine, 4-methylpyridine and 2-methylpyridine, and also their thermal analyses, have been reported [10]. We now extend the study of the inclusion compounds made from this host (**H**) with guest molecules containing nitrogen as the hydrogen-bond acceptor. We therefore report the results of thermal decomposition of the inclusion compounds of (**H**) with acetonitile (**1**) and 3-hydroxypropionitrile (**2**).

EXPERIMENTAL

The host compound was prepared as previously described [8]. Suitable crystals of the molecular complexes were obtained by slow evaporation from dilute solutions of the host (**H**) in the appropriate guest. The time required ranged from 1 week for compound (**1**) to 3 weeks for compound (**2**). Preliminary characterisation included density determination (flotation in aqueous KI), microanalysis using a Heraeus universal combustion analyser Model CHN-Rapid, melting point determination on a Linkam 600 hot stage coupled to a Linkam CO 600 temperature controller, and thermal analysis.

Differential scanning calorimetry (DSC) measurements were performed using a Perkin-Elmer DSC 7 instrument calibrated with indium and zinc. Sample masses were typically 5 mg and the heating rate was 10°C min^{-1} over the range 30–300°C, under a stream of nitrogen flowing at 40 ml min^{-1}. Thermogravimetric (TG) measurements were carried out on a Perkin-Elmer TGA 7 balance using various heating rates over the range 30–300°C. Sample masses were typically 5 mg and the sample was also under a stream of nitrogen flowing at 40 ml min^{-1}.

X-ray powder patterns of the compounds and their products after controlled decomposition were recorded on a Philips PW 1050/80 diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å) with divergence and receiving slits of 1° each. Samples were scanned at 0.1° (2θ) min^{-1} over a range 10–30° in 2θ. Preliminary cell dimensions and space group data were obtained from Weissenberg and precession photographs (Cu Kα radiation).

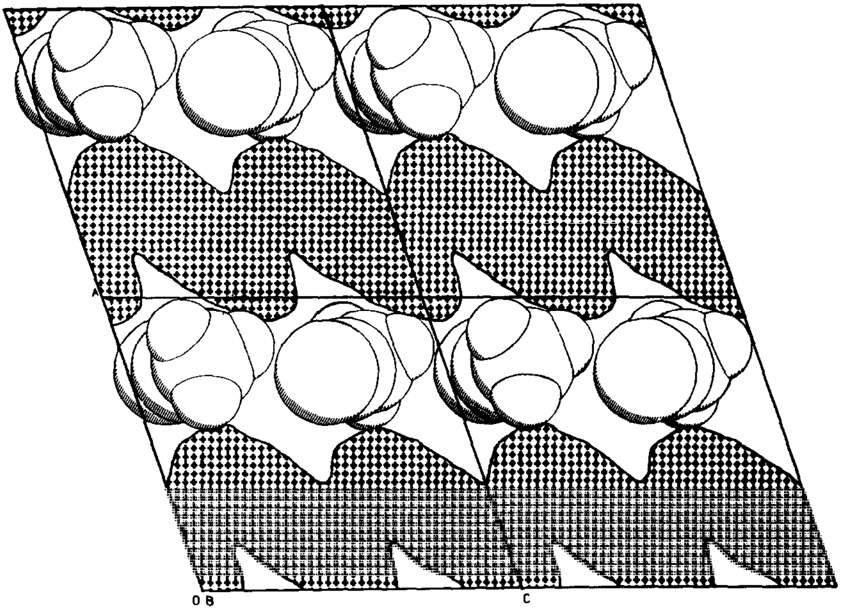

Fig. 1. OPEC drawing of the channels of (**1**) running parallel to [001].

Satisfactory intensity data were obtained with the crystals of all compounds mounted in Lindemann capillaries in the presence of a mother liquid.

STRUCTURE DETERMINATION

The crystal structures of both inclusion compounds were determined by direct methods and refined by standard least-squares techniques, using intensity data collected on an Enraf–Nonius CAD4 diffractometer. Results of the crystallographic analyses will be published in full elsewhere. As far as the thermal decompositions of (**1**) and (**2**) are concerned, attention is drawn to their most important structural feature, namely channel occupation by the guest molecules as shown in Figs. 1 and 2. These figures were obtained with program OPEC [11] which calculates the precise volume taken up by the host molecules, shown as shaded areas, while the guest molecules are displayed with van der Waals radii.

THERMAL ANALYSIS

The TG and DSC curves of compound (**1**) are shown in Fig. 3; both experiments were carried out with a heating rate of 10°C min^{-1}. The measured weight loss of 18.5% is in excellent agreement with that calculated for a compound with host : guest ratio of 1 : 2, which yields 18.4%. The DSC curve indicates that the guest is lost in a single endothermic step,

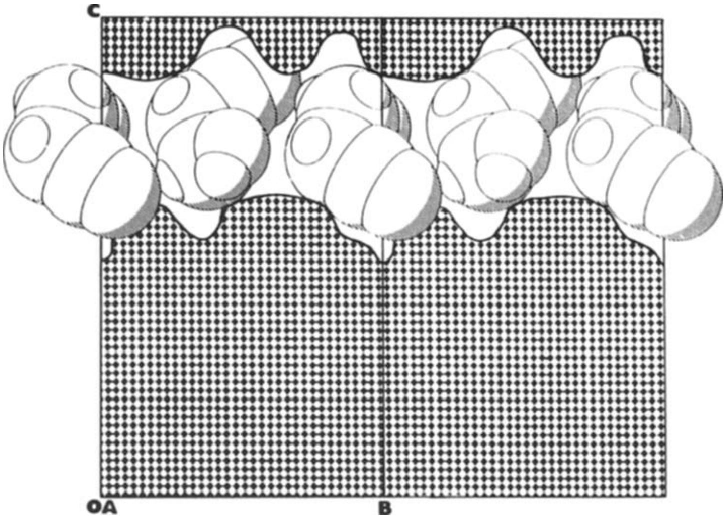

Fig. 2. OPEC drawing of the channels of (**2**) running parallel to [010].

labelled A in Fig. 3, with the enthalpy change for the guest-release reaction measured as 60.6 kJ mol^{-1}. Guest desorption commences at room temperature, 25°C, and is complete at 90°C; the host (**H**) melts at 262°C, labelled process B. The corresponding curves for compound (**2**) are shown in Fig. 4.

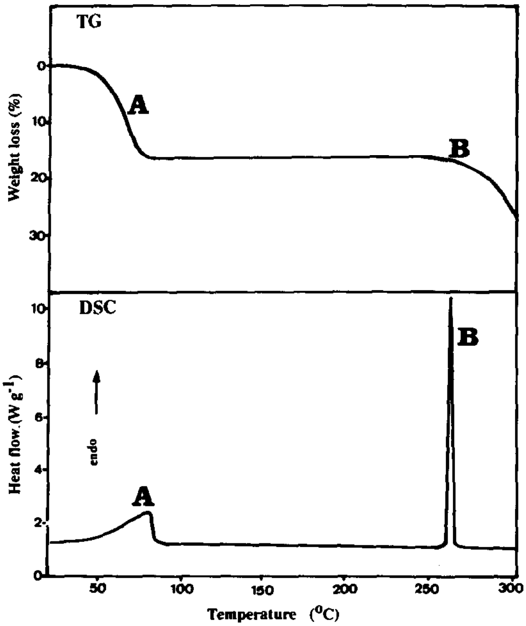

Fig. 3. TG and DSC curves for (**1**), heating rate 10°C min^{-1}.

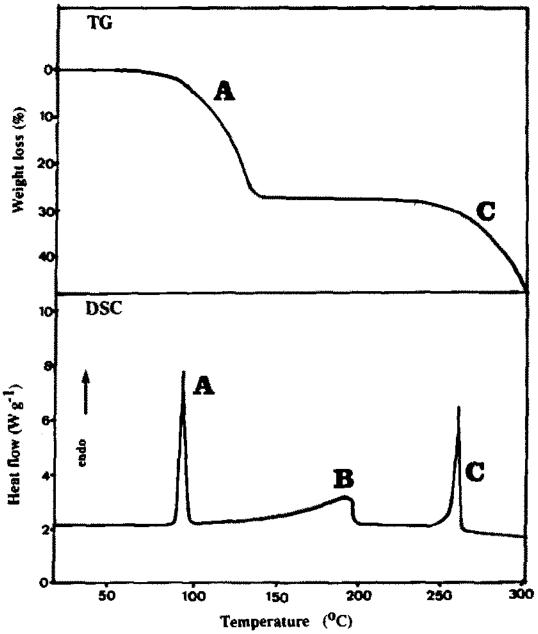

Fig. 4. TG and DSC curves for (2), heating rate 10°C min^{-1}.

The measured weight loss of 27.8% is again in good agreement with the 28.1% required for the host : guest stoichiometry of 1 : 2.

When a solid inclusion complex formed between a host and a volatile guest decomposes it may do so in several ways. The host–guest compound (β phase) may release all the guest molecules

$$\mathrm{HG}_n(\beta) \rightarrow \mathrm{H}(\alpha) + n\mathrm{G}\uparrow \qquad (1)$$

with the host compound reverting to its non-porous α phase.

Alternatively, the compound may release the guest but retain the features of the original structure, giving rise to an empty cage structure, labelled β_0. This is what occurs in the desorption of zeolites

$$\mathrm{HG}_n(\beta) \rightarrow \mathrm{H}(\beta_0) + n\mathrm{G}\uparrow \qquad (2)$$

Thirdly, the inclusion compound may release only part of the guest giving rise to a new γ phase

$$\mathrm{HG}_n(\beta) \rightarrow \mathrm{HG}_m(\gamma) + (n-m)\mathrm{G}\uparrow \qquad n > m \qquad (3)$$

The DSC curve for (2), however, reveals three endotherms. Peak A corresponds to the loss of guest, with an associated enthalpy change of 40.4 kJ mol^{-1}. This is followed by peak B, an endotherm with $\Delta H = 50.0$ kJ mol^{-1}. We ascribe this to a possible phase change in the host compound. We have observed similar behaviour in the decomposition of the inclusion compounds formed by 1,1,2,2-tetraphenylethane-1,2-diol with lutidine guests [12]. Peak C corresponds to the melting of the host compound.

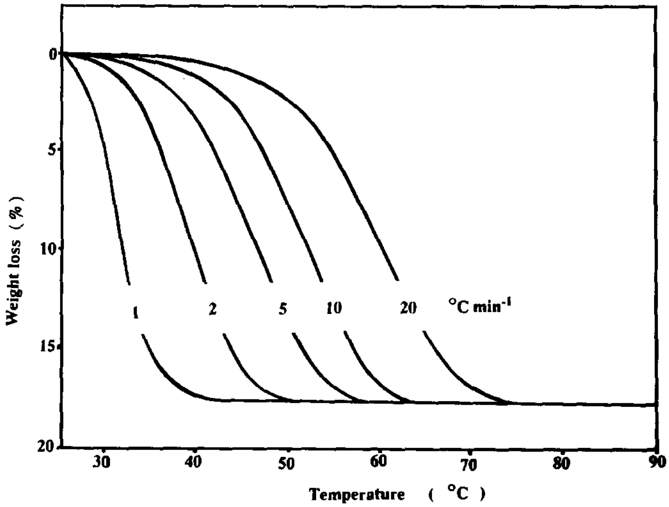

Fig. 5. TG curves of (1) at various heating rates.

We have carried out X-ray powder diffraction studies on compound (1) in the β phase and after guest loss, when the host reverts to the α phase. Similar experiments were carried out on compound (2), but powder photographs taken after partial desorption under mild conditions did not give evidence of either a β_0 or γ phase, but yielded the pattern of the α phase. We ascribe this to the fact that the inclusion compound is highly labile, and once the decomposition starts it is impossible to halt the guest loss, so that the reaction goes to completion.

Thermogravimetry at variable heating rates allowed us to estimate the activation energy of the guest-release reaction of compound (1). We used the method developed by Flynn and Wall [13], which has been applied to the decomposition of various systems, including inorganic complexes [14]. The decomposition curves recorded at various heating rates β, ranging from 1 to 20°C min^{-1} are shown in Fig. 5, and the corresponding semilogarithmic plots of log β vs. reciprocal temperature are shown in Fig. 6. The latter corresponds to several degrees of decomposition, varying between 2.5% and 15% of guest loss. The slopes of the lines correspond to a range of activation energies which vary from 83 to 115 kJ mol^{-1}. This result is not entirely unexpected in view of the fact that recent results show that the activation energy of desorption of hydrocarbons from zeolites was dependent on coverage, that is the degree to which the host lattice was covered by the guest molecules [15].

The corresponding analysis for compound (2), however, did not yield linear semilogarithmic plots, and no estimate of the activation energy for the thermal decomposition of this compound could be obtained. The reason for this could be that the guest loss is not a single-step process and

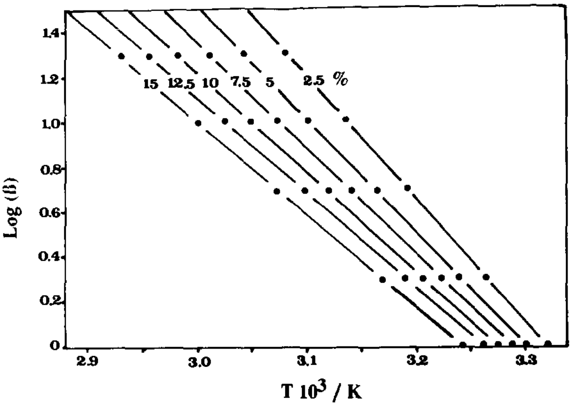

Fig. 6. Plot of log β vs. $1/T$ for several percentage decompositions.

is probably complicated by structural phase changes occurring during thermal decomposition.

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