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At room temperature trans-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid forms different clathrates with ethyl and butyl acetate in a 1:1 host-guest ratio. Increasing the formation temperature up to 40°C gives rise to pseudodimorphic clathrates with half the content of the guest component. All the clathrates studied feature intersecting channels of guest molecules within their structures.

Keywords: clathrates; crystal structures; host-guest compounds; pseudodimorphs

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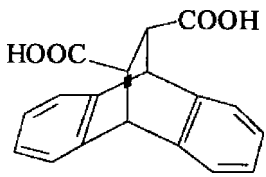
INTRODUCTION

Compounds showing versatile host properties are of great interest due to their practical applications for separation and purification [1], storage of unstable and very volatile products, as well as for controlled release of pheromones and pesticides [2] and the creation of new types of detectors [3,4]. For these applications, the topology of the space occupied by the guest component is crucial: for storage purposes guest molecules have to be located in totally enclosed voids, whereas for controlled release volatile molecules must be included in sites with a more open topology (*i.e.*, channels). In many cases, however, the clathrate obtained does not meet these requirements and it is necessary to prepare another, more suitable modification of the same host-guest complex. The study of this problem, as well as that of the possible existence of the same host-guest complex in different crystal modifications (called pseudopolymorphism due to possible change of the composition), has not been paid sufficient attention.

Our recent investigations have shown that host compounds frequently demonstrated pseudopolymorphic behavior if they were versatile hosts. Gossypol [5], 1,1′-binaphthyl-2,2′-dicarboxylic acid [6] and 2,2′-*bis*(9-hydroxy-9-fluorenyl)biphenyl [7] are examples of such compounds. Numerous cases of pseudo-dimorphic [8], -trimorphic [9] and even -tetramorphic [10] clathrates have been identified for such compounds. The specific feature of these hosts is their conformational mobility, arising from the free rotation of the two halves of the molecule relative to one another. This molecular feature may be responsible for the observed pseudopolymorphic behaviour of the compounds. There is therefore a clear motivation for investigating versatile host compounds whose molecules are not characterized by such mobility. If we neglect the possibility of slight mobility of the carboxylic acid groups relative to the molecular skeleton, the host compound *trans*-9,10-dihydro-9,10,ethanoanthracene-11,12-dicarboxylic acid (**1**, Scheme 1) can be considered as a rigid molecule. Our investigations show that clathrates of this host compound with ethyl and butyl acetate are pseudodimorphic: increasing the crystallization



SCHEME 1 Host molecule **1**.

temperature up to 40°C affords new modifications of clathrates (β-phases) from solutions of **1** in ethyl and butyl acetate. These findings attest that the conformational mobility of the molecular skeleton is not a factor governing the pseudopolymorphic behaviour of these respective inclusion complexes. Here we report on the structural features of the pseudopolymorphic clathrates of *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid with ethyl and butyl acetate.

EXPERIMENTAL

Preparation of Clathrates

Crystallization from solutions of **1** in ethyl or butyl acetate at room temperature yields clathrates with these solvents (conventional phases). To distinguish between these and possible new pseudopolymorphic modifications, the powder X-ray diffraction (XRD) patterns of the conventional clathrates were recorded and the cell parameters of their single crystals were measured to allow further comparisons. Crystallization from corresponding solutions was carried out in thermostatically controlled vessels by changing the temperature in 5°C steps from room temperature to 50°C. Powder XRD patterns were recorded for polycrystalline samples and unit cell parameters were determined in cases where it was possible to grow suitable single crystals. These characteristics of the products were compared with those of the conventional phases in order to determine whether new modifications had been prepared.

Single crystals of the conventional phase of the complex between **1** and ethyl acetate (**1a**, α-phase) were obtained by slow evaporation of the solvent from solutions in ethyl acetate at room temperature over 3 days, while the β-phase (**1b**) was obtained in thermostatically controlled vessels at 40°C over 12 hours. Crystals of the pseudopolymorphic inclusion complexes between **1** and butyl acetate were obtained at 20°C (**1c**, α-phase) and 40°C (**1d**, β-phase) over 2 days and 14 hours, respectively.

X-ray Diffraction Analyses

The single crystals selected for X-ray diffraction measurements were sealed in epoxy resin. Data collection for **1a** and **1b** was carried out on a Nonius Kappa CCD area detector diffractometer in the Centre de Diffractometrie Automatique Henri Longchambon (Mo K_α radiation, $\lambda = 0.71073$ Å, graphite monochromator) at room temperature. A total of 4093 reflections for **1a** and 3087 reflections for **1b** with $1.00^\circ < \text{theta} < 27.48^\circ$ (resolution between 20.40 and 0.77 Å) were used for unit cell refinement.

Unit cell parameters and data collection for **1c** and **1d** were performed on a Bruker SMART APEX CCD diffractometer equipped with an Oxford Cryosystems open-flow cryostat operating at 150 K and room temperature respectively. Data collection covered a hemisphere of reciprocal space by a combination of three sets of exposures with φ angles of 0, 90 or 180° and each exposure of 40 s covered 0.3° in ω. The crystal to detector distance was 6 cm and the detector swing angle was −30°. Coverage of the unique set was over 99% complete. Crystal decay was monitored by repeating the fifty initial frames at the end of data collection and analyzing the duplicate reflections, and was found to be negligible. The structure was solved by direct methods (SHELXS-97) [11] and refined by full-matrix least squares (SHELXL97) [12]. All hydrogen atoms were placed at the calculated positions. Molecular graphics utilized XP in SHELXTL-Plus [12]. Crystal data and structure determination details are given in Table 1.

DISCUSSION

Molecular Structure

The asymmetric unit for all clathrates studied and the numbering of atoms in the structures are presented in Figure 1. The conformation of host molecules is identical in all four pseudopolymorphs with the exception of the tilt of carboxylic groups relative to the ethano bridge. In **1a** and **1b**, the dihedral angles between the carboxyl group plane and the mean plane through C13, C14, C15 and C16 are similar (91.5 and 96.5°, respectively), whereas in the α- and β-phase complexes with butyl acetate the difference in dihedral angles is more marked (96.1 and 108.0°, respectively).

The guest molecules in β-phase clathrates are in the expected extended conformation with *trans*-orientation of all bonds of the alkyl chain, but in the α-phase complex the ethyl acetate and butyl acetate molecules adopt unusual and folded conformations under influence of the crystal packing forces. In clathrate **1a** the terminal methyl group C4A is displaced from the plane through the remainder of the ethyl acetate molecule, as indicated by the torsion angle of 117.5°, around O1A–C3A (the normal ideal value is 180°). Both unusual conformations are supported by weak intramolecular H-bonds C3A–H···O2A (2.510 Å, angle 105° in **1a**, and C5A–H···O1A (2.918 Å, angle 101°) in **1c** (Supplementary material). In both cases, by adopting such conformations the solvent molecules decrease their dimensions in order to match the voids of the clathrate.

TABLE 1 Crystal Data, Experimental Parameters and Selected Details of Data Collection and Structure Refinement

Compound	1a	1b	1c	1d
Crystal data				
Formula	$C_{18}H_{14}O_4 \cdot C_4H_8O_2$	$C_{18}H_{14}O_4 \cdot 0.5(C_4H_8O_2)$	$C_{18}H_{14}O_4 \cdot C_6H_{12}O_2$	$C_{18}H_{14}O_4 \cdot 0.5(C_6H_{12}O_2)$
Formula weight	382.40	337.38	410.45	352.37
$F(000)$	808	708	436	372
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	$P-1$	$P-1$	$P-1$
a/Å	13.007 (3)	8.977 (2)	8.3848 (13)	8.970 (2)
b/Å	11.934 (2)	13.057 (3)	9.4714 (15)	8.976 (2)
c/Å	14.233 (3)	16.171 (3)	13.991 (2)	11.635 (2)
α/deg	90	72.05 (3)	94.563 (2)	77.67 (3)
β/deg	112.62 (3)	78.35 (3)	100.848 (2)	77.51 (3)
γ/deg	90	82.20 (3)	100.133 (2)	85.88 (3)
V/Å^3	2039.4 (8)	1760.5 (7)	1066.9 (3)	891.2 (3)
Z	4	4	2	2
D_c/g cm^{-3}	1.245	1.273	1.278	1.313
Intensity measurement				
Radiation (λ/Å)	Mo K_α (0.71073)	Mo K_α (0.71073)	Mo K_α (0.71073)	Mo K_α (0.71073)
Temperature/K	293 (2)	293 (2)	150 (2)	293 (2)
Range of 2θ /deg	2.48–27.56	3.17–27.50	1.49–28.16	2.33–28.21
Range of hkl	−16, 16; −15, 14; −18, 18	−9, 11; −15, 16; −20, 19	−10, 10; −12, 11; −18, 18	−10, 11; −11, 10; −14, 15
Refls. collected	7551	12374	9374	5382
Unique refls.	4568	7942	4703	3810
R_{int}	0.025	0.037	0.049	0.048
Structure refinement				
Refls. with $I > 2\sigma(I)$	3013	4282	3431	3206
R_1, wR_2	0.0725, 0.2178	0.0645, 0.1980	0.0837, 0.2670	0.0676, 0.1746
Goodness of fit	1.038	1.028	1.115	1.116
Final $\Delta\rho_{max}/\Delta\rho_{min}$/eÅ^{-3}	0.41/−0.39	0.25/−0.24	0.49/−0.34	0.33/−0.30

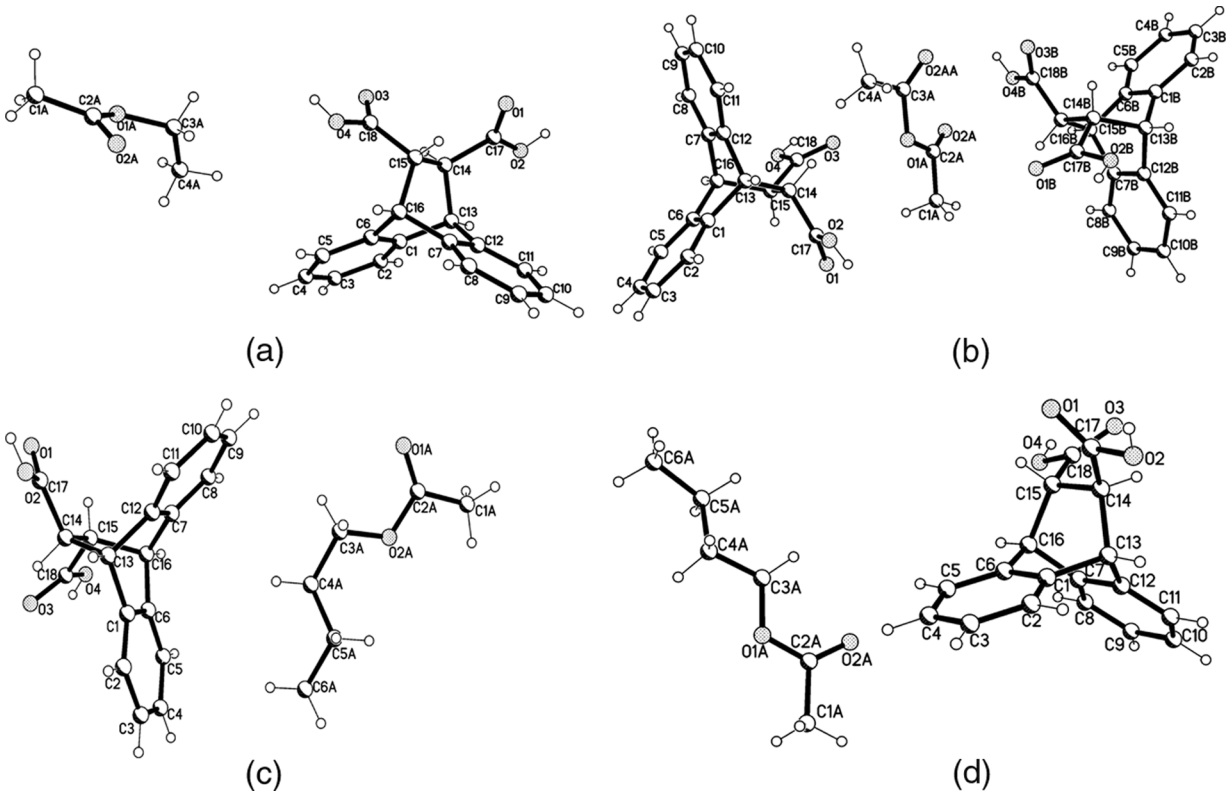
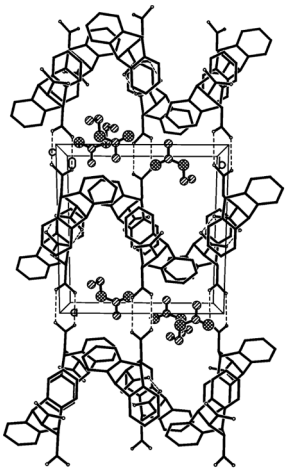


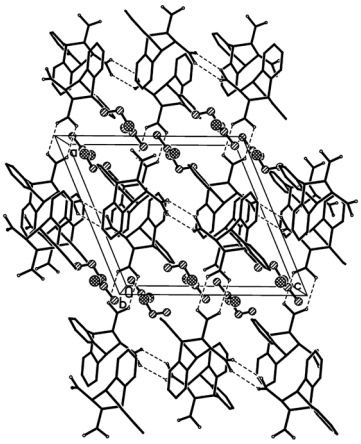
FIGURE 1 Perspective views of the asymmetric units of the studied clathrates with crystallographic numbering schemes: (a) **1a** (α-form of **1**-ethyl acetate); (b) **1b** β-form of **1**-ethyl acetate); (c) **1c** (α-form of **1**-butyl acetate); (d) **1d** (β-form of **1**-butyl acetate.

Crystal Structure

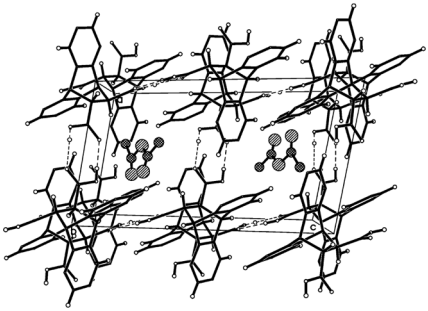
Structures of the studied clathrate modifications are shown in Figure 2 and Figure 3. The common feature of all structures is an absence of H-bonds between the host and guest components. Therefore, contrary to the expected coordinatoclathrates, for which host-guest H-bonds are characteristic, these pseudopolymorphic complexes should be considered as true clathrates showing no specific interactions between components. Self-recognition between dicarboxylic acid molecules occurs here and the host molecules are associated into zigzag type



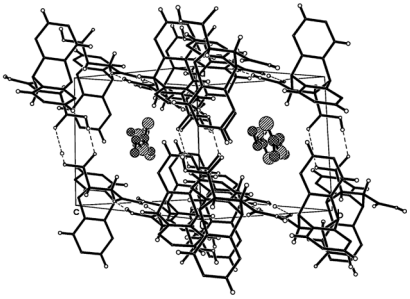
(a) Crystal structure of **1a**. View along c-axis.



(b) Crystal structure of **1a**. View along b-axis

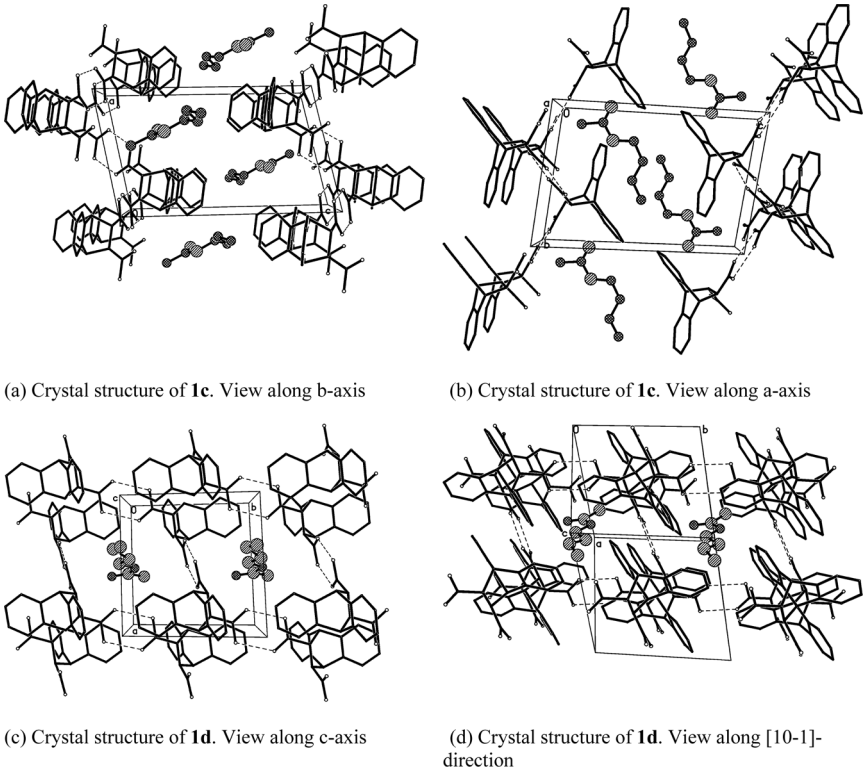


(c) Crystal structure of **1b**. View along b-axis



(d) Crystal structure of **1b**. View along [011]-direction

FIGURE 2 Packing structures of pseudopolymorphic clathrates of **1** with ethyl acetate.



(a) Crystal structure of **1c**. View along b-axis

(b) Crystal structure of **1c**. View along a-axis

(c) Crystal structure of **1d**. View along c-axis

(d) Crystal structure of **1d**. View along [10-1]-direction

FIGURE 3 Packing structures of pseudopolymorphic clathrates of **1** with buthyl acetate.

columns by a pair of centrosymmetric H-bonds between carboxylic groups. To be incorporated into infinite host columns is probably energetically preferable to forming host-guest associates.

Because of conformational rigidity of the host molecules, a small difference in the molecular structure of the individual pseudodimorphs can only be due to small rotations of the carboxylic acid groups with respect to the rest of the molecular skeleton. Different crystal structures of the pseudopolymorphic clathrates exist owing to various packing modes of the infinite zigzag type columns.

In **1a** infinite host columns running in the direction of the a-axis are formed by a pair of centrosymmetric H-bonds O2–H···O1 and O4–H···O3. Ethyl acetate molecules are located between these columns, in wide and narrow channels running in the z and y directions, respectively (Fig. 2a, b). The structure, however, may be considered from an alternative point of view. First, host molecules are linked through pairs of centrosymmetric H-bonds O2–H···O1 to give

TABLE 2 Hydrogen Bond Distances (Å) and Angles (deg.) for the investigated structures

Atoms involved	Symmetry	Donor-Acceptor	Donor-H	H···Acceptor	<Donor-H···Acceptor
1a					
O2– H···O1	1 – x, 1 – y, –z	2.647(3)	0.82	1.81	176
O4–H···O3	–x, 1 – y, –z	2.631(3)	0.82	1.83	175
1b					
O2B–H···O1B	1 – x, 1 –y, 1 –z	2.661(2)	0.82	1.84	179
O4B–H4BB···O1	1 + x, y, z + 1	2.631(3)	0.82	1.81	177
O4–H4A···O3	1 – x, – y, –z	2.698(3)	0.82	1.86	178
O2–H2A···O3B	–1 + x, y, z – 1	2.675(2)	0.82	1.88	180
1c					
O2–H2B···O1	–x, 2 –y, –z	2.662(3)	0.82	1.84	178
O4–H4B···O3	1 – x, 1 – y, –z	2.658(3)	0.82	1.84	177
1d					
O2–H2O···O1	1 – x, 1 – y, 1 –z	2.657(3)	0.82	1.84	177
O4–H4O···O3	–x, –y, 1 –z	2.646(2)	0.82	1.83	178

dimeric units. Dimers are then associated by relatively weak C–H···π and π···π H-bonds into layers parallel to the *bc* plane. Finally, these planes are bridged by centrosymmetric H-bonds O4–H···O3 to give three-dimensional networks. Guest molecules occupy the wide channels that run between the layers.

Infinite columns of the clathrate **1c**, formed also by centrosymmetric H-bonds O2–H···O1 and O4–H···O3, extend in the [1–10] direction. Van der Waals forces link columns into layers parallel to (110) plane. Butyl acetate molecules are located in the channels between these layers which run parallel to the *a*-axis. The existence of weak interactions between phenyl groups of the adjacent layers characterises this complex as a tubulate (channel) type structure, rather than an intercalate (layer). It is worth noting that there is another system of channels running in the direction of the *y*-axis (Fig. 3a, b).

The structures of the high temperature clathrate modifications are very similar. Both of them are characterized by a host-guest ratio of 2:1, in contrast to the 1:1 ratio seen for the low temperature modifications. In the β-phase, the clathrates with ethyl acetate and butyl acetate have infinite columns formed in the same way that run parallel to the directions [2–11] and [110], respectively. Again there are two types of channel in clathrates **1b** and **1d**, running in the directions [010] and [011] (Fig. 2c, d) as well as [001] and [10–1] (Fig. 3c, d), respectively. In **1b** the guest molecules are statistically disordered over two positions while in the **1d** butyl acetate molecules lie across an inversion centre.

In summary, increasing the crystallization temperature of the clathrates with ethyl and butyl acetate does not lead to formation of a new type of host association: in all structures infinite host columns are observed. However, different clathrate structures arise from the adoption of differing packing modes for the columns. The specific feature of these clathrates is the presence of two sets of intersecting channels having different dimensions. Moreover, it is demonstrated that conformational rigidity of the host molecule is consistent with pseudo-polymorphic behaviour of clathrate formation.

Supplementary Material

Relating to this article are deposited with the British Library as supplementary publication No 217711–217714.

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