

Selective Clathrate Formation with the New Host Systems *cis*- and *trans*-9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Acid:† Inclusion Properties and X-Ray Structure of an Encapsulated Acetic Acid Dimer

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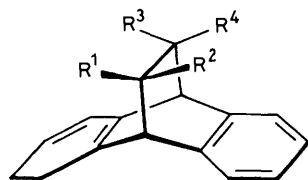
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2+4 Cycloaddition of fumaric or maleic acid to anthracene produces the novel host molecules (1) and (2) respectively, which readily form inclusion compounds with a variety of solvents, among which acetic acid, as demonstrated by its crystal structure, gives true clathrate formation with encapsulated dimeric guest units.

A novel class of host compounds termed as coordinatoclathrands¹ have been shown to be a basis for a rational clathrate design.^{2,3} Their space filling properties and the presence of functional groups, coupled with special molecular symmetry, offers some advantageous possibilities. The title compounds (1) and (2), distinguished by a roof-shaped molecular backbone, are a new type of host molecule and demonstrate these principles. Compounds (1) and (2) were obtained from 2+4 cycloaddition of fumaric or maleic acid respectively to anthracene.⁴

Recrystallization leads to the formation of inclusion compounds with a variety of solvents (Table 1), ranging from OH- and CH- acidic to less polar or even non-polar guest substrates (tetrahydrofuran, dioxane). The stoichiometries



- (1) R¹, R⁴ = CO₂H; R², R³ = H
 (2) R¹, R³ = CO₂H; R², R⁴ = H

(host : guest) found for the different aggregates largely correspond with the expected ratios; thermal stabilities in most cases are relatively high (*cf.* ref. 2, 3). A remarkable finding is that low-volume substrate species, *e.g.* methanol, ethanol, or acetonitrile (*cf.* benzonitrile) do not act as suitable guest components for the host lattices formed by (1) and (2) (*cf.* ref. 3). Results from solvent competition experiments with (1) (recrystallization from 1:1 solvent mixtures) are as follows.

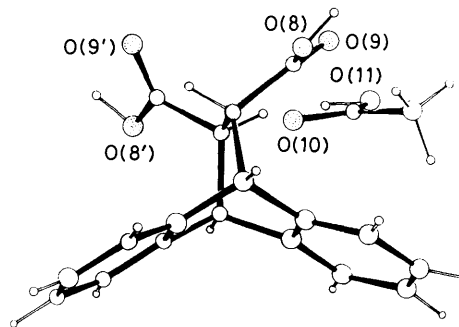


Figure 1. Perspective view of the title clathrate. Characteristic mean bond lengths of the structure (where averaged over more than three values, r.m.s.d.'s are indicated in parentheses; e.s.d.'s for individual bond lengths range from 0.002 to 0.003 Å): C(sp³)-C(sp³) 1.559(8), C(sp³)-C(sp²) 1.506(2), C(sp²)-C(sp²) 1.384(9), C=O 1.226, C-O 1.297 Å.

† Here *cis* and *trans* refer to the relative positions of the carboxy groups in (1) and (2).

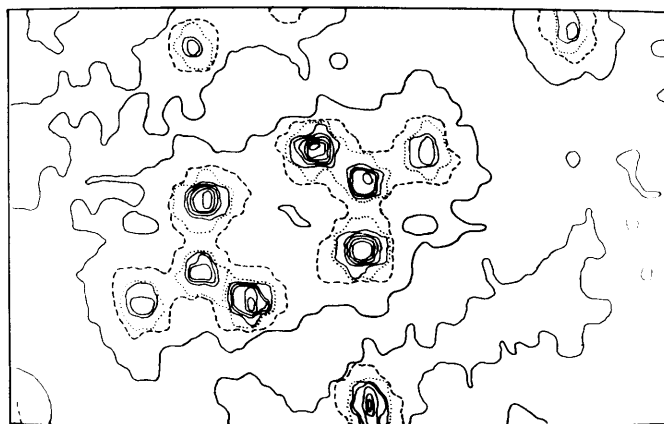


Figure 2. Cross-section of electron density near the plane of the acetic acid dimer. First contour line is at $0.4 \text{ e}\text{\AA}^{-3}$ level while the subsequent ones are arbitrarily chosen values (1, 2, 3, and $4 \text{ e}\text{\AA}^{-3}$).

Table 1. Inclusion compounds of the new clathrate hosts.

Guest solvent	Inclusion compound			
	with (1)		with (2)	
	Ratio	Decomp./°C	Ratio	Decomp./°C
Pr ⁿ OH	1:1 ^a	^b		
Bu ⁿ OH	1:1	110—115		
Bu ^t OH	1:1			
n-C ₈ H ₁₇ OH	2:1	110—115		
HO[CH ₂] ₂ OH	1:2	130—135		
MeO[CH ₂] ₂ OH		^c		
MeCO ₂ H	1:1	120—125		
MeCOSH		^c		
HSCH ₂ CO ₂ H	1:1	120—130		
MeCH(OH)CO ₂ H		^c		
DMF	1:1	175—185		
MeCN		^c		
PhCH ₂ CN	1:1	195—200	1:2	185—200
Dimethyl sulphoxide	1:1	145—155	1:2	80—90
Pyridine			1:1	100—104
Tetrahydrofuran	1:2	110—120		^c
Dioxane	2:1	140—145	2:1	165—170
MeO[CH ₂] ₂ OMe		^c		

^a Host: guest stoichiometry; determined by n.m.r. integration of the isolated crystals after a drying period of 4 h (room temperature) at 15 Torr (including a control test). ^b Range of thermal decomposition; value in front indicates the onset of opacity or the release of the gaseous guest component. If not specified, difficulties in detecting the decomposition point exist. ^c Does not analyse stoichiometrically after the specified drying period.

Higher alcohols (normal and branched) are clearly favoured over the lower analogues as inclusion candidates. Dimethylformamide, DMF, is preferred to BuⁿOH, but acetic acid is preferred over DMF; ethylene glycol is preferred over acetic acid.

Table 1 shows that the inclusion properties of the host (2) compared with (1) are restricted, especially in the uptake of hydroxylic guests. This, along with some discrepancies in the host: guest stoichiometries *e.g.* the inclusion of (1) and (2), respectively, with benzonitrile and dimethyl sulphoxide (1:1 vs. 1:2, *cf.* Table 1), suggests a different lattice build-up for each system and for the examples studied previously (*cf.* ref. 2, 3).

In view of this general interest we investigated the structure of the (1)·MeCO₂H host-guest aggregate by *X*-ray diffraction. This clathrate was prepared by dissolving (1) in hot acetic acid.

A single crystal of dimensions $0.3 \times 0.7 \times 0.7 \text{ mm}$ was sealed in a glass capillary and used for *X*-ray analysis.

Crystal data: (1)·MeCO₂H, C₁₈H₁₄O₄·C₂H₄O₂, *M* = 354.36, monoclinic, space group *P*2₁/*n*, *a* = 9.717(2), *b* = 14.462(2), *c* = 13.038(3) Å, β = 104.27(1)°, *Z* = 4, *D*_x = 1.325 Mg m⁻³; 5168 unique reflections were measured with monochromatized Mo-*K*_α radiation. The structural model (Figure 1) was refined to a final *R* value of 0.046 against 3042 absorption and extinction corrected observed reflections using the least-squares technique. Relevant hydrogen atomic positions were deduced from difference Fourier maps while the others were geometrically positioned.‡

The molecular structure of (1)·MeCO₂H is shown in Figure 1. Surprisingly there are no interactions between host and guest molecules other than those derived from steric barriers. In this respect the structure corresponds to a clathrate lattice build-up in the conventional sense.⁵ The -CO₂H groups of the racemic host establish a dimer between symmetry centre-related molecules of (1) which, in turn, are arranged as infinite chains *via* hydrogen bonding {O(8)–H(O8) 0.99, H(O8) ··· O(9)_[–x, –y, 2–z] 1.67, O(8')–H(O8') 1.02, H(O8') ··· O(9')_[1–x, –y, 1–z] 1.67 Å, O(8)–H(O8) ··· O(9) 171.0, O(8')–H(O8') ··· O(9') 168.8°}. The guest molecules appear in a hydrogen-bonded dimeric form in the crystal interspace across centres of symmetry at 0, 0, $\frac{1}{2}$ and $\frac{1}{2}$, 0 {O(11)–H(O11) 0.95, H(O11) ··· O(10)_[–x, –y, 1–z] 1.72 Å, O(11)–H(O11) ··· O(10) 178.3°}. These entities are then enclosed in the intercoil cavities formed by the chains of (1).

As Figure 2 shows, the fit between a dimer of guests and the encircling host matrix is a tight one. The so-formed rectangular cavity has a maximum cross-section of $5.1 \times 11.6 \text{ \AA}$. This arrangement suggests why a 'true' clathrate^{1,5} occurs in this case. The guest component as a dimeric entity is the preferred grouping to satisfy the steric and electronic requirements of the host intercoil cleft. Such an occurrence of the acetic acid dimer in the solid state is rare.⁶ To our knowledge there is only one other reported structure⁷ which possesses a similar subunit, however, in contrast with the present situation, it is not planar.

The packing in the crystal seems mainly influenced by the internal twofold symmetry of the host molecule⁸ which serves

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

in propagating the building elements of the lattice. As a precondition for dicarboxylic acids having such symmetry, the molecular symmetry operator is almost perpendicular to the crystallographic glide plane n (cf. ref. 2, 3). The host molecule (2) does not have a respective twofold symmetry operator, and that is possibly why its inclusion properties are less pronounced.

In summary, the V-shaped constitution of the host molecule, the H-bond donor/acceptor functionality, and the special twofold molecular symmetry have been demonstrated as effective principles for the design of new clathrates.

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