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Determination of the structure of 2(benzene-1,3,5-tricarboxylic acid)·1.5(pyrene)·2(methanol) and comparison with that of 2(benzene-1,3,5-tricarboxylic acid)·pyrene·2(ethanol)

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The structure of the title methanol complex ($P\bar{1}$, $Z = 2$) has been determined and compared with that of the title ethanol complex ($C2/c$, $Z = 8$) using published data. Both complexes have layer structures, the (essentially planar) layers being constructed from rings of six TMA molecules, hydrogen bonded through four 'carboxyl dimers' and two 'interrupted dimers', where methanol (ethanol) is included in the $R_4^4(12)$ (graph set) ring. The packing of the layers differs in the two complexes, leading to different three-dimensional structures. In the methanol complex, one pyrene molecule is located within the layer and the other, at a centre of symmetry, between the layers in one type of interlayer space, while the methyls of methanol protrude into the other type of interlayer space. In the ethanol complex, the superpositioning of the layers is such that two types of stack are formed; one of these is mixed, containing pyrene and one of the independent TMA molecules in alternating sequence, while the other stack contains only the second type of TMA. Spectroscopic study is needed to establish whether the partial mixed stack arrangement in the crystalline ethanol complex implies donor–acceptor interaction.

1. Introduction

Trimesic acid (TMA; benzene-1,3,5-tricarboxylic acid; not ionized) forms many interesting binary and ternary inclusion complexes with neutral guest molecules (Herbstein, 1996; Sharma & Zaworotko, 1996; those with charged species will not be discussed here). The most precise structure determination among this group appears to be that of 2(TMA)·pyrene·2(ethanol) at 198 K (Kolotuchin *et al.*, 1995; refcode SURYUZ; Kolotuchin *et al.*, 1999; SURYUZ10; refcodes and data are retrieved from the Cambridge Structural Database, CSD; Allen *et al.*, 1991; Allen & Kennard, 1993). The rather intricate SURYUZ structure suggests that the ethanol component might be replaced by analogous solvent molecules without a drastic change in the overall arrangement. A first step towards checking this prediction has been taken by preparing the methanol analogue and determining its crystal structure. This work illustrates a point made by Görbitz & Hersleth (2000): 'finding the right solvent molecules may be of critical importance for obtaining crystals, and even apparently minor changes, such as repositioning a methyl group.....may be sufficient'. Here a methyl group is removed on going from one structure to the other. Describing what happens requires detailed comparison of the two structures; understanding may come later.

2. Experimental

Slow cooling of saturated solutions of equimolar proportions of TMA and pyrene in methanol, propan-1-ol and propan-2-ol gave well faceted crystals of the methanol complex of excellent diffraction quality, while poor crystals were obtained from propan-1-ol and no results from propan-2-ol. Only the methanol complex was studied further; the triclinic crystals had the composition 2TMA·1.5(pyrene)·2(methanol) (abbreviated as TMPYME; this is not a refcode). Structure solution and refinement were by standard methods (Table 1); full details of the TMPYME structure have been deposited;[1] information about SURYUZ is available from the CSD.

3. Molecular and crystal structures of the two complexes

3.1. Introduction

As the structure of TMPYME is more precise and simpler than that of SURYUZ, we treat it first in our parallel description of both structures. After a brief description of the overall arrangement of the three components, we give an overview of molecular dimensions and hydrogen bonding and then return to a more detailed discussion of the packing.

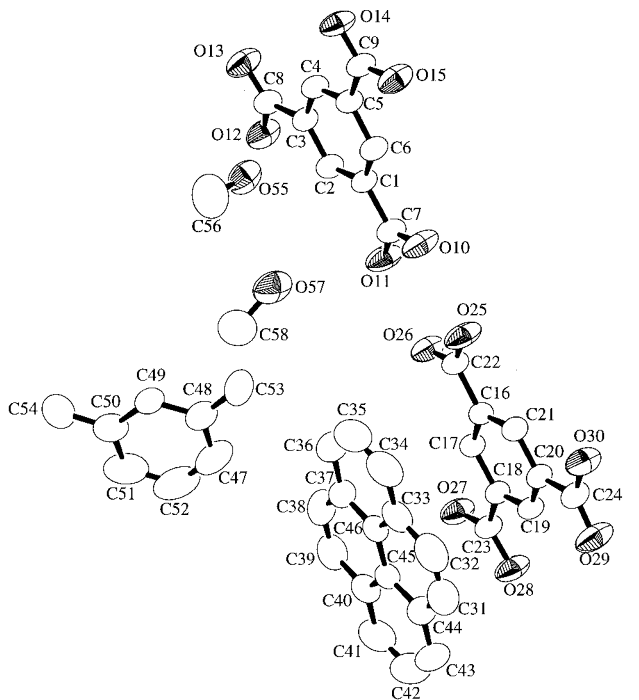

Figure 1
TMPYME. *ORTEP*II (Johnson, 1976) diagram of the asymmetric unit, showing 50% probability ellipsoids. Atomic numbering: pyrene *A* at general position: C31—C46; pyrene *B* about a centre of symmetry C47—C54; TMA-*A* O10—O15, C1—C8; TMA-*B* O2—O30, C16—C24; MeOH-*A* O55—C56; MeOH-*B* O57—C58.

3.2. Overall description of the crystal structures

TMPYME: there are two crystallographically independent TMA (*A* and *B*) and methanol (*A* and *B*) molecules in the asymmetric unit, with one pyrene (*A*) at a general position and a second (*B*) located about a centre of symmetry [Wyckoff position ‘g’ (0,1/2, 1/2); Fig. 1]. TMA, methanol and pyrene-*A* molecules are arranged in planes approximately parallel to (−1, 1, −1) (Fig. 2). The independent TMA molecules are linked by hydrogen bonds between carboxyl groups in the 1- and 3-positions [‘carboxylic acid dimers’; $R_2^2(8)$ graph set; Grell *et al.*, 1999]; the carboxyl dimers are essentially disordered, the longest C—O distance (of the eight independent values) being 1.274 (3) Å and the shortest 1.244 (3) Å. The remaining (5-) carboxyl of TMA-*A* is linked through the hydroxyls of the two crystallographically independent methanols to the 5-carboxyl of TMA-*B* [$R_4^4(12)$ graph set; Fig. 3]. The second type of linkage (Fig. 4) has been termed an interrupted, expanded or bridged dimer by different authors. Thus, all hydrogen bonding capabilities are utilized. The two independent TMAs are linked; there is no linkage between similar TMAs. Pyrene and the methyl groups of the methanols fill the remaining space in a manner to be described later. Interrupted dimer hydrogen bonding similar to that found here has been reported in SURYUZ and in the 1:2 molecular complexes of 1,1′-binaphthyl-2,2′-dicarboxylic acid with methanol, ethanol and 2-propanol by Weber *et al.* (1984), who quote earlier work. In this group the methanol complex differed in structure from the ethanol and 2-propanol complexes, which were isomorphous.

The basic building block of the structure is the layer of hydrogen-bonded TMA and methanol molecules shown in Fig. 3. This layer contains pyrene-*A* molecules which are coplanar with the planar hydrogen-bonded rings of six TMA and four methanol molecules. However, the overall layers are not completely planar, as there is tilting at the methanols of the interrupted dimer ring (Fig. 4). The layers are stacked with interspersed pyrene (*B*) molecules between them on one side and protruding methyl groups of methanols on the other side.

SURYUZ:[2] the large unit cell [$a = 28.128$ (5), $b = 16.550$ (3), $c = 14.725$ (4) Å, $\beta = 95.13$ (2)°, $Z = 8$] means that even the projection down the shortest axis is difficult to decipher, but relief is obtained by noting that the TMA and pyrene molecules are arranged in planes parallel to (101) (see Fig. 2B of

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0091). Services for accessing these data are described at the back of the journal.

[2] The SURYUZ structure was described as follows: ‘...monoclinic with a large unit cell that contained 16 molecules of trimesic acid, eight of pyrene and 16 of ethanol. The structure consists of stacked layers of noninterpenetrated hydrogen-bonded networks that superficially resemble the chicken-wire motif found in trimesic acid. In actuality, the hydrogen-bonded network is expanded. Thus, ‘infinite’ ribbons are formed wherein each trimesic acid is linked to two other trimesic acids by standard carboxylic dimers. The layers are formed by linking the remaining carboxylic acids with two ethanol molecules in a 12-membered hydrogen-bonded ring...The holes created by these ‘expanded’ carboxylic acid dimers reside within one layer and are filled by one pyrene molecule and the ethyl groups of two ethanol molecules from an adjacent layer.’ ‘$Z = 40$’ was given in footnote [8](a) of SURYUZ, but this printing error was corrected to ‘8’ in SURYUZ10. Atom numbering for SURYUZ is: pyrene: C1—C16; TMA-*A* O1—O6, C15—C25; TMA-*B* O7—O12, C26—C34; EtOH-*A* O13—C35—C36; EtOH-*B* O14—C37—C38.

SURYUZ10). The basic building block of the structure is the same layer of hydrogen-bonded TMA and (here) ethanol molecules as is found in TMPYME (see Fig. 1 of SURYUZ or Fig. 2A of SURYUZ10), with pyrene molecules and the protruding ethyl groups of ethanol interspersed between the layers, as described below. The layers are not completely planar because of tilting at the hydroxyls of the ethanols, with both ethyl groups protruding in the same direction (Fig. 5).

3.3. Structure of the TMA molecules

In TMPYME the carbon skeletons of the TMA molecules are planar to within 0.005 Å, and the mean C—C bond length in the benzene rings is 1.389 [4] Å, where the sample ($n - 1$) standard uncertainty is given in square brackets. The least squares s.u. is 0.003 Å. The extra-ring C—C bonds to carboxyls have a mean length of 1.485 [4] Å. The corresponding values for SURYUZ are 1.392 [5] and 1.481 (13) Å.

3.4. Structure of pyrene

The C—C bond lengths in both structures are qualitatively similar to those found in pyrene-pyromellitic anhydride at 19 K (Herbstein *et al.*, 1994), but the peripheral bonds are systematically shorter, suggesting greater thermal motion in the present complexes, also illustrated in Fig. 1. Detailed discussion is not warranted.

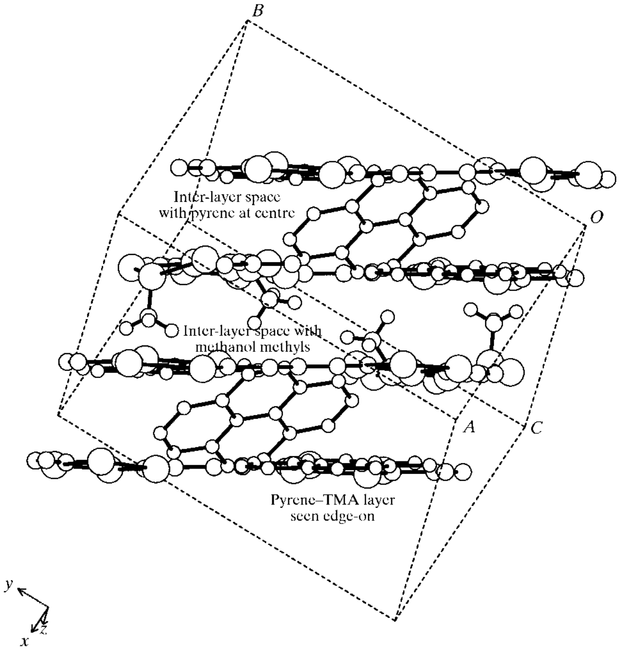

Figure 2
TMPYME. Edge-on view of the layer structure. The arrangement of component molecules within a single layer is shown in Fig. 3. The two different types of space separating the layers are indicated (type *A*: interlayer pyrene *B* molecules; type *B*: methyl groups of methanols). The larger circles represent O atoms and the smaller circles C atoms; the H atoms (shown only for the methanol methyls) are the smallest circles. The layer plane is approximately parallel to (−1, 1, −1).

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{44}H_{35}O_{14}$
Chemical formula weight	787.72
Cell setting, space group	Triclinic, $P\overline{1}$
a, b, c (Å)	9.5330 (5), 13.5400 (7), 14.6440 (9)
α, β, γ (°)	93.880 (2), 95.020 (2), 90.140 (3)
V (Å^3)	1878.57 (18)
Z	2
D_x (Mg m^{-3})	1.393
Radiation type	Mo $K\alpha$
No. of reflections for cell parameters	7840
θ range (°)	2.0–25.04
μ (mm^{-1})	0.105
Temperature (K)	293 (2)
Data collection	
No. of measured, independent and observed parameters	6639, 6639, 3827
Criterion for observed reflections	$I > 2\sigma(I)$
$R_{\rm int}$	0.0000
$\theta_{\rm max}$ (°)	25.04
Range of h, k, l	$0 \rightarrow h \rightarrow 11$ $-16 \rightarrow k \rightarrow 16$ $-17 \rightarrow l \rightarrow 17$
Refinement	
Refinement on	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0577, 0.1409, 1.021
No. of reflections and parameters used in refinement	6639, 655
H-atom treatment	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0580P)^2 + 0.2978P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$	0.005
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.238, −0.166
Extinction method	*SHELXL*97 (Sheldrick, 1997)
Extinction coefficient	0.018 (3)

Computer programs used: *KappaCCD* (Nonius, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXL*97 (Sheldrick, 1997), *TEXSAN* (Molecular Structure Corporation, 1993), *CrystalMaker* (Palmer, 1999).

3.5. Structures of methanol and ethanol

The experimental values are compatible with results from the literature, but systematic errors due to thermal motion make detailed discussion unprofitable.

3.6. Details of hydrogen bonding

All H atoms were found experimentally in TMPYME and refined (with isotropic displacement factors). As is usual, the d(C—H) and d(O—H) values were systematically shorter than those found (in other structures) by neutron diffraction. For SURYUZ 'carboxyl and hydroxyl H atoms were located and refined but appeared disordered; idealized positions were used for contributions of remaining H atoms'.[3] The locations of all hydroxyl H atoms in both structures can be inferred unequivocally from C—O bond lengths. The carboxyl dimers are indeed disordered, as shown by the near-equality of the

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[3] The s.u.'s of the hydrogen coordinates given by the CSD are (mostly) no larger than those of the non-H atoms. Some error appears to have occurred. Hydrogens in TMPYME are not considered explicitly, apart from inferring their locations from C—O bond lengths.

C—O bond lengths and of the O···O distances. However, the interrupted dimers are ordered, the pattern of interatomic distances being the same in both crystals, although the detailed values differ somewhat (Fig. 4).

3.7. Packing in TMPYME

The edge-on view of the layers (Fig. 2) shows that there are two different types of interlayer space, which alternate along the normal to the layer plane. The centrosymmetric pyrene (*B*) is ensconced in one type of space, and methyl groups of methanols in the second type of interlayer space. Pyrene *A* is essentially coplanar with the TMA-methanol net, with a 3.4° angle between the normals to the pyrene *A* plane and the plane through the six inner C atoms of the TMA molecules of the hydrogen-bonded ring; the angle between pyrene *B* and the inner-carbon plane is 59.6°. The two pyrenes have different crystallographic roles, while TMA-*A* and -*B* fill much the same crystallographic function, as do the two methanols. TMPYME can be described as an inclusion complex, albeit of an unusual kind. One type of pyrene (*A*) is included within the layers, while the second kind (*B*) is between the layers.

3.8. Packing in SURYUZ

The layer of molecules parallel to (101) is shown in Fig. 1 of SURYUZ and Fig. 2A of SURYUZ10. Seen edge-on (Fig. 2B of SURYUZ10), it is clear that there are two types of space between the layers. One type of space is free of intervening groups; the other type of space contains the ethyl groups protruding up and down from adjacent layers. Adjacent (101) layers are similar, but with different mutual positioning of the hydrogen-bonded nets and the pyrene molecules. It is the combination of mutually offset adjacent layers which provides the key to the complete description of the packing. When adjacent layers are superimposed, one sees that pyrene molecules lie above and below TMA-*A* in mixed stacks, while TMA-*B* packs in segregated stacks. This was not mentioned in the earlier (SURYUZ) description of the structure, but included in SURYUZ10. The two types of stack are shown edge-on in Fig. 5. Thus, in SURYUZ the two independent TMAs, although having the same crystallographic role in the construction of the layers, have different functions when the overall packing is considered. Mixed stacks are found in π–π^* donor–acceptor molecular compounds (Herbstein, 1971) and are usually taken to indicate a charge-transfer interaction between the adjacent components in a stack, accompanied by a striking colour change. The colour of the SURYUZ crystals has not been reported, while those of TMPYME are fawn coloured. A spectroscopic study of solutions and crystals is needed to determine whether the formation of mixed stacks in SURYUZ is a packing phenomenon or indicative of a charge-transfer interaction.

4. Discussion

Trimesic acid and ROH form ternary host–guest complexes where the *R*OH component (R = H, CH_3, C_2H_5 *etc.*) has an

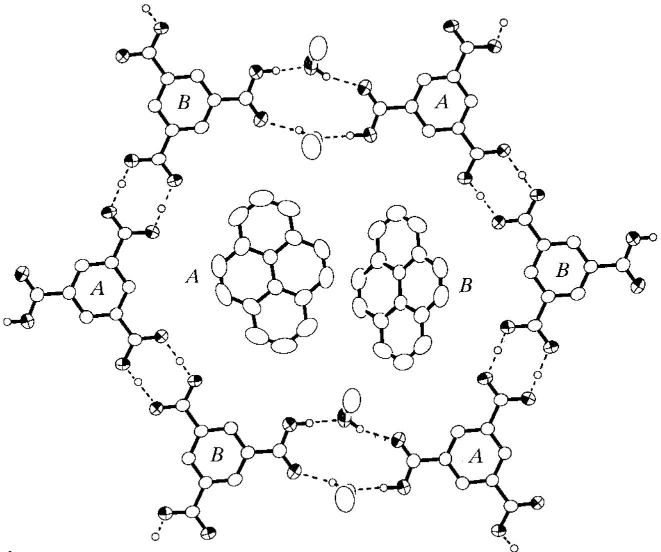

Figure 3
TMPYME. *ORTEP*II (Johnson, 1976) diagram of a single layer showing the hydrogen-bonding scheme; 50% probability ellipsoids are shown. Pyrene *A* is at general positions and is (essentially) coplanar with the TMA and the hydroxyls of the methanol molecules; pyrene *B*, which extends out of the plane of the page between the layers, is located about centres of symmetry. The crystallographically independent TMA molecules are designated *A* and *B*. Adjacent layers are mutually offset, the degree depending on whether they are separated by pyrene *B* or methanol methyls.

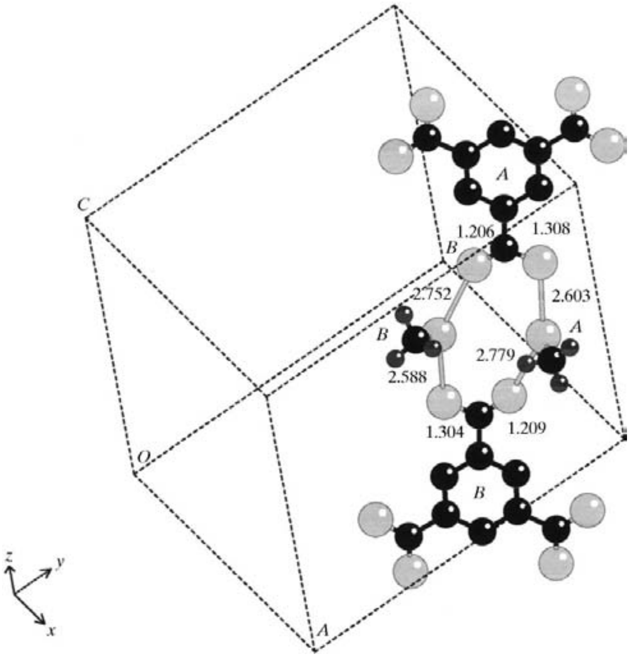

Figure 4
The similar patterns of interrupted hydrogen bonds in TMPYME (shown) and SURYUZ, which, however, differ in detail. The C atoms are the darkened spheres and the O atoms the lighter spheres; only the methyl H atoms are shown. The interatomic distances (Å) shown are for TMPYME, the s.u.'s being 0.003 Å. The corresponding values for SURYUZ are (reading clockwise from TMA-*A*): 1.306, 2.505, 2.689, 1.210, 1.312, 2.582, 2.757, 1.211 Å, with s.u.'s 0.004 Å.

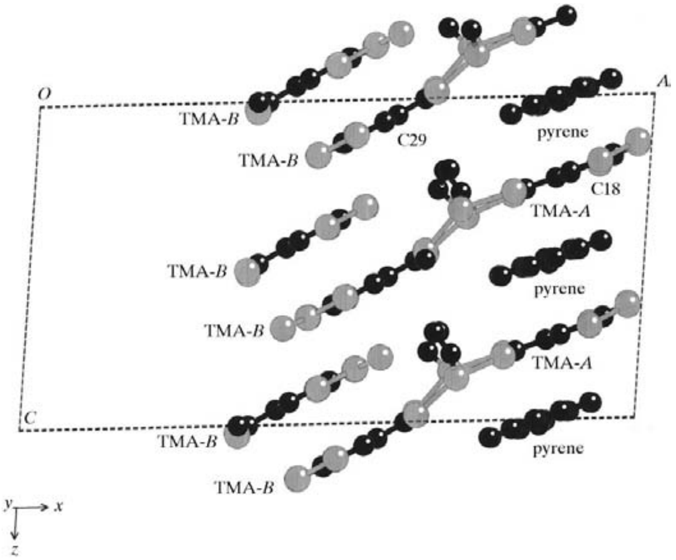

Figure 5
SURYUZ. Edge-on view of mixed TMA-*A*/pyrene stacks on the right and TMA-*B*/TMA-*B* stacks on the left. The stacks are linked *via* the interrupted dimer, the layer thus formed not being completely planar. The ethyl groups protrude from the layer in the same direction. H atoms have been omitted. A similar, but smaller, tilting at the methanol hydroxyls is found in TMPYME. Here too the methyl groups protrude from the layer in the same direction.

essential structural role. Small (substituted) aromatics (picric acid, durene) can be incorporated as guests in TMA·H_2O complexes, but, so far, pyrene is the only guest reported when R = CH_3 and C_2H_5, while complexes have not yet been reported for other *R*OH components. The TMA·H_2O complexes are best described as channel inclusion complexes (Herbstein & Marsh, 1977; Herbstein, 1987) and are different structurally from the similar TMA·CH_3OH and TMA·C_2H_5OH complexes of pyrene discussed here, which are best described as layer inclusion complexes. Comprehensive experiments varying both R and 'guest' are needed, hopefully supplemented by determination of ternary phase diagrams.

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