

The Crystal Structures of Trimesic Acid, its Hydrates and Complexes.

IV. Trimesic Acid–Dimethyl Sulphoxide

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$C_9H_6O_6 \cdot C_2H_6SO$ is monoclinic, with $a = 8.743$ (4), $b = 6.803$ (4), $c = 10.677$ (5) Å, $\beta = 96.24$ (4)°, $Z = 2$, space group $P2_1$ or $P2_1/m$. The structure was refined to $R = 8.4\%$ (in space group $P2_1$) for 1751 counter reflections. There are hydrogen bonds both between pairs of TMA molecules (but carboxylic acid dimers are not formed) and between TMA and DMSO molecules. O atoms of the DMSO molecules are part of the walls of channels formed by the TMA molecules, while the methyl groups of the DMSO molecules lie within the channels; the lone pair of the DMSO S atom is stereochemically active in the sense that it appears to influence the intermolecular arrangement.

Introduction

Trimesic acid (TMA) molecules can form hydrogen bonds mutually, as in α -TMA (Duchamp & Marsh, 1969), or both mutually and with other molecules, as in $TMA \cdot H_2O \cdot \frac{2}{3}PA$ (PA = picric acid), $TMA \cdot \frac{5}{6}6H_2O$ (Herbstein & Marsh, 1977) and $TMA \cdot H_2O \cdot dioxane$ (Herbstein & Kapon, 1978). Among the many molecular complexes formed by TMA is $TMA \cdot DMSO$ (DMSO = dimethyl sulphoxide). Although TMA and water act as both acceptors and donors of hydrogen bonds, dioxane and DMSO can serve only as acceptors. Furthermore, the methyl groups form a voluminous hydrophobic region in the DMSO molecule. It is not easy to predict which of these features will determine the component arrangement in the $TMA \cdot DMSO$ complex and we have therefore determined its crystal structure.

Experimental

Light-yellow prisms were obtained by slow cooling of a saturated solution of TMA in water to which 8 mol% DMSO had been added. Crystal data are given in Table 1. Intensities of 1751 reflections (90 with $I_o = 0$) ($h0l$ – $h6l$ layers) were measured with a Stoe Weissenberg diffractometer (Mo $K\alpha$ radiation, graphite monochromator) and reduced to structure factors (absorption corrections were not applied as $\mu t \sim 0.1$). E statistics calculated with *MULTAN* (Germain, Main & Woolfson, 1971) favoured $P2_1/m$. In these circumstances the TMA molecules lie in the mirror planes

at $y = \frac{1}{4}, \frac{3}{4}$ and the DMSO molecules have m symmetry. As there is a pyramidal arrangement of bonds about S, this implies that S and O atoms are in the mirror planes, with methyl groups above and below them. The structure was solved on this basis with *MULTAN*, and refined to convergence at $R = 0.092$ (26 reflections were excluded at this stage because of errors in their measured intensities). The space group was then changed to $P2_1$ and refinement continued to convergence at $R = 0.084$. Hamilton's (1965, 1974) test was applied: $\mathcal{R} = R(P2_1/m)/R(P2_1) = 1.095$, while for 1725 reflections, 171 variables in $P2_1$ and 60 parameters constrained in $P2_1/m$, a value of $\mathcal{R} = 1.02$ would be significant at the 2.5% level.

This result suggests that the correct space group is $P2_1$ despite the E statistics. However, there is some doubt about the correctness of this decision because the two S–C distances in DMSO have different values ($\Delta \sim 0.08$ Å) if the $P2_1$ coordinates are used. We have therefore decided to report the structure in terms of

Table 1. Crystal data for $TMA \cdot DMSO$ (all dimensions measured on a Weissenberg diffractometer)

Light-yellow prisms	$C_9H_6O_6 \cdot C_2H_6SO$ †
Monoclinic	FW 288.27
Space group $P2_1$ or $P2_1/m$ *	$D_m = 1.51$ g cm ⁻³
$a = 8.743$ (4) Å	$D_x = 1.50$
$b = 6.803$ (4)	$Z = 2$
$c = 10.677$ (5)	$F(000) = 300$
$\beta = 96.24$ (4)°	$\mu(\text{Mo } K\alpha) = 3.02$ cm ⁻¹
$V = 635.1$ (6) Å ³	$\lambda(\text{Mo } K\alpha) = 0.71069$ Å

* See text.

† Chemical analysis (wt%): C: 45.73 (found), 45.83 (calculated); H: 4.11, 4.20; O: 39.23, 38.85; S: 10.93, 11.12.

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Table 2. Atomic coordinates ($\times 10^4$) of atoms found by refinement in space group $P2_1$; *e.s.d.'s* in parentheses are given for the least significant digit

H atom coordinates are not refined; for refinement in space group $P2_1/m$ the *x,z* coordinates are changed by only small amounts while the *y* coordinates are all $\frac{1}{2}$, except for $\nu[C(10)]$ which becomes 0.4457.

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	-3967 (4)	2572 (18)	2 (4)
C(2)	-2864 (4)	2521 (19)	1045 (4)
C(3)	-1313 (4)	2594 (20)	874 (4)
C(4)	-835 (4)	2521 (21)	-320 (4)
C(5)	-1936 (4)	2546 (21)	-1363 (4)
C(6)	-3500 (5)	2521 (22)	-1192 (4)
C(7)	-5649 (5)	2537 (22)	153 (4)
C(8)	-145 (4)	2482 (21)	1994 (4)
C(9)	-1496 (5)	2528*	-2667 (4)
O(1)	-6639 (4)	2553 (20)	-723 (4)
O(2)	-5910 (4)	2595 (20)	1340 (4)
O(3)	-739 (4)	2575 (22)	3071 (3)
O(4)	1246 (4)	2527 (21)	1942 (4)
O(5)	-10 (4)	2672 (23)	-2722 (3)
O(6)	-2447 (5)	2680 (25)	-3594 (3)
S	2896 (1)	2564 (14)	5115 (1)
O(7)	1146 (4)	2581 (23)	5079 (3)
C(10)	3542 (8)	4453 (17)	6121 (9)
C(11)	3505 (10)	545 (16)	6142 (8)
HC(2)	-3180	2450	1920
HC(4)	280	2430	-430
HC(6)	-4300	2530	-1940
HO(2)	-7000	2600	1400
HO(3)	200	2600	3600
HO(5)	200	2600	-3400
HM(11)	4800	4400	6400
HM(12)	2990	4300	6910
HM(13)	3240	5700	5700
HM(21)	4600	600	6400
HM(22)	3310	-770	5690
HM(23)	2950	530	6910

* Held fixed in $P2_1$.

$P2_1$, but to note the changes that would be required if the space group were $P2_1/m$.

Atomic coordinates are given in Table 2.*

Results and discussion

Crystal structure

An ORTEP (Johnson, 1965) view of the structure looking approximately down [010] is shown in Fig. 1 and a view of a single layer in Fig. 2. TMA molecules are hydrogen bonded to one another in ribbons along [100] through single and approximately linear C=O...H-O interactions. In the [001] direction, adjacent

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33293 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

TMA molecules are hydrogen bonded through the O atoms of those DMSO molecules whose S and O atoms lie nearly in the same layer as the atoms of the TMA molecules. The cavity that remains between the TMA molecules is occupied by the S atom and methyl groups of the DMSO molecule. The structure is thus similar to that of a channel-inclusion complex but the usual clear-cut distinction between host and guest molecules [*cf.* TMA.H₂O. $\frac{2}{3}$ PA and TMA. $\frac{2}{3}$ H₂O (Herbstein & Marsh, 1977)] has disappeared because the O atom of the DMSO is an essential part of the channel wall while the rest of the DMSO molecule forms the contents of the channel.

There do not appear to be many examples of channel-inclusion or clathrate complexes where host and guest do not have separate structural roles. Two examples from among the polyhedral clathrate hydrates are (*i*-C₅H₁₁)₄N⁺F⁻.38H₂O (Feil & Jeffrey, 1961) and (*n*-C₄H₉)₄N⁺.C₆H₅COO⁻.39 $\frac{1}{2}$ H₂O (Bonamico, Jeffrey & McMullan, 1962). In both these crystals the anions participate in the polyhedral frameworks while the cations are contained in the cavities. Two other examples are *trans*-dichlorobis(ethylenediamine)-cobalt(III) chloride-tris(thiourea) (Simonov, Landa, Proskina, Malinovskii & Ablov, 1973) and NiI₂-deca-kisurea (Suleimanov, Porai-Koshits, Antsyshkina & Sulaimankulov, 1971). In the first of these the Cl⁻ ion forms part of the channel walls together with the thiourea molecules, while the cation is contained in the channel. In the second there appears to be appreciable interaction between the Ni²⁺ and I⁻ inside the framework and the urea molecules which constitute the channel walls.

The hydrogen-bonding scheme requires comment. Firstly, no carboxylic acid dimers are formed, which is unusual among the carboxylic acids (Leiserowitz, 1976). Secondly, the four atoms of the hydrogen-bonded group C=O...H-O are approximately collinear, whereas \angle C=O...O is usually $\sim 130^\circ$. These uncommon, but not unprecedented, features of the arrangement do not appear to affect the O...O distances which are essentially the same (~ 2.64 Å) irrespective of whether the carboxyl groups are bonded through one or both O atoms, or whether the arrangement is collinear or bent. The values of $d(O...O)$ for the -OH...O $\begin{matrix} \text{S} \\ \parallel \\ \text{HO} \end{matrix}$ hydrogen bonds are 2.56 and 2.66

Å in the present complex, in good agreement with the values found for -OH...OH₂ bonds in TMA.H₂O. $\frac{2}{3}$ PA and TMA. $\frac{2}{3}$ H₂O (Herbstein & Marsh, 1977). A more detailed discussion of the hydrogen-bond dimensions has been given in the preceding paper. Two of the carbonyl groups in each TMA molecule of TMA.DMSO do not participate in hydrogen bonds, but all available hydroxyl groups are hydrogen-bond donors.

The hydrogen bonding of DMSO and related

moieties (either complexed or as part of a molecular structure) appears to follow two patterns. In the first, which concerns us here, there are two hydrogen-bond donors bonded to the O atom of the DMSO molecule, and the arrangement of the three groups (S and two OH) about the DMSO O atom is trigonal planar. This pattern is found in TMA. DMSO and 5-bromouridine-DMSO (Iball, Morgan & Wilson, 1968). In the second pattern, found in *p*-carboxyphenyl azoxycyanide-DMSO (Viterbo, Gasco, Serafino & Mortarini, 1975), cloxacillin sulphoxide-dioxane-mono hydrate (Blanpain & Durant, 1976) and diethylstilboestrol-DMSO (Busetta, Courseille & Hospital, 1973), only one of the hydrogen-bond donors is present. We have compared the torsion angles about the S-O bond in TMA. DMSO and 5-bromouridine-DMSO (Fig. 3); they are quite different and this suggests that there is little mutual interaction between the electron distributions in the S-O and S-C regions of the DMSO molecule.

Molecular structures

TMA. The geometry of the TMA molecule is essentially identical to that found in an earlier work (Herbstein & Marsh, 1977). Detailed discussion is not given because of the lower accuracy of the present results. The carboxyl groups take up the synplanar O=C-OH conformation that seems to be frequently found, the only known exceptions being those in which the hydroxyl group participates in an intramolecular hydrogen bond (Leiserowitz, 1976). The TMA molecule does not have $3/m$ symmetry, owing to the requirements of the hydrogen bonding.

DMSO. The DMSO molecule has the expected pyramidal shape (Fig. 4). The most accurate dimensions available for DMSO are those obtained by gas-phase microwave spectroscopy on various isotopically-substituted species (Feder, Dreizler, Rudolph & Typke, 1969): $d(\text{S-O}) = 1.485(6)$ Å, $d(\text{S-C}) = 1.799(5)$ Å, $\angle \text{C}'\text{-S-C} = 96.57(3)^\circ$,

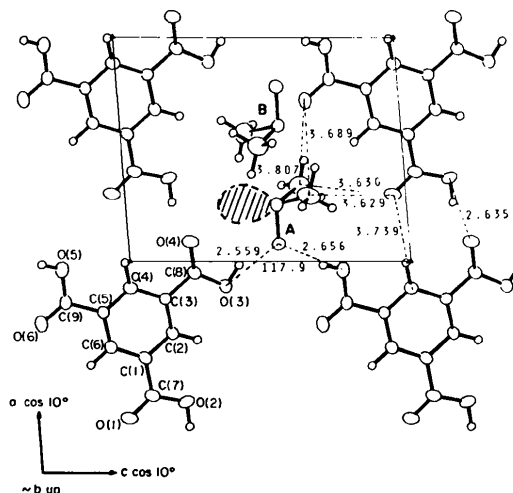


Fig. 2. Projection of the layer at $y = \frac{1}{4}$, viewed approximately along [010]. A slight tilt has been introduced in order to separate the two methyl groups of the DMSO molecules. The atoms of the reference molecules are numbered. The DMSO molecule labelled *B* is related to DMSO *A* by the 2_1 axis along [010] and is in the layer translated above (or below) that shown by $\frac{1}{2}b$. For space group $P2_1/m$ all the atoms are in the plane at $y = \frac{1}{4}$, except for the two methyl groups (of DMSO *A*) which are disposed symmetrically above and below this plane. For space group $P2_1$ there are small deviations of the atoms along y . The stereochemically-active lone pair is indicated schematically in the diagram.

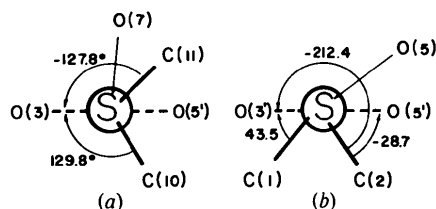


Fig. 3. Torsion angles ($^\circ$) about the S-O bond of the DMSO molecule in two complexes containing hydrogen-bonded DMSO: (a) TMA. DMSO and (b) 5-bromouridine-DMSO. The numbering of the atoms conforms to the original papers. The hydrogen bonds are shown by dashed lines.

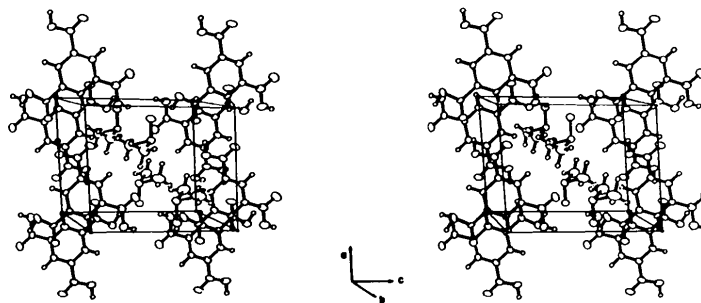


Fig. 1. ORTEP (Johnson, 1965) stereodiagram of the TMA. DMSO structure, viewed approximately along [010]. The reference molecules (i.e. those whose coordinates are given in Table 2) can be identified from Fig. 2.

$\angle C-S-O = 106.65 (3)^\circ$. These values agree well with the crystallographic results obtained for various aliphatic, aromatic and mixed sulphoxides (Svinning, Mo & Bruun, 1976; Viterbo, Gasco, Serafino & Mortarini, 1975; Pelizzi, Michelon & Bonivento, 1976; Pelizzi, Coghi, Michelon & Bonivento, 1976). In terms of these dimensions, we can infer that a systematic error of $\sim 0.07 \text{ \AA}$ has occurred in the position of C(10), mainly in its y coordinate [this is for space group $P2_1$; a comparison of values obtained for $d(S-C)$ in the two refinements is given in the caption to Fig. 4].

The dimensions of the DMSO moiety can be usefully compared with those of the sulphone and sulphoxide moieties (Alléaume, Gulko, Herbstein, Kapon & Marsh, 1976). The value of $d[S-C(sp^3)]$ is the same for both moieties, although the C atom hybridization state affects this value more in the sulphones than in the sulphoxides. There is a significant difference between the values of $d(S-O)$ found for the two groups of compounds; for the sulphones the mean is 1.44 \AA (range $\sim 0.03 \text{ \AA}$), with a π -bond order (Cruickshank, 1961) of 0.6. For the sulphoxides the π -bond order corresponding to $d(S-O)$ of 1.49 \AA is 0.4. More recent CNDO/2 calculations, explicitly taking the d orbitals into account, show an appreciably larger $3d$ contribution to the S-O bond in sulphones than in sulphoxides (Guimon, Goubeau & Pfister-Guillouzo, 1973).

DMSO is sometimes described as having a quasi tetrahedral shape, with the lone pair of the S atom occupying the fourth tetrahedral position; however, there is appreciable bond-angle distortion with $\angle C-S-C$ reduced to 97° . In the sulphones there is a smaller distortion of the R_1-S-R_2 angles to $\sim 104^\circ$, but this falls to 97° in three compounds containing S^{IV}

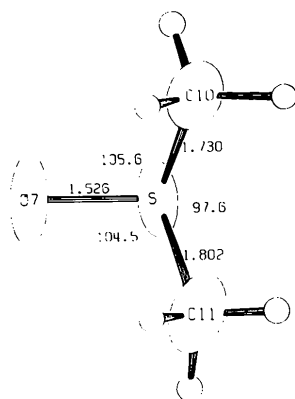


Fig. 4. Dimensions of the DMSO molecules as found from refinement in space group $P2_1$; the thermal ellipsoids represent 50% probability envelopes. The lack of equality between S-C(11) and S-C(10) is ascribed to a systematic error in the position of C(10). In space group $P2_1/m$ these distances are necessarily equal and $d(S-C)$ was found to be 1.773 \AA (the average for $P2_1$ is 1.766 \AA).

(rather than S^{VI}), viz, butadiene sulphone, β -isoprene sulphone and *cis*-perhydrocyclopenta[1,2-*c*:3,4-*c'*]-dithiophene S,S',S',S' -tetroxide (Alléaume *et al.*, 1976); the corresponding O-S-O angle remains at 117° . Thus the S lone pair in DMSO appears to occupy a site corresponding to one of the O atom positions in the sulphones. This lone pair appears to be stereochemically active and occupies the region shown schematically for DMSO *A* in Fig. 2. Similar stereochemical activity of an S lone pair has recently been demonstrated by Durand, Galigné & Cot (1977) in their comparison of the isostructural $(NH_4)_2SO_3 \cdot H_2O$ and $(NH_4)_2PO_3F \cdot H_2O$ and is also found in the diphenyl sulphone-diphenyl sulphoxide system, where the solid solution 0.09 sulphone-0.91 sulphoxide still has the diphenyl sulphone structure, an O atom of the sulphone being replaced by the (smaller) lone pair of the sulphoxide (Abrahams & Silverton, 1956).

Thermal stability

The crystals of TMA.DMSO are reasonably stable in air at room temperature, but lose DMSO on heating to $\sim 230^\circ C$. In this sense they contrast with 5-bromouridine-DMSO (Iball *et al.*, 1968) which decomposes immediately on exposure to the atmosphere, as does TMA.H₂O.dioxane (Herbstein & Kapon, 1978). These differences in stability are puzzling and none of the crystal structures provides much in the way of explanation. The lengths (and hence the strengths) of analogous hydrogen bonds are similar in all complexes (Herbstein & Kapon, 1978) while the arrangements of the components do not appear to be such as to differentially hinder or facilitate the escape of solvent molecules. Furthermore, TMA.H₂O.dioxane was crystallized from nominally anhydrous dioxane, and yet it incorporated water, whereas TMA.DMSO was crystallized from an aqueous solution of DMSO, as was 5-bromouridine-DMSO, and yet neither contains water. Determination of the ternary phase diagrams, which we do not contemplate, may throw light on these questions.

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A Simple Refinement of Density Distributions of Bonding Electrons. IV. The Distribution of Valence Electrons in Cyanuric Acid

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The new proposed refinement for density distributions of bonding electrons has been applied to the crystal structure of cyanuric acid. R becomes 2.62 or 2.52% (LQ1, LQ2). Constrained populations for the bonding electrons (LQ3–LQ5) seem to be less suitable for obtaining agreement with the X-ray data. In these three refinements, fixed population factors ($n = 2$, $n = 3$, and $n = 2$ or 4) for the charge clouds of the bonding electrons have been introduced. A comparison with the atom- and bond-population parameters obtained with atomic-orbital functions, shows that there are differences in the population values. In both cases, however, the difference maps and the bonding electrons outside the spherical arrangement of the core electrons are similar.

Introduction

In the first paper of this series (Hellner, 1977) the refinement procedure is explained. The electron density is split into core electrons (c), bonding electrons (v) and non-bonding electrons (o). For the core electrons the atomic form factors (f_c) and the occupation factors for the first main row elements ($n = 2$) are known, whereas a Gaussian distribution is used for the charge clouds of the bonding and non-bonding electrons. The shape of

the charge clouds is then described by the factors β_{ij} which also include the true temperature factor. At low temperature this part is less than 10% of the total β_{ij} . A correction of the β_{ij} with respect to the temperature factor will be described in a subsequent publication with the aim of transforming the dynamic electron density into a static one. This will be possible even without the knowledge of neutron diffraction data, because it turns out that the xyz and the β_{ij} for the core electrons are very similar to those obtained by neutron diffraction.