allow effective discrimination against such erroneous indications.

The problem of observational errors in $|F_p|$ and $|F_{PH}|$, and hence in E_h, is likely to be the major limitation to the technique, and is presumed to underlie the difficulties encountered with the Hg derivative of phosphorylase b. Errors in the observed magnitudes of the E_h will reduce the reliability of the triple-product phase relations. To arbitrarily increase the value of N is not the ideal solution to this problem, as the ensuing fractional reduction in $\kappa(h,k)$ is independent of the moduli and identity of the terms involved – while the errors will almost certainly be dependent upon them. Furthermore this approach does not provide an objective evaluation of the reliability.

A fundamental improvement should result if the errors inherent in the observations and those inherent in the relations were to be combined to produce an overall reliability measure. This would allow a rational decision as to whether phase determination by *MULTAN* would be likely to produce satisfactory results for a particular problem. A modification to the tangent formula which will allow for experimental error in the observations will be proposed later (French & Wilson, in preparation).

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The Crystal Structures of Trimesic Acid, its Hydrates and Complexes. III.* Trimesic Acid—H₂O—1,4-Dioxane

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$C_9H_6O_6 \cdot H_2O \cdot C_4H_8O_2$ is triclinic, $a = 9.528$ (3), $b = 9.535$ (3), $c = 8.031$ (3) Å, $\alpha = 89.68$ (5), $\beta = 95.01$ (5), $\gamma = 92.03$ (4)°, $Z = 2$, space group $P\bar{1}$. The structure was refined to $R = 0.113$ for 2890 counter reflections. It consists of planar ribbons of composition TMA.H₂O extending along |100|; these ribbons are hydrogen-bonded to one another *via* two crystallographically independent groups of bridging dioxane molecules. The framework formed in this way can be described in terms of an infinite series of steps running approximately about the (011) planes.

1. Introduction

Trimesic acid (TMA) forms complexes with many organic molecules. The two structures reported to date

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* Part II: Herbstein & Marsh (1977).

(Herbstein & Marsh, 1977) are of the channel inclusion type without hydrogen bonding between host and guest. However, other arrangements are possible and we are studying some of them to obtain an overall view of the crystal chemistry of TMA molecular complexes.

TMA crystallized from dioxane gives a ternary

complex which also contains water; the structure analysis shows that the arrangement of the components is an intricate one, with some of the features of the TMA.H_2O framework (Herbstein & Marsh, 1977), but with additional complications due to the ability of the dioxane to form hydrogen bonds with both TMA and water molecules. The resulting structure cannot be described as a channel inclusion complex.

2. Experimental

Transparent triclinic prismatic crystals, elongated along [001], were obtained by slow evaporation (almost to dryness) of a saturated solution of TMA in dioxane. The crystals are unstable and become opaque after a few minutes in the atmosphere; they are stable if sealed in a capillary with some dioxane. An approximate composition TMA–dioxane was deduced from preliminary crystallographic work and density measurement (Table 1). The correct formula, which includes an additional water molecule, was established by the structure analysis. The unexpected composition suggests that the dioxane used was not completely dry. Intensities of 3246 unique reflections (356 unobserved) of the $hk0$–$hk9$ layers were measured in the ω–2θ mode on a Stoe semi-automatic Weissenberg diffractometer, with graphite-monochromated Mo $K\alpha$ radiation (crystal size $0.4 \times 0.3 \times 0.4$ mm).

Intensities were reduced to structure factors by standard methods (no absorption correction). E statistics applied to the measured F's indicated that the cell was centrosymmetric. Unsuccessful attempts were made to solve the structure with MULTAN (Germain, Main & Woolfson, 1971) and SHELX (Sheldrick, 1977). E maps obtained from the best sets of signs showed honeycomb-like arrays of peaks from which unambiguous recognition of TMA or dioxane molecules was impossible. A similar problem arose in the structure of avicennin (Lai & Marsh, 1974). Thus we tried a combination of Patterson and search

techniques. The 022 reflection is exceptionally strong, suggesting that the TMA molecular plane is approximately parallel to (011). It follows that Patterson sections through the origin and 3.4 Å above the origin (normal separation of aromatic rings), parallel to (011), should show respectively the typical intramolecular and intermolecular TMA vector patterns. The orientation of the TMA molecules was established from these arrays of peaks. Packing considerations showed that the TMA molecules cannot occupy planes passing through the origin but must lie in planes 1.7 Å above and below these planes. The search was carried out on the assumption that the TMA molecule was planar with standard dimensions. Possible positions of the TMA molecules were taken in turn from the peaks in the intermolecular vector array. Each of these peaks gives a possible value for the coordinates of the tip of the intermolecular

Table 1. *Crystal data for* TMA.H_2O.*dioxane*

All dimensions were measured on a Stoe Weissenberg diffractometer.

$C_9H_6O_6$.H_2O.$C_4H_8O_2$*
Triclinic
Space group $P\bar{1}$*
$a = 9.528\,(3)$ Å
$b = 9.535\,(3)$
$c = 8.031\,(3)$
$\alpha = 89.68\,(5)°$
$\beta = 95.01\,(5)$
$\gamma = 92.03\,(4)$

$M_r = 316.27$
$V = 726.4$ Å^3
$D_m\dagger = 1.46$ g cm^{-3}
$D_c = 1.44$
$Z = 2$
$F(000) = 332$
μ(Mo $K\alpha$) = 0.81 cm^{-1}
λ(Mo $K\alpha$) = 0.71069 Å

* From structure analysis.
† Suspension in CCl_4–cyclohexane mixture.

Table 2. *Final fractional coordinates*
($\times 10^4$; *for* H $\times 10^3$)

E.s.d.'s in parentheses are in units of the least significant digit. H atoms are numbered as the atoms to which they are bonded. H coordinates were not refined.

	x	y	z
C(1)	175 (4)	1638 (4)	1120 (5)
C(2)	1387 (4)	979 (4)	1762 (5)
C(3)	1293 (3)	−196 (4)	2756 (5)
C(4)	−10 (3)	−716 (4)	3178 (5)
C(5)	−1231 (3)	−46 (4)	2517 (5)
C(6)	−1144 (3)	1107 (4)	1520 (5)
C(7)	347 (4)	2844 (4)	−15 (6)
C(8)	2623 (4)	−907 (4)	3323 (6)
C(9)	−2631 (3)	−644 (4)	2967 (6)
O(10)	−873 (3)	3314 (3)	−696 (5)
O(11)	1463 (3)	3304 (4)	−369 (6)
O(12)	3706 (3)	−625 (4)	2705 (5)
O(13)	2496 (3)	−1823 (3)	4503 (4)
O(14)	−2768 (3)	−1542 (3)	3974 (5)
O(15)	−3681 (3)	−39 (4)	2079 (5)
OD(1)	−4999 (4)	−4258 (4)	−1500 (6)
CD(2)	−4264 (7)	−5556 (7)	−1265 (9)
CD(3)	−4929 (7)	−6451 (6)	−71 (10)
OD(1')	−323 (4)	−5094 (4)	−3328 (5)
CD(2')	−1325 (6)	−4658 (6)	−4632 (9)
CD(3')	−1086 (6)	−5245 (7)	−6241 (9)
OW	−5127 (3)	−2931 (4)	5429 (5)
HC(2)	234	122	119
HC(4)	−8	−142	399
HC(6)	−192	153	100
HO(10)	−80	373	−156
HO(13)	292	−203	520
HO(15)	−425	0	281
HCD2(1)	−465	−616	−237
HCD2(2)	−320	−524	−89
HCD3(1)	−589	−665	−90
HCD3(2)	−443	−745	47
HCD2'(1)	−224	−495	−420
HCD2'(2)	−126	−355	−436
HCD3'(1)	−107	−637	−403
HCD3'(2)	−161	−513	−725
HOW(1)	−492	−312	639
HOW(2)	−452	−269	495

vector through the inversion centre at the origin. With the molecular orientation deduced from the Patterson map, this enabled us to calculate (*via* a program written by MK) atomic coordinates in the crystal axis system for input to *CRYM* (Duchamp, Trus & Westphal, 1969) for structure factor calculations. 30 strong peaks were scanned and R's calculated for 73 low-angle reflections. The most promising set of coordinates gave $R = 0.49$. A difference synthesis with 1040 reflections ($R = 0.56$) showed five new peaks which were ascribed to the dioxane molecules. There was an immediate drop in R. A difference map was sufficient to locate all dioxane atoms and the water O atoms. The dioxane O atoms were identified unambiguously after all hydrogen bonds had been found from the full interatomic distances list.

The structure was refined by least squares with the *SHELX* 76 package. Isotropic and then anisotropic refinement was performed with 2890 reflections (356 unobserved reflections were excluded) until convergence was reached at $R = 0.130$. Unit weights were applied to all reflections. Scattering factors for C and O atoms were taken from Cromer & Mann (1968), and for H from Stewart, Davidson & Simpson (1965). 26 reflections having $(F_o - F_c) > 2\sigma$ were omitted. A difference synthesis revealed the positions of all 16 H atoms. After they were introduced, the structure was refined further for the non-hydrogen atoms only until refinement ceased at $R = 0.113$. A difference map based on the final parameters showed no features of chemical significance. The relatively high R is attributed to inaccuracies in the intensity measurements. Atomic coordinates are given in Table 2.*

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33285 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

3. Results

3.1. Description of the structure

An *ORTEP* (Johnson, 1965) stereoview of the structure normal to the TMA molecular plane (*i.e.* approximately along [011]) is shown in Fig. 1 and a corresponding projection down the normal to the TMA plane in Fig. 2. There are ribbons of composition TMA.H_2O extending along [100]; the shaded ribbon is the *reference ribbon*, while the numbered atoms belong to the reference molecules whose coordinates are given in Table 2. The geometry of the TMA.H_2O ribbon is very similar to that of the analogous parts of TMA.H_2O.$\frac{2}{3}$PA and TMA.$\frac{5}{6}H_2O$ (Herbstein & Marsh, 1977). The two edges of a TMA.H_2O ribbon are made up of different arrangements of atoms and hence the intermolecular bonding in the two directions normal to the ribbon length (but in its plane) are different. Edges of the same kind are always juxtaposed in adjacent ribbons in the same sheet, as these ribbons are related by centres of symmetry. The reference ribbon is bonded to the next ribbon, proceeding down the page, by dioxane A molecules which bridge between water molecules. The vector between the O atoms of dioxane and water molecules is intermediate between axial and equatorial. The planes of these two ribbons are separated by ~ 1.4 Å. The bonding on the other edge of the reference ribbon is not shown directly for the reference ribbon in Fig. 2 but for the centrosymmetrically related ribbon below it. Here dioxane B bridges between carboxyl groups, with the O(dioxane)–O(hydroxyl) vectors directed equatorially. The planes of these two ribbons are separated by a normal distance of ~ 1.9 Å. The stepped nature of each sheet of ribbons (the rise of the step being at the bridging dioxane molecules) is shown in the stereoview. The three-dimensional structure is obtained by stacking the stepped sheets one above the other. The super-
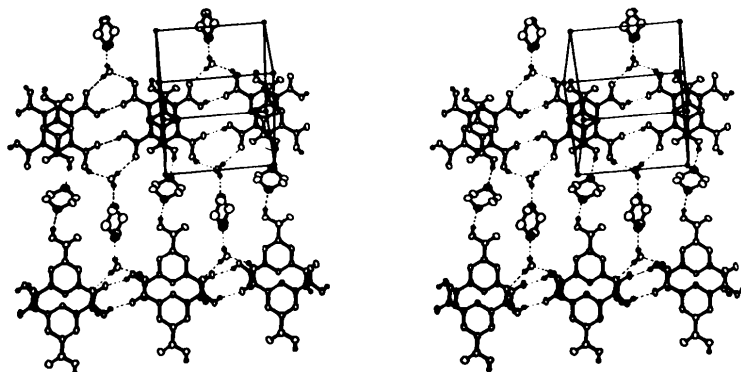

Fig. 1. *ORTEP* (Johnson, 1965) stereodiagram of TMA.H_2O. 1,4-dioxane viewed normal to the TMA plane (approximately along [011]). The origin is at the lower left-hand corner of the upper face of the cell, *a* is horizontal and *b* and *c* point above and below the line normal to the plane of the paper. Dioxane O atoms are shaded and hydrogen bonds marked with broken lines.
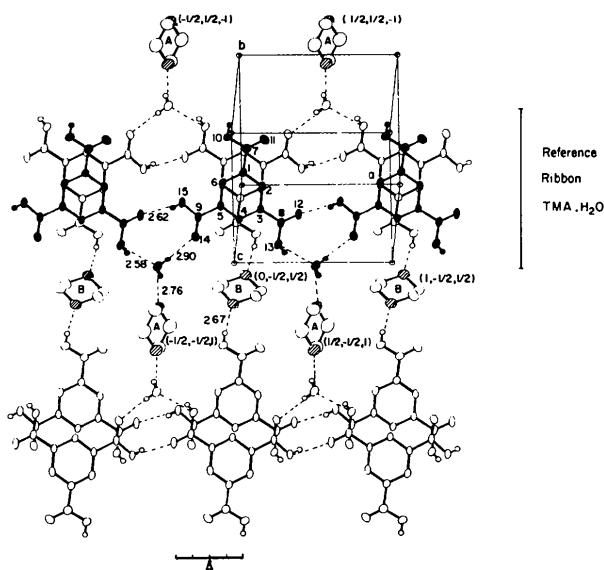
Fig. 2. Projection of two superimposed stepped sheets normal to the TMA planes (approximately along [011]). The atoms of the reference molecule are numbered [TMA C(1)—C(9), O(10)—O(15); O atoms of dioxane molecules are shown hatched]. The two crystallographically independent dioxane molecules are labelled A and B.

position of TMA molecules for the reference ribbon and its neighbouring ribbons is similar to that found in TMA.H₂O.⅔PA, but there is almost complete offsetting in the pair of ribbons shown in the lower part of Fig. 2. The superposed TMA molecules are separated by the normal interplanar distance of 3·4 Å; as the steps rise in the same directions, but the two step heights differ by 0·5 Å, the planes of the offset TMA molecules are separated by 2·9 Å, which is, of course, too short to allow more direct overlap.

The TMA carboxyl O(11) is not involved in any hydrogen bonding. Instead it makes normal van der Waals contacts with both dioxanes A and B. All available hydroxyl groups act as hydrogen-bond donors.

3.2. Geometry of the TMA molecule

The results are close to those reported by Herbstein & Marsh (1977) but less accurate and therefore are not discussed in detail. All hydrogen bonds are ordered. All TMA C atoms are coplanar within experimental error; the mean torsion angles of the carboxyl groups are −13 [about C(3)—C(8)], 9 [about C(5)—C(9)], and −3° [about C(1)—C(7)].

3.3. Geometry of the dioxane molecules

The molecular geometries of the two crystallographically independent dioxane molecules are shown in Fig. 3. Both molecules are in the stable chair
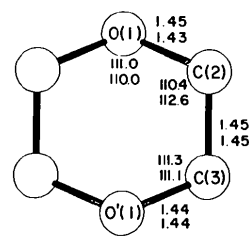

Fig. 3. Dimensions of the two crystallographically independent dioxane molecules. Upper figures are for dioxane A and lower for dioxane B.

conformation. The exact point group is C_i ($\bar{1}$) but they aproximate C_{2h} (2/m). The various C—O distances (1·43–1·45 Å) are close to the corresponding values found in the complex between 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane and 1,4-dioxane (Cobbledick & Small, 1973) and in bispropionato-copper(II).0·5dioxane (Borel & Leclaire, 1976) (average distance 1·43 Å). However, the C—C distances of 1·45 Å are considerably shorter than the average of 1·51 Å derived from these structures and from two structures of dichloro derivatives of dioxane (Altona & Romers, 1963; Altona, Knobler & Romers, 1963). This unusual shortening of the C—C lengths is believed to arise from thermal libration of the molecules about an axis through the hydrogen-bonded O atoms. Support for this supposition can be found in the relatively high e.s.d.'s of C atom coordinates and their somewhat higher thermal parameters.

4. Discussion

Although the TMA.H₂O.dioxane structure is clearly not of the host–guest type, there are, nevertheless, close resemblances between the arrangement of TMA and water molecules in the ribbons along [100] and that found in the appropriate parts of the TMA.H₂O framework in the host–guest complexes TMA.H₂O.⅔PA and TMA.⅚H₂O (Herbstein & Marsh, 1977). There is a lesser resemblance between the arrangements of dioxane and water molecules in TMA.H₂O.dioxane and in cloxacillin sulphoxide–dioxane–monohydrate C₁₉H₁₈ClO₆N₃S.C₄H₈O₂.H₂O (Blanpain & Durant, 1976); in the present complex dioxane A bridges the two water molecules to which it is bonded (and dioxane B between two carboxyl groups) while in the cloxacillin sulphoxide complex only one O atom of the dioxane molecule is bonded to a water molecule. A comparison of O···O distances in the hydrogen bonds between particular pairs of moieties (Table 3) suggests that there are rather constant pairwise interactions between analogous groups. For example, the distance between carboxyl and hydroxyl O atoms in two carboxyl groups is about 2·6 Å while that between

Table 3. *Typical values of d*(O⋯O) (Å) *found in hydrogen bonds in related structures*

Type (hydrogen-bond between groups)	TMA.H₂O.⅔PA and TMA.⅔H₂O	TMA.H₂O. dioxane	Cloxacillin sulphoxide.H₂O. dioxane	TMA.DMSO*
(1) C–OH and O=C in carboxyl groups	2·64[a]	2·62[b]	–	2·64[b]
(2) Carboxyl OH and water O	2·59[c]	2·58	2·60	–
(3) Carboxyl OH, DMSO O[d] or dioxane O	–	2·67 (dioxane B)	2·69	2·66, 2·56
(4) Water OH and dioxane O	–	2·76 (dioxane A)	2·76	–
(5) Water OH and carboxyl O=C	2·87[e]	2·90	–	–
Reference	Herbstein & Marsh (1977)	Present paper	Blanpain & Durant (1976)	Herbstein, Kapon & Wasserman (1978)

Notes

(a) Bonds a, b of Herbstein & Marsh (1977), who also give details of the spread of values found in these structures. These are hydrogen bonds in carboxylic acid dimers.

(b) These are bonds between carboxylic acid groups joined by single hydrogen bonds.

(c) Bond e of Herbstein & Marsh (1977).

(d) The corresponding value in p-carboxyphenol azoxycyanide. DMSO is 2·53 Å (Viterbo, Gasco, Serafino & Mortarini, 1975). In 5-bromouridine. DMSO (Iball, Morgan & Wilson, 1968), the values found for C–OH⋯O=S < are 2·66, 2·74 Å.

(e) Bonds c and d of Herbstein & Marsh (1977).

* Dimethyl sulphoxide.

carboxyl O in a carboxyl group and HO in a water molecule is about 2·9 Å.

The results suggest that there are only a few ways of constructing hydrogen bonds between these particular groups, and that these are utilized to the maximum extent possible in the construction of the lowest free-energy framework for the complex as a whole. Such a hypothesis could explain both the resemblances and differences between the arrangements found in complexes of partly but not completely similar chemical compositions. It requires testing, however, against many more examples.

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