

## The Crystal Structure of Trimesic Acid (Benzene-1,3,5-tricarboxylic Acid)\*

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The crystal structure of one modification of trimesic acid (benzene-1,3,5-tricarboxylic acid) has been determined. The crystals are monoclinic, space group  $C2/c$ , with  $a = 26.52$ ,  $b = 16.42$ ,  $c = 26.55$  Å, and  $\beta = 91.53^\circ$ ; there are 48 molecules in the cell and, hence, 6 in the asymmetric unit. Intensities were estimated visually from Weissenberg photographs; about 11,500 were recorded of which 3200 were too weak to be observed. The structure was derived by consideration of Patterson maps, optical transforms and molecular packing; refinement was by multiple-matrix least squares. In all, 979 parameters were refined, including anisotropic temperature factors for the heavy atoms and coordinates and isotropic temperature factors for the hydrogen atoms. The final  $R$  index is 0.068 and the standard deviation of fit is 1.49. The basic structural motif is a continuous, two-dimensional network comprising large, open rings formed by six molecules of trimesic acid bonded together through pairs of  $O-H \cdots O$  hydrogen bonds. The networks are not planar, pleats involving dihedral angles of about  $70^\circ$  being formed by means of a twisting of some of the hydrogen-bonding carboxyl groups out of the planes of their benzene rings. The networks continually interpenetrate one another; through each large ring of one network pass three parallel rings of other networks. The average C(ring)-C(ring) distance is 1.390 Å, and the average C(ring)-C(carboxyl) distance is 1.489 Å; none of the individual values differs significantly from the average. On the other hand, there is a wide spectrum of C-O distances. For the carboxyl groups that are severely twisted out of the plane of the benzene rings, the C-O(H) and C=O distances differ greatly, the average values being 1.319 and 1.218 Å; for the carboxyl groups that are only slightly twisted, the distances are more nearly equal (1.279 and 1.245 Å). For a third category of carboxyl groups the hydrogen atoms are disordered, some in ratios of 2:1 and others 1:1. In these, the C-O distances reflect the disorder.

### Introduction

Our attention was first directed to trimesic acid – benzene-1,3,5-tricarboxylic acid,  $C_6H_3(COOH)_3$  – by Professor H. McConnell and Dr G. R. Liebling. Their e.p.r. experiments indicated that trimesic acid may be damaged by X-radiation to produce a 'relatively high concentration of stable, long-lived free radicals' (Liebling, 1965); they also pointed out that knowledge of the crystal structure was essential to the precise interpretation of their observations.

### Experimental

Large prismatic crystals of trimesic acid were kindly furnished by Dr Liebling. Preliminary oscillation and Weissenberg photographs showed them to be monoclinic, space group  $Cc$  or  $C2/c$  ( $hkl$  absent for  $h+k$  odd,  $h0l$  absent for  $l$  odd), with approximate cell dimensions  $a = c = 26.5$ ,  $b = 16.35$  Å,  $\beta = 91.6^\circ$ . (More accurate values, obtained subsequently from a least-squares treatment of measurements of  $h0l$  and  $0kl$  Weissenberg photographs prepared in a Straumanis-type camera, are given in Table 1.) The density meas-

ured by flotation is  $1.46 \pm 0.02$  g.cm<sup>-3</sup>, indicating 48 molecules in the unit cell.\*

Table 1. *Crystal data*

Trimesic acid	$C_9H_6O_6$
Formula weight	210.14
Monoclinic,	Space group $C2/c$
$a = 26.520 \pm 0.002$ Å	
$b = 16.420 \pm 0.001$	
$c = 26.551 \pm 0.002$	
$\beta = 91.53 \pm 0.01^\circ$	
$D_x = 1.449$ g.cm <sup>-3</sup>	$Z = 48$
$D_m = 1.46$ g.cm <sup>-3</sup>	$F(000) = 5184$

\* Many of the crystals were found to be twinned about the (101) or (10 $\bar{1}$ ) planes. In an attempt to obtain additional untwinned crystals, some of the material was recrystallized from water. However, this resulted in crystals of a different modification – also monoclinic, space group  $Cc$  or  $C2/c$ , but with approximate cell dimensions  $a = 26.2$ ,  $b = 7.8$ ,  $c = 21.9$  Å,  $\beta = 102^\circ$ . On oscillation photographs about the  $b$  (needle) axis, the odd layer lines were much weaker than the even; moreover, Weissenberg photographs of these odd levels showed the spots to be extensively smeared along the reciprocal lattice rows parallel to  $c^*$ , indicating disorder. These crystals probably contain water, as the density calculated on the basis of 16 molecules of trimesic acid per unit cell is only 1.3 g.cm<sup>-3</sup>. A study of the weighted reciprocal lattice suggested that the rings are approximately perpendicular to the  $b$  axis with one edge parallel to  $c^*$ . No further work on this modification was undertaken.

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A number of preliminary observations encouraged us to proceed with the structure analysis. A rotation photograph about the *b* axis (Fig. 1) showed a rather clear transform of a benzene ring, and suggested that at least some of the molecules are parallel to **b**. The *h*0*l* Weissenberg photographs had almost exact *mm* symmetry, the mirror planes being (101) and (10 $\bar{1}$ ). (On upper-layer photographs this *mm* pseudosymmetry disappears.) Moreover, some extremely strong *h*0*l* reflections indicated the orientations, in projection, of the rings; they also suggested the presence of a center of symmetry and, hence, that the space group is *C*2/*c* rather than *C**c*. For space group *C*2/*c*, the asymmetric unit contains six molecules of trimesic acid.

Complete intensity data were collected by the multiple-film equi-inclination Weissenberg technique using Cu *K* $\alpha$  radiation. For this purpose, two large, untwinned crystals were eventually found and ground into spheres by the method of Bond (1951). One, 0.43 mm in diameter, was mounted about the *b* axis and layer lines 0–14 were recorded; it was later remounted about **a** and layer lines 0–4 were recorded. The second crystal, about the same size, accidentally cleaved into two equal hemispheres during the grinding. It was mounted perpendicular to the cleavage plane (101) – that is, parallel to the [10 $\bar{1}$ ] axis – and the zero level was recorded in order to permit correlation of the data from the other axes (because of the *C* centering, the odd layers about **b** have no reflections in common with the even layers about **a**, and *vice versa*). The intensities were estimated visually. Approximately 11,000 reflections were recorded on the photographs about the *b* axis, 2500 about **a**, and 200 about [10 $\bar{1}$ ]; in all, 11,563 independent reflections were measured, of which 3172 were too weak to be observed. The reciprocal sphere for copper radiation contains approximately 12,500 reflections.

The data reduction, as well as all subsequent calculations, was carried out on an IBM 7094 computer using subroutines of the CRYRM system (Duchamp, 1964). The intensity values as estimated on each film (and which ranged from about 2 to 65 for the comparison strip we used) were read into the computer and each was immediately assigned a standard deviation according to the function

$$\sigma(I) = \left( 0.833 + mI + \frac{0.1I^2}{(65 - I)^2} \right) \{ 1 + 0.25 \times \exp[-50(0.5 - \sin^2\theta)^2] \}. \quad (1)$$

Within the first factor, the constant term increases the uncertainties when *I* is small and the quadratic term increases the uncertainties when *I* is large (if *I* is equal to or greater than the limiting value 65,  $\sigma$  is set to a very large value and the weight of that observation becomes essentially zero); the second factor increases the uncertainties of reflections occurring in the region

where the  $\alpha_1$ – $\alpha_2$  splitting begins. The linear coefficient *m* was at first assigned the value 0.1.

These standard deviations were used in the calculation of the intensity factors relating different films of a particular layer. Empirical values of *m* (equation 1) were also calculated at this time, from a comparison of different measurements of the same reflections. The values were 0.043 for data collected about the *a* axis, 0.059 for data about **b**, and 0.166 for data about [10 $\bar{1}$ ]. New standard deviations were assigned, based on these empirical values of *m*; these standard deviations were propagated through all subsequent corrections and scaling for use later in least-squares weighting. All the data within each layer were then scaled together, averaged, and multiplied by 1/*Lp*. No absorption correction seemed necessary ( $\mu t \approx 0.5$ ).

The final step of the scaling procedure was the determination of the scale factors (*C*<sub>1</sub>...*n*) relating the various sets of films. These factors were calculated by a method which minimizes  $\sum w_i(C_k I_{ik} - C_l I_{li})^2$ , the sum-

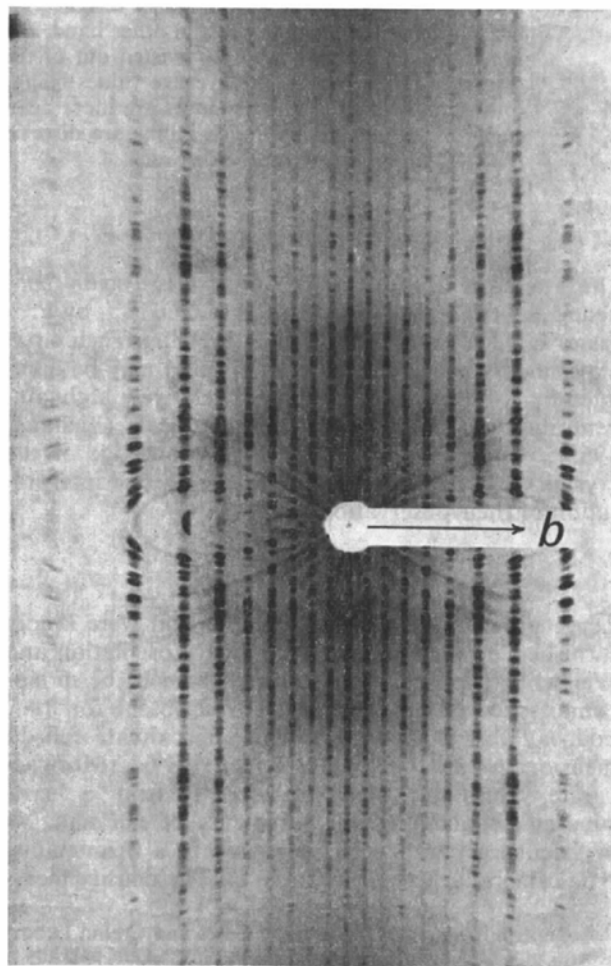


Fig. 1. A rotation photograph (Cu *K* $\alpha$ ) of trimesic acid. The rotation axis (*b*) is horizontal.

mation being over all reflections  $i$  common to film sets  $k$  and  $l$ . Using these factors, an averaged intensity and standard deviation was assigned to each of the 11,563 independent reflections.

### Determination of the structure

Several different methods of attack were used in deriving a trial structure. Perhaps the biggest clue came from comparing the Fourier transform of the molecule (synthesized optically by means of an apparatus constructed by Professor J.H. Sturdivant and making use of two 12" spherical lenses) with zero-level precession photographs prepared at 15° intervals about the  $b$  axis. This comparison confirmed the previous observation that at least some molecules are parallel to  $\mathbf{b}$ , and suggested three possible orientations: approximately perpendicular to  $\mathbf{a}$ , to  $\mathbf{c}$ , and to (10 $\bar{1}$ ).

In view of the length of the  $b$  axis and the observed orientations of some of the rings, it now appeared probable that one of the features of the structure was the formation of planar ribbons of molecules, hydrogen bonded together through their COOH groups; these ribbons presumably were parallel to  $\mathbf{b}$  and in the orientation suggested by the molecular transform work. When viewed down the  $b$  axis, many of the atoms within these ribbons would be closely superimposed, and hence Patterson projections on to (010) were expected to have many of the advantages of a heavy-atom map. Sharpened and unsharpened Patterson projections were calculated; and while they differed from one another in many important features, both were in agreement with the proposed ribbon-like arrangement.

Consideration of possible intermolecular arrangements as viewed down the  $b$  axis eventually led to a satisfactory structure in projection. The planar ribbon hypothesis and the possible orientations deduced from the molecular transform work were used as a starting point. The Patterson maps were used to check each step and to give hints on how to proceed. The three-dimensional implications for each possible arrangement were also studied. The only arrangement satisfying all criteria was one in which all six molecules in the asymmetric unit were parallel to the  $b$  axis, three being approximately perpendicular to  $\mathbf{a}$  and three to  $\mathbf{c}$ .

Three cycles of full-matrix least-squares refinement of the  $x$  and  $z$  coordinates were calculated, using only the  $h0l$  data. Even though this refinement proved to be rather unstable, necessitating careful evaluation of the indicated shifts, the  $R$  index for the  $h0l$  reflections was reduced from 0.61 to 0.38 by this method. Significant shifts in the centers of the molecules resulted, as well as twists of 4 of the 18 carboxyl groups out of the planes of their benzene rings.

The  $y$  coordinates of the centers of the six molecules were derived from a sharpened three-dimensional Patterson map. Coordinates for all the 90 heavier atoms in the asymmetric unit were then calculated assuming standard bond distances and angles, and structure fac-

tors were calculated for the complete three-dimensional data set; the  $R$  index ( $R = \sum ||F_o| - s|F_c|| / \sum |F_o|$ ) was 0.51.

### Three-dimensional refinement

Refinement was primarily by least squares, the quantity minimized being  $\sum w(F_o^2 - s^2F_c^2)^2$  (where  $1/s$  is the scale factor). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). There was one false start: the structure derived from the Patterson maps required that some of the carboxyl groups of structurally equivalent molecules be hydrogen bonded to one another across twofold axes, and hence that the hydrogen atoms be disordered. An alternate ordered structure with hydrogen bonding across centers of symmetry (and identical in projection down  $\mathbf{b}$ ) could be generated by translating the origin to  $x = \frac{1}{4}$ ,  $z = \frac{1}{4}$ . Initial refinement was based on this alternate structure. However, reflections with  $(k+l)$  odd showed continuing poor agreement between observed and calculated structure factors; the agreement improved markedly when the original structure was considered.

The amount of core storage available limited the number of parameters that could be included in a single matrix to approximately 200, and accordingly the parameters being refined were distributed among a number of smaller matrices. In the early stages, when only the coordinates and isotropic temperature factors of the carbon and oxygen atoms were being adjusted, the coordinates of the atoms in four molecules (180 parameters) could be combined in one matrix, the remaining parameters being held fixed; alternatively, four matrices could be collected: three, of 90 parameters, each containing the coordinates of two molecules and the fourth, of 91 parameters, containing the scale and temperature factors. Other set-ups were also used.

Initial calculations were based on the 1070 reflections with  $\sin^2\theta/\lambda^2 < 0.08$ , and with the weighting scheme  $w = 1/F_o^2$  for  $F_o \geq 15$ ,  $w = 1/15F_o$  for  $F_o \leq 15$ . After several cycles of refining only the coordinates, refinement was speeded up by applying the least-squares method of Waser (1963), in which constraints – in the form of additional, heavily weighted observational equations – were introduced to insure that the molecules retained their expected geometry. In these calculations the benzene rings and the carboxyl groups were required to be planar, but not necessarily coplanar. The coordinates and isotropic temperature factors were then refined using an increased amount of data and weights equal to  $1/\sigma^2(F_o^2)$ . Eventually the  $R$  index for the complete set of data was reduced to 0.16.

At this stage anisotropic thermal parameters for the 90 heavy atoms were introduced. For the carbon atoms, the starting values were the isotropic parameters from the preceding cycles; since the thermal motions of the oxygen atoms were expected to be quite anisotropic (larger than average in directions perpendicular to the planes of the carboxyl groups and smaller than average along the C–O bonds), their starting values were esti-

mated anisotropic coefficients. The complete set of data (11,563 reflections) was included in the remaining refinement cycles, and weights were taken equal to  $1/\sigma^2(F_o^2)$  (see *Experimental*). Since the number of parameters was now up to 811 (270 coordinates, 540 temperature parameters, and a scale factor), further subdivision of the matrices was necessary. We also found it efficient to carry out the least-squares refinement cycles in pairs: in the second cycle only the shift vectors were calculated, the inverse matrices of the normal equations being saved from the first cycle.

Four cycles of block-matrix refinement (two matrices, one for the coordinates and the other for the  $b_{ij}$ 's, for each atom) reduced the  $R$  index to 0.10. However, the molecular geometry was not entirely satisfactory, and it was apparent that convergence was being prevented by a small number – less than a dozen – of reflections with large residuals  $\sqrt{w(F_o^2 - sF_c^2)}$ , and that in most cases the residuals were probably due to the neglect of the hydrogen atoms. A three-dimensional difference map was therefore calculated; it indicated unambiguously the positions of the ring hydrogen

atoms, but not of the carboxyl hydrogen atoms. This map had a rather high noise level, undoubtedly due to incorrect parameters of the heavier atoms.

Nine more refinement cycles, with the ring hydrogen atoms included only in the structure factors, led to an  $R$  index of 0.079. Once again, several matrix arrangements were tried; one of the most efficient procedures seemed to be to include the coordinates of all the atoms of one molecule in a single matrix at the expense of reducing the sizes of the temperature-factor matrices. However, satisfactory convergence was still not attained.

Further attention was now given to the problem of locating the hydrogen atoms of the carboxyl groups. Difference maps were calculated through the ten sets of four oxygen atoms involved in the hydrogen bonding between carboxyl groups. These maps clearly showed the positions of two of the three hydrogen atoms [H(5) and H(6)] of each molecule; the third hydrogen atom [H(4)] of each molecule appeared to be disordered. For molecules *A* and *B*, the hydrogen bonding is across a twofold axis and accordingly H(4)

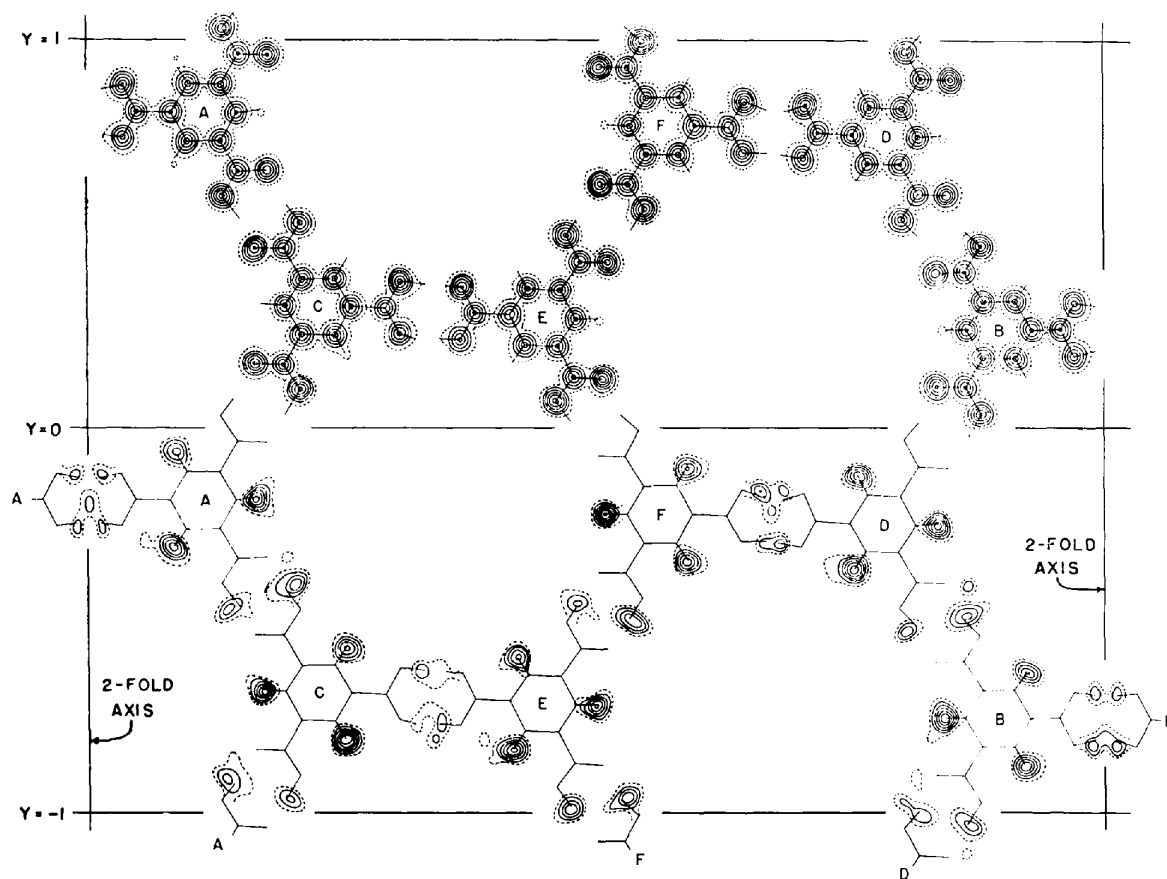


Fig. 2. Composite electron-density maps calculated at the conclusion of the refinement. Top: Sections evaluated in the planes of the benzene rings and, where necessary, in parallel planes containing carboxyl oxygen atoms. Contours are at intervals of  $2 \text{ e.}\text{\AA}^{-3}$  beginning with  $1.0 \text{ e.}\text{\AA}^{-3}$  (dashed). Bottom: Similar sections of difference maps, the contributions of the hydrogen atoms being omitted from the  $F_c$ 's. Contours are  $0.1$  (dashed),  $0.2$ ,  $0.3 \dots \text{ e.}\text{\AA}^{-3}$ . The  $b$  axis is vertical; for the left half of the Figure the view is roughly along  $c$  while for the right half it is roughly along  $a$ . Thus there is a fold (not shown) of about  $70^\circ$  between the plane of molecules *A*, *C*, and *E* and that of *B*, *D*, and *F*.

must be disordered in the form of two half-atoms. For molecules *C*, *D*, *E*, and *F*, H(4) appeared to be only partially disordered, one of the two positions being favored over the other. The apparent disorder of these four atoms was tentatively ignored, each atom being placed in the more favorable of the two positions.

Eight more least-squares cycles were now calculated. In the first four, the coordinates of the hydrogen atoms were included in a single ( $114 \times 114$ ) matrix; in the next four, isotropic temperature factors of the hydrogen atoms were included in an additional  $38 \times 38$  matrix. During these cycles, the hydrogen atoms H(4) for molecules *C*, *D*, *E*, and *F* shifted to positions approximately midway between the two hydrogen-bonding oxygen atoms. Another set of difference maps was therefore calculated for these atoms. These maps strongly suggested that the four hydrogen atoms are disordered in a ratio of about 2 to 1; that is, it appeared as though  $\frac{2}{3}$  of an atom should be placed in one site (in each case, the position 'favored' in the preceding map) and  $\frac{1}{3}$  in the alternate site adjacent to the other oxygen atom.

Two more least-squares cycles completed the refinement. A total of 979 parameters were adjusted: three coordinates and six temperature factors for each of 90 heavy atoms, three coordinates and one temperature factor for each of 42 hydrogen atoms (five whole atoms and one split atom for each of the six molecules), and a scale factor. Calculation time on an IBM 7094 computer was approximately 2 hours for the first cycle and 15 minutes for the second (in which only the structure factors and the shift vectors were calculated).

During the last cycle, the shifts in the heavy-atom parameters were small – almost invariably less than  $0.1\sigma$ . Three coordinates and one temperature factor of disordered hydrogen atoms shifted by approximately  $1.5\sigma$ . The final *R* index is 0.068; the 'goodness of fit' ( $= [\sum w(F_o^2 - s^2 F_c^2)^2 / (m - s)]^{1/2}$ ) is 1.49. Of 3172 reflections too weak to be observed, 86 calculated larger than the threshold value.

In Fig. 2 are shown electron-density and difference maps calculated at the conclusion of the refinement. In the upper half is shown a composite of a number of electron-density sections; these were calculated in the least-squares planes of the carbon atoms of each molecule except for those oxygen atoms which lie more than  $0.20 \text{ \AA}$  from the plane, in which case a parallel plane through the center of the oxygen atom was calculated. In the bottom half is shown a composite of difference sections calculated with the hydrogen atoms omitted from the structure factors; for the ring hydrogen atoms these sections were calculated in the planes of the benzene rings, while for the carboxyl hydrogen atoms the sections are in the least-squares planes of the four oxygen atoms involved in hydrogen bonding between pairs of carboxyl groups.

Observed and calculated structure factors are listed in Table 2; the final atomic parameters and their standard deviations are listed in Table 3. The standard deviations were calculated in the usual way from the

residuals and the diagonal elements of the inverse matrices of the normal equations; since these matrices were incomplete, the standard deviations are presumably underestimated. However, the agreement between the many different measurements of chemically equivalent bond distances suggests that this underestimation is not serious (see *Discussion*).

## Discussion of the results

### *Bond distances and angles*

The bond distances and most of the bond angles are shown in Fig. 3, which is a representation of a portion of the structure viewed normal to the planes of the molecules except that a fold, running vertically between molecules of types *E* and *F* and involving a dihedral angle of approximately  $70^\circ$ , is not shown. The interior angles of the benzene rings are not given in this Figure; they range from  $119.2^\circ$  to  $121.0^\circ$ , and there seems to be no systematic difference between angles opposite carboxyl groups and those opposite hydrogen atoms.

The standard deviations in positional parameters (Table 3) correspond to e.s.d.'s in the C–C and C–O distances of about  $0.004 \text{ \AA}$  and of about  $0.4^\circ$  in the angles. There are 36 structurally distinct ring C–C distances, all of which may be expected on chemical grounds to be equal. The scatter of these 36 measurements from their average value of  $1.390 \text{ \AA}$  leads to an internal standard deviation of  $0.0058 \text{ \AA}$  ( $\pm 0.0007 \text{ \AA}$ ); similarly, the scatter among the internal bond angles leads to a standard deviation of  $0.43^\circ$  ( $\pm 0.05^\circ$ ). We feel that this agreement between the two sets of standard deviations is satisfactory, and suggests that the refinement has been carried essentially to completion.

Least-squares planes were calculated through the six ring atoms of each molecule (with all six atoms weighted equally). Equations for these planes are given in Table 4, together with the out-of-plane distances of the various atoms in each molecule. Each group of six ring atoms of molecules *A*, *B*, *C*, and *D* is probably coplanar within experimental error; for molecules *E* and *F* they are slightly, but significantly, not coplanar. None of the carboxyl groups is coplanar with its benzene ring; the largest deviations are for the carboxyl groups C(8) and C(9) of molecules *E* and *F*, which are twisted about the C(ring)–C(carboxyl) bonds by amounts ranging up to  $27^\circ$ . These twists correspond to the folds in the hydrogen-bonded network, as will be discussed later. Besides being twisted about the C–C bonds, the carboxyl groups are also displaced through a bending of these bonds out of the planes of the benzene rings.

The C–O distances suggest three distinct types of carboxyl group: those involving C(8) and C(9) of molecules *A*, *B*, *C*, and *D*; those involving C(8) and C(9) of molecules *E* and *F*; and those involving C(7) of all six molecules. The carboxyl groups of the first type are approximately coplanar with their benzene rings; for them, the two C–O distances are not greatly different (av-

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Table 2. Observed and calculated structure factors

The three columns contain values, reading from left to right, of  $h$ ,  $F(\text{obs})$  and  $F(\text{cal})$ . A minus sign preceding  $F(\text{obs})$  should be read 'less than'; asterisks indicate reflections omitted from the refinement.

$h$	$F(\text{obs})$	$F(\text{cal})$	$h$	$F(\text{obs})$	$F(\text{cal})$	$h$	$F(\text{obs})$	$F(\text{cal})$	$h$	$F(\text{obs})$	$F(\text{cal})$	$h$	$F(\text{obs})$	$F(\text{cal})$	$h$	$F(\text{obs})$	$F(\text{cal})$	$h$	$F(\text{obs})$	$F(\text{cal})$
0	100	100	10	10	10	20	20	20	30	30	30	40	40	40	50	50	50	60	60	60
1	10	10	11	10	10	21	20	20	31	30	30	41	40	40	51	50	50	61	60	60
2	10	10	12	10	10	22	20	20	32	30	30	42	40	40	52	50	50	62	60	60
3	10	10	13	10	10	23	20	20	33	30	30	43	40	40	53	50	50	63	60	60
4	10	10	14	10	10	24	20	20	34	30	30	44	40	40	54	50	50	64	60	60
5	10	10	15	10	10	25	20	20	35	30	30	45	40	40	55	50	50	65	60	60
6	10	10	16	10	10	26	20	20	36	30	30	46	40	40	56	50	50	66	60	60
7	10	10	17	10	10	27	20	20	37	30	30	47	40	40	57	50	50	67	60	60
8	10	10	18	10	10	28	20	20	38	30	30	48	40	40	58	50	50	68	60	60
9	10	10	19	10	10	29	20	20	39	30	30	49	40	40	59	50	50	69	60	60
10	10	10	20	10	10	30	20	20	40	30	30	50	40	40	60	50	50	70	60	60
11	10	10	21	10	10	31	20	20	41	30	30	51	40	40	61	50	50	71	60	60
12	10	10	22	10	10	32	20	20	42	30	30	52	40	40	62	50	50	72	60	60
13	10	10	23	10	10	33	20	20	43	30	30	53	40	40	63	50	50	73	60	60
14	10	10	24	10	10	34	20	20	44	30	30	54	40	40	64	50	50	74	60	60
15	10	10	25	10	10	35	20	20	45	30	30	55	40	40	65	50	50	75	60	60
16	10	10	26	10	10	36	20	20	46	30	30	56	40	40	66	50	50	76	60	60
17	10	10	27	10	10	37	20	20	47	30	30	57	40	40	67	50	50	77	60	60
18	10	10	28	10	10	38	20	20	48	30	30	58	40	40	68	50	50	78	60	60
19	10	10	29	10	10	39	20	20	49	30	30	59	40	40	69	50	50	79	60	60
20	10	10	30	10	10	40	20	20	50	30	30	60	40	40	70	50	50	80	60	60
21	10	10	31	10	10	41	20	20	51	30	30	61	40	40	71	50	50	81	60	60
22	10	10	32	10	10	42	20	20	52	30	30	62	40	40	72	50	50	82	60	60
23	10	10	33	10	10	43	20	20	53	30	30	63	40	40	73	50	50	83	60	60
24	10	10	34	10	10	44	20	20	54	30	30	64	40	40	74	50	50	84	60	60
25	10	10	35	10	10	45	20	20	55	30	30	65	40	40	75	50	50	85	60	60
26	10	10	36	10	10	46	20	20	56	30	30	66	40	40	76	50	50	86	60	60
27	10	10	37	10	10	47	20	20	57	30	30	67	40	40	77	50	50	87	60	60
28	10	10	38	10	10	48	20	20	58	30	30	68	40	40	78	50	50	88	60	60
29	10	10	39	10	10	49	20	20	59	30	30	69	40	40	79	50	50	89	60	60
30	10	10	40	10	10	50	20	20	60	30	30	70	40	40	80	50	50	90	60	60
31	10	10	41	10	10	51	20	20	61	30	30	71	40	40	81	50	50	91	60	60
32	10	10	42	10	10	52	20	20	62	30	30	72	40	40	82	50	50	92	60	60
33	10	10	43	10	10	53	20	20	63	30	30	73	40	40	83	50	50	93	60	60
34	10	10	44	10	10	54	20	20	64	30	30	74	40	40	84	50	50	94	60	60
35	10	10	45	10	10	55	20	20	65	30	30	75	40	40	85	50	50	95	60	60
36	10	10	46	10	10	56	20	20	66	30	30	76	40	40	86	50	50	96	60	60
37	10	10	47	10	10	57	20	20	67	30	30	77	40	40	87	50	50	97	60	60
38	10	10	48	10	10	58	20	20	68	30	30	78	40	40	88	50	50	98	60	60
39	10	10	49	10	10	59	20	20	69	30	30	79	40	40	89	50	50	99	60	60
40	10	10	50	10	10	60	20	20	70	30	30	80	40	40	90	50	50	100	60	60

Table 2 (cont.)

11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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Table 2 (cont.)

12	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	105	110	115	120	125	130	135	140	145	150	155	160	165	170	175	180	185	190	195	200	205	210	215	220	225	230	235	240	245	250	255	260	265	270	275	280	285	290	295	300	305	310	315	320	325	330	335	340	345	350	355	360	365	370	375	380	385	390	395	400	405	410	415	420	425	430	435	440	445	450	455	460	465	470	475	480	485	490	495	500	505	510	515	520	525	530	535	540	545	550	555	560	565	570	575	580	585	590	595	600	605	610	615	620	625	630	635	640	645	650	655	660	665	670	675	680	685	690	695	700	705	710	715	720	725	730	735	740	745	750	755	760	765	770	775	780	785	790	795	800	805	810	815	820	825	830	835	840	845	850	855	860	865	870	875	880	885	890	895	900	905	910	915	920	925	930	935	940	945	950	955	960	965	970	975	980	985	990	995	1000
----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	------



Table 2 (cont.)

A large table with multiple columns and rows of numerical data, including various mathematical expressions and symbols.



Table 3. *The final parameters and their standard deviations (in parentheses)*

The coordinates of the heavy atoms have been multiplied by  $10^4$ ; those of the hydrogen atoms, by  $10^3$ . The anisotropic temperature parameters of the heavy atoms are of the form  $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$ , and have been multiplied by  $10^5$ . For the hydrogen atoms the values listed are of the isotropic temperature parameters  $B$ .

	x	y	z	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$		x	y	z	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$		x	y	z	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$			
(C1)	1295(13)	2076(17)	7167(19)	86(5)	305(11)	95(4)	-1(4)	-1(4)	-1(6)	(C1)	1629(13)	2277(15)	4084(19)	93(5)	385(10)	93(1)	-1(2)	-1(2)	-1(2)	-1(2)	(C1)	1629(13)	2277(15)	4084(19)	93(5)	385(10)	93(1)	-1(2)	-1(2)	-1(2)		
(C2)	1261(13)	1483(16)	4816(16)	81(5)	263(10)	115(4)	19(3)	-1(3)	1(10)	(C2)	1684(13)	2076(15)	3633(19)	117(5)	211(10)	106(4)	4(3)	4(3)	4(3)	4(3)	-1(2)	(C2)	1702(13)	2076(15)	3633(19)	96(5)	263(10)	115(4)	19(3)	-1(3)	-1(3)	
(C3)	2092(13)	1497(15)	7076(19)	81(5)	279(10)	100(4)	-1(3)	-1(3)	-1(10)	(C3)	1769(13)	2076(15)	4096(19)	96(5)	276(10)	99(4)	4(3)	4(3)	4(3)	4(3)	4(3)	-1(2)	(C3)	1771(13)	2033(16)	9476(19)	126(5)	242(12)	98(3)	24(3)	24(3)	-1(10)
(C4)	2297(13)	1773(16)	2732(19)	81(5)	279(10)	100(4)	-1(3)	-1(3)	-1(10)	(C4)	1800(13)	1596(15)	4298(19)	75(5)	251(10)	90(4)	14(3)	14(3)	14(3)	14(3)	14(3)	-1(2)	(C4)	1825(13)	2562(16)	3738(19)	86(5)	268(11)	105(4)	1(3)	1(3)	1(3)
(C5)	2026(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C5)	1677(13)	1564(15)	3377(19)	56(5)	257(11)	99(4)	27(3)	27(3)	27(3)	27(3)	-1(2)	(C5)	1873(13)	1999(16)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	-1(3)	
(C6)	1135(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C6)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C6)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C7)	1135(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C7)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C7)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C8)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C8)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C8)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C9)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C9)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C9)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C10)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C10)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C10)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C11)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C11)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C11)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C12)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C12)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C12)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C13)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C13)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C13)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C14)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C14)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C14)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C15)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C15)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C15)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C16)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C16)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C16)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C17)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C17)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C17)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C18)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C18)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C18)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C19)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C19)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C19)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C20)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C20)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C20)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C21)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C21)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C21)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C22)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C22)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C22)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C23)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C23)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C23)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C24)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C24)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C24)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C25)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C25)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C25)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C26)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C26)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C26)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C27)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C27)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C27)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C28)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C28)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C28)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C29)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C29)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C29)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C30)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C30)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C30)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C31)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C31)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C31)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C32)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C32)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C32)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C33)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C33)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)	1(3)	-1(2)	(C33)	1859(13)	1806(16)	3143(19)	124(6)	285(10)	99(4)	-1(3)	-1(3)	-1(3)	
(C34)	2355(13)	1773(16)	2632(19)	81(5)	266(10)	98(4)	6(3)	-9(8)	-1(6)	(C34)	1834(13)	1564(15)	3143(19)	114(7)	288(11)	99(4)	1(3)	1(3)	1(3)													

Table 4. *Least-squares planes through atoms C(1), . . . , C(6)*

Direction cosines	A	B	C	D	E	F
cos (a)	-0.1989	-0.9843	-0.2262	-0.9787	-0.2241	-0.9806
cos (b)	+0.0090	-0.0020	+0.0171	-0.0295	+0.0418	+0.0006
cos (c)	+0.9849	+0.2021	+0.9795	+0.2287	+0.9792	+0.2216
Origin to plane distance	6.5365	1.2893	7.0457	1.2363	9.6147	-1.8295
Deviations						
C(1)	-0.004	+0.002	+0.008	-0.009	+0.019	-0.013
C(2)	+0.004	+0.001	+0.002	+0.010	-0.018	-0.004
C(3)	+0.001	-0.006	-0.010	-0.001	-0.000	+0.019
C(4)	-0.006	+0.007	+0.008	-0.009	+0.017	-0.016
C(5)	+0.007	-0.004	+0.001	+0.010	-0.017	-0.001
C(6)	-0.002	-0.001	-0.009	-0.001	-0.001	+0.016
C(7)	-0.005	+0.012	-0.031	+0.037	+0.044	-0.043
C(8)	+0.053	-0.056	-0.148	+0.060	+0.117	+0.018
C(9)	+0.075	-0.058	-0.070	+0.131	-0.031	-0.095
O(1)	-0.006	+0.028	-0.249	-0.135	+0.218	+0.169
O(2)	-0.025	+0.026	+0.130	+0.228	-0.099	-0.244
O(3)	+0.100	-0.086	-0.309	+0.163	-0.301	+0.296
O(4)	+0.068	-0.095	-0.128	+0.043	+0.599	-0.230
O(5)	+0.187	-0.158	-0.104	+0.173	+0.260	-0.600
O(6)	+0.045	-0.024	-0.126	+0.228	-0.362	+0.383
H(1)	-0.013	-0.084	+0.049	+0.076	+0.020	-0.080
H(2)	+0.017	+0.027	+0.043	-0.008	-0.012	+0.053
H(3)	-0.046	+0.002	-0.033	-0.007	+0.097	-0.049

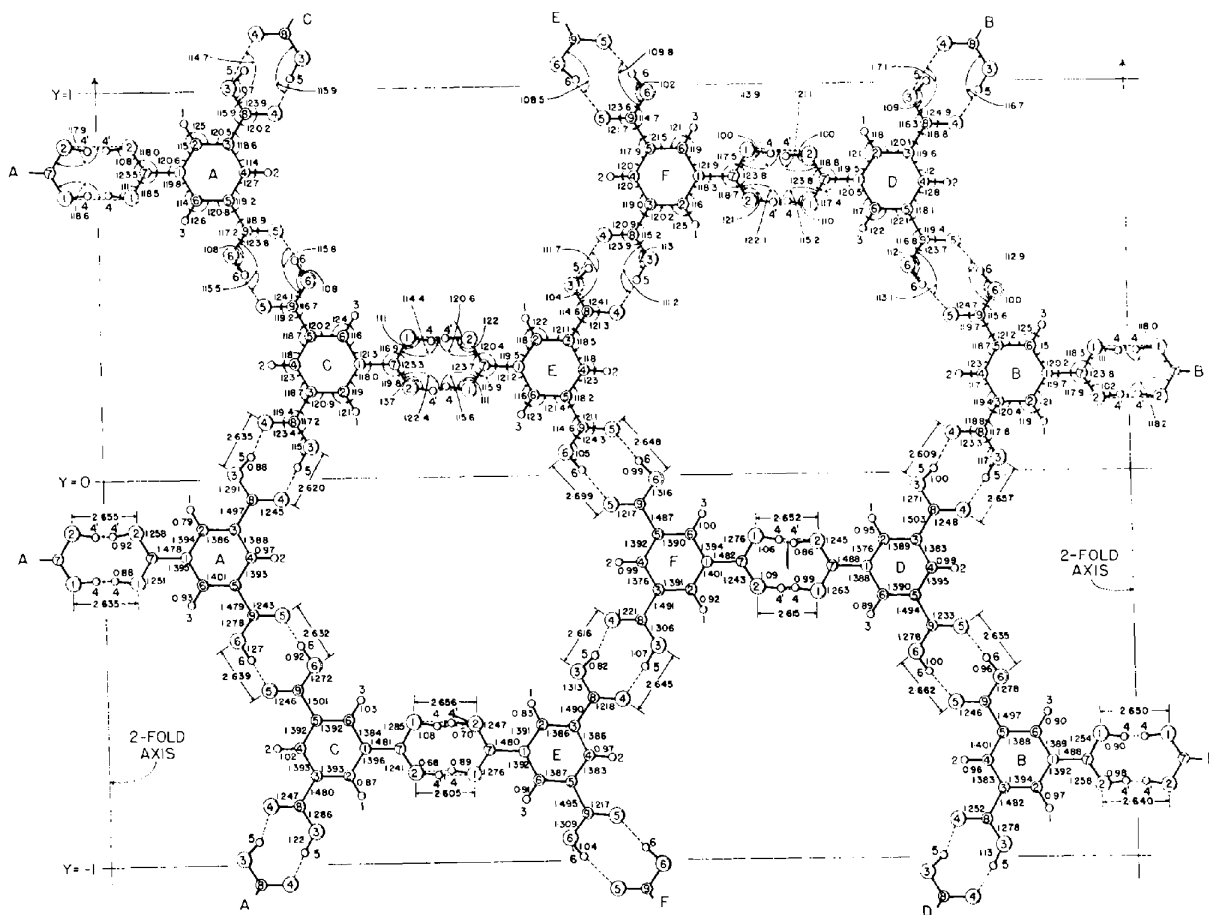
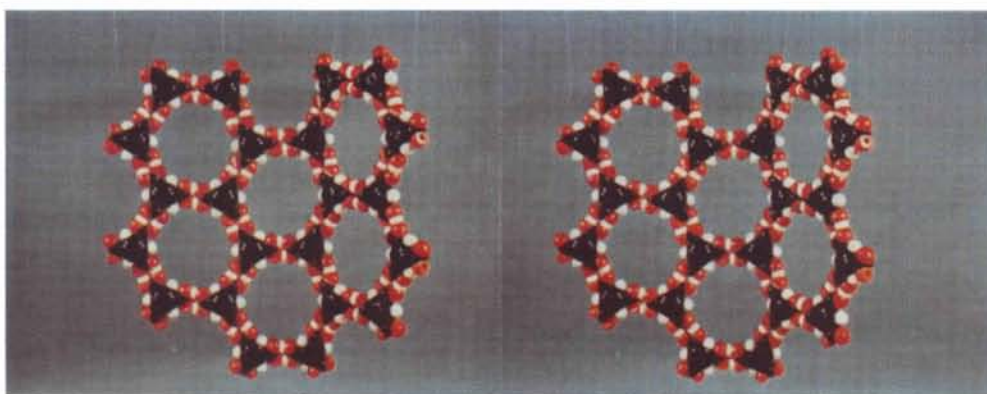


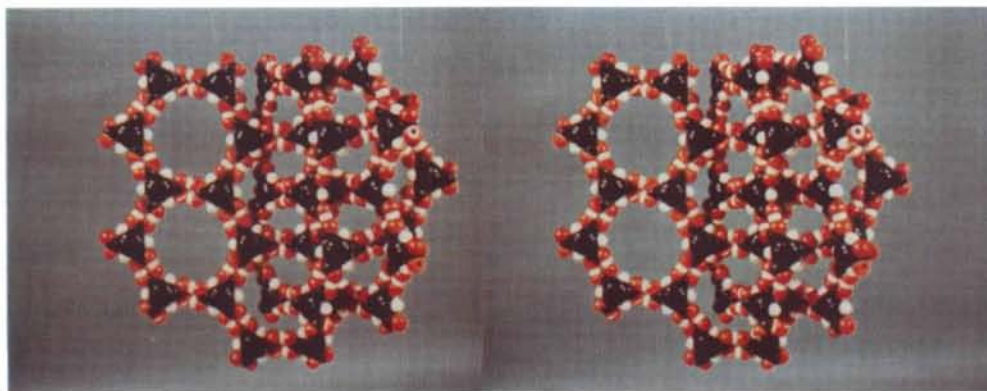
Fig. 3. The bond distances and angles for one asymmetric unit. The interior angles of the benzene rings are not given; they range from  $119.2^\circ$  to  $121.0^\circ$ . The view is the same as for Fig. 2



(a)

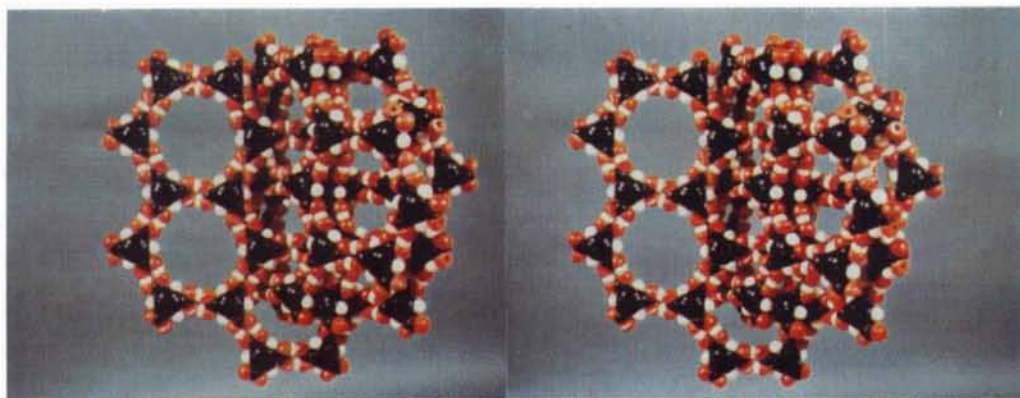


(b)

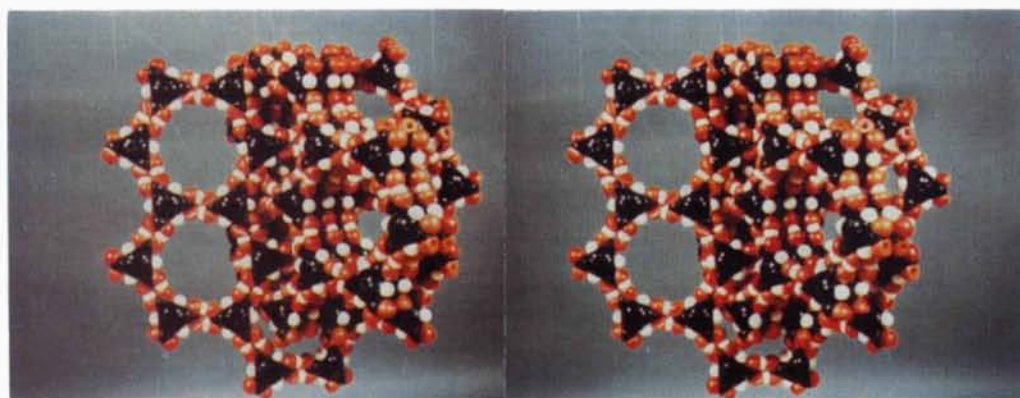


(c)

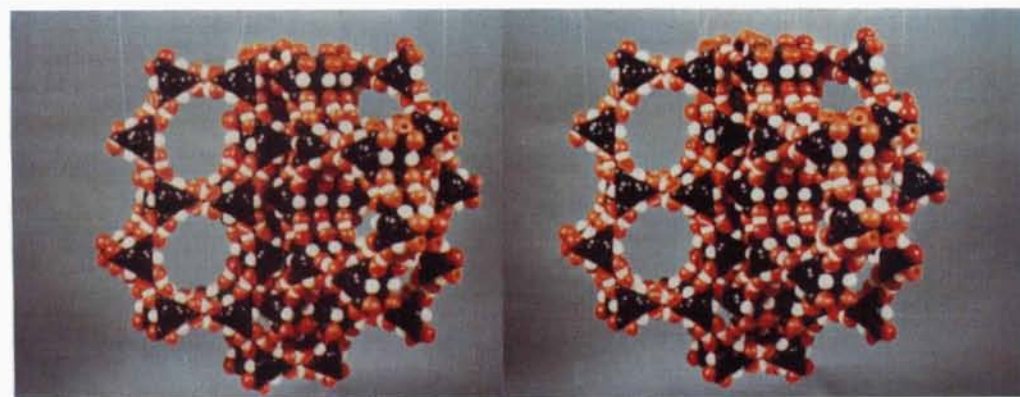
Fig. 4. Photographs of a model of the structure. (a) The trimesic acid molecule. (b) . . . (f) Stereographic photographs of portions of the three-dimensional structure. (b) A portion of a single 'chicken-wire' network, showing the large six-molecule rings and the fold in the network. (c) Two interlocking networks.



(d)



(e)



(f)

Fig. 4 (*cont.*) (d) Three networks. (e) Four networks. Here can be seen the interpenetration of one network by parallel portions of three other networks. (f) Six networks, showing the mutual interlocking of three parallel networks with three others in a different orientation.

The basic motif is that shown in Fig. 5 – an open framework, much like chicken wire, comprising rings of six molecules of trimesic acid hydrogen bonded together through pairs of O–H...O hydrogen bonds between carboxyl groups. A brief consideration of molecular models makes it clear that this motif is the only reasonable array that can be formed by planar trimesic acid molecules; however, it results in large holes in the centers of the six-molecule rings, and these holes must be filled if satisfactory packing is to be attained. The filling is accomplished through a mutual interpenetration of different chicken-wire frameworks. Through each hole of one framework pass, at an angle of about 70°, three parallel six-molecule rings of other frameworks; in turn, the original framework is one of three arrays that pass through the holes in the second set of frameworks.

The details of this interpenetration are shown in Fig. 6, which is a schematic view down the *b* axis. Mol-

ecules of type *A*, *C*, and *E* are hydrogen-bonded to one another, as shown in Figs. 2 and 3, to form three parallel, planar arrays approximately perpendicular to the *c* axis, while molecules *B*, *D*, and *F* form similar arrays approximately perpendicular to *a*. These arrays interpenetrate one another. Moreover, hydrogen bonds between molecules of types *E* and *F* connect one array directly to the other, this connection involving a dihedral angle of approximately 70°; thus, each chicken-wire array is folded into pleats. The pleating occurs between carboxyl groups C(8) and C(9) of molecules of types *E* and *F*, and is accomplished by means of the large out-of-plane twists of these carboxyl groups from the planes of their benzene rings.

The dihedral angles between planes of adjacent molecules within a three-molecule stack are 2.6° for *A* and *E*, 3.8° for *A* and *C'* (related to *C* by a  $Z_1$  axis), 1.6° for *F* and *B*, and 2.5° for *B* and *D'*

Table 5. Principal axes of the thermal ellipsoids

Columns are the magnitudes, *B*, and the direction cosines ( $\times 10^3$ ) with respect to the crystallographic axes, *a*, *b*, and *c* respectively.

	A	B	C	D	E	F
c(1)	3.45 -012 1000 013 2.65 -539 -019 856 2.41 842 006 517	3.43 -168 -974 029 2.72 -761 100 661 2.31 639 -050 750	3.27 -650 -178 756 3.04 -153 983 106 2.70 754 047 646	3.26 -312 -887 348 3.05 -577 439 593 2.30 666 060 726	3.37 -387 643 671 2.95 -368 -765 538 2.34 845 -039 510	3.33 -509 -741 451 2.74 -492 668 571 2.16 706 -068 626
c(2)	3.26 -290 109 958 2.95 -326 -945 016 2.53 900 -306 285	3.07 -354 842 416 3.01 -768 -512 406 2.28 532 -176 813	3.47 -491 204 860 2.90 473 079 060 2.42 731 -432 508	3.23 -717 584 399 2.83 -272 -737 626 2.41 641 341 670	3.51 -716 -136 704 2.82 608 362 690 2.55 344 -922 168	3.64 -816 194 566 2.70 578 305 741 2.42 019 -393 360
c(3)	3.02 -531 -298 807 2.71 -384 919 099 2.46 756 297 582	3.20 -486 721 507 2.91 -695 -661 300 2.43 530 -207 808	3.30 -816 109 589 2.77 372 -652 650 2.44 442 750 480	3.07 -348 804 491 2.91 -557 -591 597 2.40 754 -066 634	3.18 -622 -495 623 2.59 -222 854 475 2.38 751 -157 621	3.04 -552 -308 789 2.65 -307 939 163 2.38 775 153 592
c(4)	3.23 -282 -697 666 2.81 -395 710 593 2.30 874 096 453	3.35 -230 -973 023 3.01 -901 221 397 2.16 367 -071 917	3.15 -049 -940 339 2.78 -073 341 939 2.43 996 -022 069	3.36 -779 622 100 2.95 -556 -767 279 2.42 225 158 955	3.23 -526 -099 869 2.81 -015 994 107 2.22 860 -043 501	3.19 -791 -346 526 2.60 -258 936 245 2.21 555 -068 815
c(5)	2.96 -574 -505 659 2.84 -274 861 437 2.53 772 -071 611	3.32 -471 865 186 2.90 -835 -501 250 2.51 284 -038 960	3.12 -542 -130 844 2.69 -153 987 038 2.39 826 098 533	3.37 -894 014 471 2.67 115 -959 257 2.41 432 284 844	3.43 -708 140 711 2.56 640 541 528 2.15 299 -829 464	2.98 -363 439 831 2.75 -735 -677 056 2.27 572 -591 553
c(6)	3.17 -458 798 404 3.07 -445 -558 628 2.40 770 136 603	3.41 -643 -765 054 3.22 -637 563 543 2.45 424 -315 838	3.47 -609 -388 724 2.76 -510 860 010 2.31 608 363 690	3.82 -751 354 578 2.90 -354 -921 079 2.35 538 -163 812	3.33 -650 317 708 2.98 512 854 077 2.64 561 -413 702	3.27 -474 -656 600 2.61 093 626 772 2.50 816 -421 213
c(7)	3.77 -178 355 922 3.51 -425 -582 265 2.29 807 -345 282	3.75 -937 -292 219 3.43 -288 956 216 2.25 200 011 974	3.99 -293 424 865 3.16 -262 -893 362 2.35 920 -120 349	3.45 -963 -090 278 3.10 111 -091 066 2.37 244 097 968	3.62 -372 104 932 3.36 -146 -998 066 2.42 917 -115 358	3.41 -282 -291 373 2.99 -282 965 065 2.41 376 036 915
c(8)	3.55 -317 -539 789 3.06 -479 801 371 2.78 819 260 490	3.55 -889 193 439 3.35 -201 -979 030 2.56 412 -062 898	3.48 -097 -041 997 2.91 809 575 081 2.44 587 -809 008	3.82 -755 613 251 3.20 -558 -787 278 2.52 343 070 927	3.40 -817 -253 540 3.08 557 -114 807 2.50 -149 961 238	3.09 -740 204 660 2.89 645 -064 745 2.70 -189 -978 097
c(9)	3.88 -341 -210 985 2.83 057 968 242 2.48 938 -135 293	3.53 779 -625 023 3.15 -640 -761 124 2.78 027 111 992	3.56 -412 -304 870 3.31 -027 946 322 2.51 911 -110 374	3.76 -922 -103 397 3.20 119 -993 018 2.60 367 064 918	3.07 -476 766 445 2.98 -750 -611 272 2.52 458 -205 853	2.96 168 -648 738 2.70 -834 309 450 2.46 528 695 474
c(1)	10.16 -196 066 983 4.10 347 -929 123 2.39 917 365 134	9.61 -981 003 218 4.58 078 921 350 2.30 175 -390 899	6.20 -184 191 969 6.97 214 -902 223 2.40 939 249 108	8.66 -962 -198 215 4.13 -099 897 433 2.27 265 -395 875	10.88 -253 237 944 3.85 211 -933 286 2.36 944 272 161	4.87 -910 -168 403 3.78 280 -924 254 2.25 306 344 879
c(2)	7.27 -298 -010 962 4.22 281 965 090 2.33 912 -297 257	7.24 -965 -126 256 4.50 158 -970 169 2.25 202 206 952	10.34 -225 241 950 4.23 -433 -893 136 2.31 873 -330 282	6.03 -931 -306 223 4.04 348 -910 218 2.57 111 280 950	5.44 -349 034 945 3.80 394 912 103 2.31 650 -409 309	9.04 -968 150 229 3.82 212 920 323 2.53 138 -361 918
c(3)	8.13 -430 -065 912 3.57 899 059 409 2.16 -077 997 027	7.15 -916 -009 426 3.26 400 -118 698 2.67 039 993 312	6.83 -245 -150 965 3.35 943 196 244 2.64 -228 969 100	7.46 -957 -019 316 2.93 291 -099 944 2.61 010 995 100	5.44 -757 082 668 3.15 612 274 695 2.28 118 -968 257	5.43 -715 038 717 3.09 699 037 695 2.18 -001 -999 053
c(4)	6.43 -206 -189 965 3.39 -606 796 044 2.70 769 575 257	6.10 -957 044 312 3.76 146 927 342 2.43 250 -373 882	6.77 -257 -117 970 3.51 517 -856 049 2.63 252 504 242	6.96 -968 158 222 3.35 187 973 154 2.56 169 -171 966	6.34 -374 -076 934 2.98 521 -842 124 2.64 767 535 338	5.40 -968 082 299 3.07 170 -606 773 2.43 230 792 559
c(5)	6.86 -314 -064 955 3.51 499 838 209 2.59 807 -543 210	6.54 -969 161 213 3.57 016 -714 699 2.71 247 681 683	6.81 -338 -077 917 3.31 693 618 286 2.59 631 -758 148	7.16 -939 007 368 4.01 134 -825 436 2.59 307 466 821	4.82 -258 221 947 3.06 849 517 089 2.25 461 -827 308	5.76 -928 -042 395 3.13 306 451 813 2.55 213 -876 428
c(6)	7.14 -369 028 939 3.16 897 -242 340 2.52 235 970 068	7.31 -916 -010 425 3.26 388 227 843 2.61 100 -974 202	8.82 -386 025 933 3.35 634 -232 365 2.11 230 971 063	7.48 -975 067 236 3.78 209 -009 972 2.80 012 997 012	5.33 -717 -010 716 3.07 693 -113 693 2.32 072 994 086	5.34 -690 056 737 3.10 722 013 672 2.21 -050 -996 072

(related to  $D$  by a center of symmetry). The average distance between molecules within a stack is about 3.1 Å.

Pairs of molecules of type  $A$  are hydrogen bonded to one another across a twofold axis (see Fig. 6), as are molecules of type  $B$ . The hydrogen atoms involved in these bonds must, then, be disordered (the  $O \cdots O$  distances are far too long to represent symmetric hydrogen bonds). It is interesting that the other hydrogen bonds oriented perpendicular to the  $b$  axis – those between carboxyl groups  $C(7)$  of molecules  $C$  and  $E$  and of molecules  $D$  and  $F$  – also appear to be disordered, although in these cases one of the two arrangements seems to be favored over the other. The remaining hydrogen bonds – those between carboxyl groups  $C(8)$  and  $C(9)$  of different molecules – show no such disorder. Moreover, each of the twelve  $C(8)$ – $C(9)$  carboxyl groups is oriented such that its hydrogen atom is at the maximum distance along  $b$  from the center of its respective molecule. The result of this systematic arrangement of hydrogen bonds is that the holes in the centers of the six-molecule rings are slightly ellip-

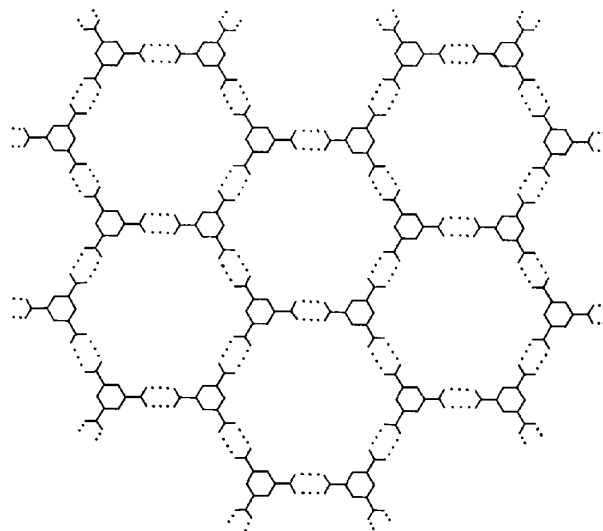


Fig. 5. The basic chicken-wire motif – a two-dimensional network of six-molecule rings. Dashed lines represent hydrogen bonds.

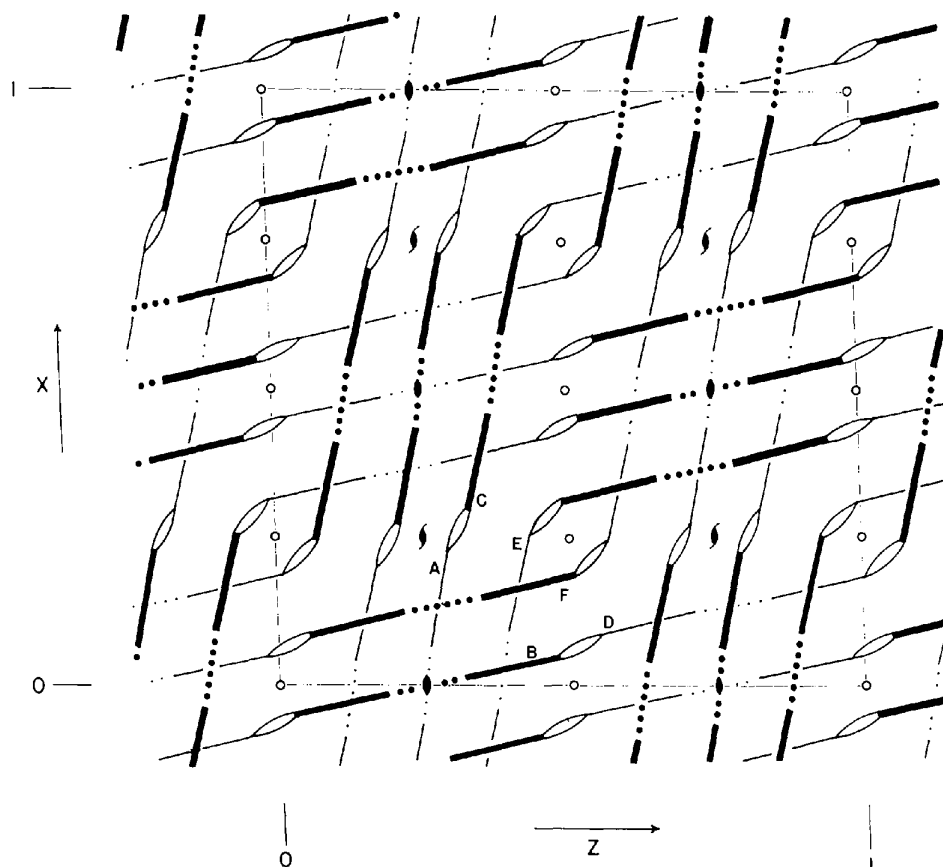


Fig. 6. A schematic representation of the structure viewed down the  $b$  axis. Individual trimesic acid molecules are represented by straight, solid lines. Dotted lines represent hydrogen bonds between molecules having similar  $y$  coordinates; these horizontal hydrogen bonds all involve disordered hydrogen atoms (see Figs. 2 and 3). The pairs of curved lines represent hydrogen bonds between molecules lying at different heights along  $b$ ; for these, the hydrogen atoms seem to be entirely ordered. The molecules labelled  $A$  through  $F$  are those whose coordinates are listed in Table 3.



tical, the diameter being greater perpendicular to the  $b$  axis than parallel to  $b$ .

This work represents part of the graduate thesis of DJD (Duchamp, 1965), who is indebted to the National Science Foundation for a Cooperative Fellowship. We are also indebted to Mrs Eva Browder for constructing the model from which the stereographic photographs (Fig. 4) were prepared, and to Professor J. H. Sturdivant for help and advice in using the optical transform apparatus.

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## The Crystal Structures of Copper Tetrammine Complexes A. $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{NH}_3)_4\text{SeO}_4^*$

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The room temperature crystal structures of two copper tetrammine complexes have been refined by the full-matrix least-squares method using three-dimensional Mo  $K\alpha$  intensity data. The space group for  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  is  $Pnam$  with lattice constants  $a_0 = 10.651$ ,  $b_0 = 11.986$ , and  $c_0 = 7.069$  Å; that for  $\text{Cu}(\text{NH}_3)_4\text{SeO}_4$  is  $P2_1/n$  with lattice constants  $a_0 = 10.313$ ,  $b_0 = 10.259$ ,  $c_0 = 7.405$  Å and  $\beta = 104.43^\circ$ . In both complexes, the copper ion is surrounded by four ammonia molecules ( $\sim 2.0$  Å) in a near square planar arrangement and by two more distant oxygen atoms (but at unequal distances from the copper ion). The copper ions are connected *via* the oxygen atoms in a chain-like arrangement, and a network of hydrogen bonds hold these chains and ions together.

### Introduction

The magnetic and thermal properties of  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  (CTASUL) have been extensively studied and have been interpreted as those of a substance containing a magnetic linear chain structure (Saito & Kanda, 1967; Rogers, Carboni & Richards, 1967). Recently Saito & Kanda (1967) conducted proton nuclear magnetic resonance studies on this material in the paramagnetic and ordered state. Unfortunately the lack of proton positions prevented a quantitative interpretation of these data. Since the early crystallographic study by Mazzi (1955) reported a structure based on projected data (with overlapping atomic sites) and indicated an unusual coordination about the copper ion, a detailed structure determination was considered necessary for any future quantitative interpretation of the observed resonance data.

Our attempts to crystallize an isostructural selenate compound proved to be unsuccessful; however, we isolated several other copper tetrammine complexes. The crystal structure of one of these complexes,  $\text{Cu}(\text{NH}_3)_4\text{SeO}_4$  (CTASEL), was determined and the coordination about the copper was shown to be distorted in a similar manner to that found in CTASUL. The room temperature X-ray diffraction studies on these two compounds reported here are part of a program to gain an understanding of the relationship be-

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tween chemical bonding and magnetic properties in materials containing linear chain structures.

### Experimental

The deep blue crystals of both compounds were grown in the interface between an alcohol layer and an aqueous solution, prepared by adding an excess of  $\text{NH}_3$  to the required copper salt solution. Crystals were examined by X-ray photographic techniques to insure that a single-crystal specimen rather than a twin was selected for our measurements. The space groups were selected on the basis of the observed extinctions on Mo  $K\alpha$  precession photographs and the absence of a piezoelectric response. In addition, the statistics of the normal structure factors calculated from the intensity data on CTASEL corroborated a centrosymmetric space group. The final agreement between the observed and calculated structure factors indicate that the space groups selected are the correct choice. The cell edges have been selected to conform to Donnay's (1943) rules, and hence, may not agree with other published results. Specific values found from our experimental procedures are summarized in the following section.

The lattice constants for these complexes were obtained with Cu  $K\alpha$  radiation ( $\lambda$  for  $K\alpha_1 = 1.54050$  Å) by least-squares fit of high  $2\theta$  values measured on films taken with a 115 mm diameter Weissenberg camera utilizing Straumanis film loading.

Three-dimensional Mo  $K\alpha$  intensity data were measured using the  $\theta$ - $2\theta$  scan technique on a Picker dif-

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