

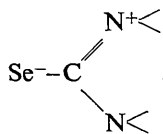
Table 8. Coefficients in the expression $Ax + By + Cz = D$ referred to crystallographic axes and distances from planes [molecule (b)]

	A	B	C	D
I(b)	-0.5070	-0.4365	0.8834	1.9952
II(b)	0.9964	0.0834	-0.4105	-0.4286
III(b)	-0.5512	-0.3882	0.8967	1.9730

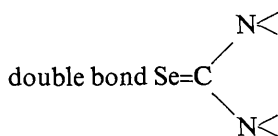
Deviation from plane

Se(2)	0.002 Å	I
C(10)	-0.006	I
N(3)	0.002	I
N(4)	0.002	I
C(11)	-0.024	II
C(12)	0.023	II
C(13)	-0.025	II
C(14)	0.026	II
C(15)	-0.020	II
C(16)	0.021	II
N(3)	0.014	III
C(17)	-0.042	III
C(18)	0.012	III
O(2)	0.015	III

The observed value, 1.87 Å, for the Se-C bond indicates a considerable contribution by the structure



. The sum of the covalent bond radii for Se-C is 1.94 Å for the single bond, and 1.74 Å for the



The N(2)-H...O(1) and N(4)-H...O(2) hydrogen bonds, 2.70 and 2.73 Å respectively, are consistent with the assumption of a positive charge placed on the NH group. It is suggested that the possibility of the NH group forming a hydrogen bond may account for the difference between the bond distances C(1)-N(2) and C(1)-N(1) for the molecule (a) and the bond distances C(10)-N(4) and C(10)-N(3) for the molecule (b).

We are very grateful to Dr Sagrario Martinez Carrera for making crystallographic programs available to us and also for help in running them. Our thanks to Dr M. Cubero for her helpful discussions and suggestions during the course of this work.

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The Crystal Structure of Trisethylsulphonylmethane

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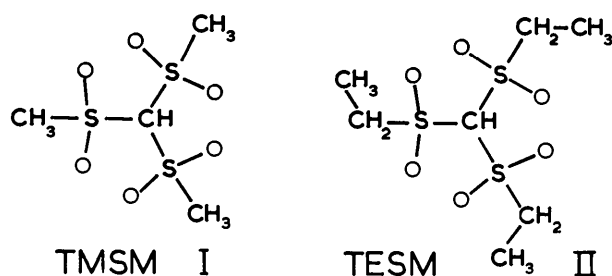
(Received 1 April 1968)

Trisethylsulphonylmethane (TESM) crystallizes with six molecules in a unit cell belonging to the hexagonal system with $a=14.97$, $c=9.81$ Å. The space group is $R3c$, and the required molecular symmetry 3. The crystal structure has been determined and refined to $R=0.085$ for 636 independent reflexions whose intensities were measured on an automatic diffractometer. The structure resembles that of trimethylsulphonylmethane (TMSM), but the crystals are not isomorphous. They differ in the manner of lateral packing of very similar stacks of molecules along c . The crystals of TESM are also free from the disorder which gives rise to spectacular diffuse scattering from TMSM. These differences are discussed. The principal bond-lengths, with standard deviations in parentheses are as follows: C-S=1.834 (4); S-O (mean)=1.442 (7); S-CH₂=1.785 (10); H₂C-CH₃=1.496 (15) Å.

Introduction

The crystal structure of trimethylsulphonylmethane (TMSM, I) has been studied by Silverton, Gibson & Abrahams (1965). This study was motivated not only by the interesting chemical properties of TMSM, but also by the remarkable diffuse reflexions observed in

its X-ray diffraction patterns (Abrahams & Speakman, 1956). Dr Gibson presented us with a sample of the analogous trisethylsulphonylmethane (TESM, II). Interest quickened when we found that this compound crystallizes in the same trigonal space group as TMSM, with similar unit-cell dimensions, but that its X-ray photographs were free from diffuse reflexions.



The diffuse reflexions from TMSM were explained in terms of disorder. Molecules are stacked, at intervals of $c/2$, along the threefold axis and any single stack is regularly ordered; the disorder arises because the stacks do not all point in the same direction, as would be required by the space group $R3c$. The idealized structures, with all stacks pointing up, or all down, c , are referred to respectively as A and B . The explanation supposes that A and B occur in the proportion 61:39; by postulating a specified type of lateral packing of A and B stacks, the observed pattern of diffuse spectra can be accounted for.

We started our study of TESM with the supposition that its crystals were isomorphous with those of TMSM, and therefore that TESM would have only one of the (physically equivalent) structures A or B . In fact, the structure of TESM proved different from that of TMSM. The crystals are not isomorphous, though the difference is subtle.

Experimental

TESM is easily soluble in water from which it can be crystallized as hexagonal prisms. Table 1 compares our crystal data, obtained with $\text{Cu K}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$), with those for TMSM (Silverton, Gibson & Abrahams, 1965). The diffraction symbol is R^*c . We assumed the space group to be $R3c$ (No. 161), which corresponds to either of the A or B structures of TMSM, and this assumption was borne out by our analysis. It implies that the asymmetric unit consists of one third of a molecule, with the central C atom, with its attached H atom, occupying a special position on a threefold axis. These atoms, together with one S, two O, two C, and five H atoms constitute the crystal-chemical unit (CCU).

Table 1. Comparison of crystal data

	TMSM $\text{C}_4\text{H}_{10}\text{O}_6\text{S}_3$	TESM $\text{C}_7\text{H}_{16}\text{O}_6\text{S}_3$
M	250.3	292.4
a (\AA)	12.89	14.965 (20)
c	9.53	9.81 (2)
V (\AA^3)	1371	1903
D_o	1.83	1.55
Z	6	6
D_c	1.818	1.531
μ ($\text{Mo K}\alpha$, cm^{-1})	—	5.83

Three-dimensional intensity data were collected on a Hilger-Watts linear diffractometer, using $\text{Mo K}\alpha$ radiation with balanced filters. To avoid recording the preponderance of systematically absent reflexions in $R3c$, each reciprocal-lattice net ($hk0-hk13$) was appropriately re-indexed. During processing of the diffractometer output, conventional indexing was restored, and the intensities of equivalent reflexions averaged (McGregor, 1967); 636 independent $|F_o|$ values were finally available.

Our expectation was that the crystal structure of TESM, so far as corresponding atoms are concerned, would be almost identical with that of TMSM in one of its forms. When this led to difficulties, we decided to solve the structure of TESM *ab initio*. With heavy atoms present, this proved to be straightforward, and it was, to a large extent, carried out with Glasgow ASS-system. This consortium of KDF 9 programs for Automatic Structure Solution has been developed principally by McGregor (1967), Muir (1967), Pollard (1968) and Sime (1967).

Structure factors, calculated for S atoms only, gave $R = 0.28$. The O and C atoms were found by computer-search of an electron-density synthesis phased on the S atom. Refinement proceeded by least-squares analysis (the program being due to Cruickshank, Smith & Sime), using first isotropic and then anisotropic vibrational parameters. The weighting scheme (due to McGregor, 1967) has been described elsewhere (Currie, Curry & Speakman, 1967); that it was satisfactory is shown by the uniform distribution of $w\Delta^2$ with respect to both $\sin \theta$ and $|F_o|$, and is supported by the analysis of structure factors given in Table 6. All H atoms appeared in a difference electron-density synthesis. They were included, in chemically acceptable positions, in subsequent structure-factor calculations, though their parameters were not refined. The atomic-scattering functions were taken from *International Tables for X-ray Crystallography* (1962).

$R3c$ is a polar space group. In the analysis of TMSM it was nevertheless possible to fix a unique origin along c because of the two partial structures A and B . Had these occurred in equal proportions and completely at random, the effective space group would have been $R\bar{3}c$, which includes points of $\bar{3}$ symmetry. Such a point could still be chosen as origin though the structures were unequal in proportion and not randomly disordered. With TESM the z coordinate cannot be fixed by reference to symmetry elements. It was prevented from 'floating' by putting the z coordinate of the S atom equal to zero, and inhibiting refinement of this parameter.

The molecule of TESM existing in the crystal is dissymmetric. This is of no chemical interest because the operation of the glide-planes produces D and L molecules in equal numbers. The crystal is a racemate. (In any case, inversion of any molecule will occur readily in solution, as the dissymmetry depends only on conformation.) Nevertheless the molecular dimensions

found are liable to errors due to anomalous dispersion (Ueki, Zalkin & Templeton, 1966; Cruickshank & McDonald, 1967). Such errors particularly affect the position found for the S atom, when this is derived

from data which do not cover a complete sphere in reciprocal space. The actual chirality of the molecule including the CCU is therefore relevant at this level. In other words, it matters whether reflexions are in-

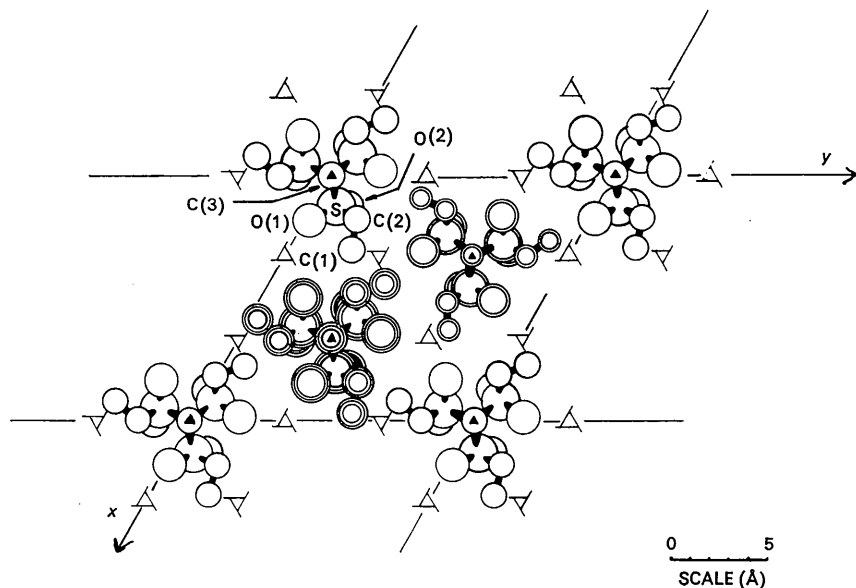


Fig. 1. The crystal structure of TESM seen in its c axial projection. The atoms of the CCU are numbered, and only one of the two molecules within the primitive translation c is shown.

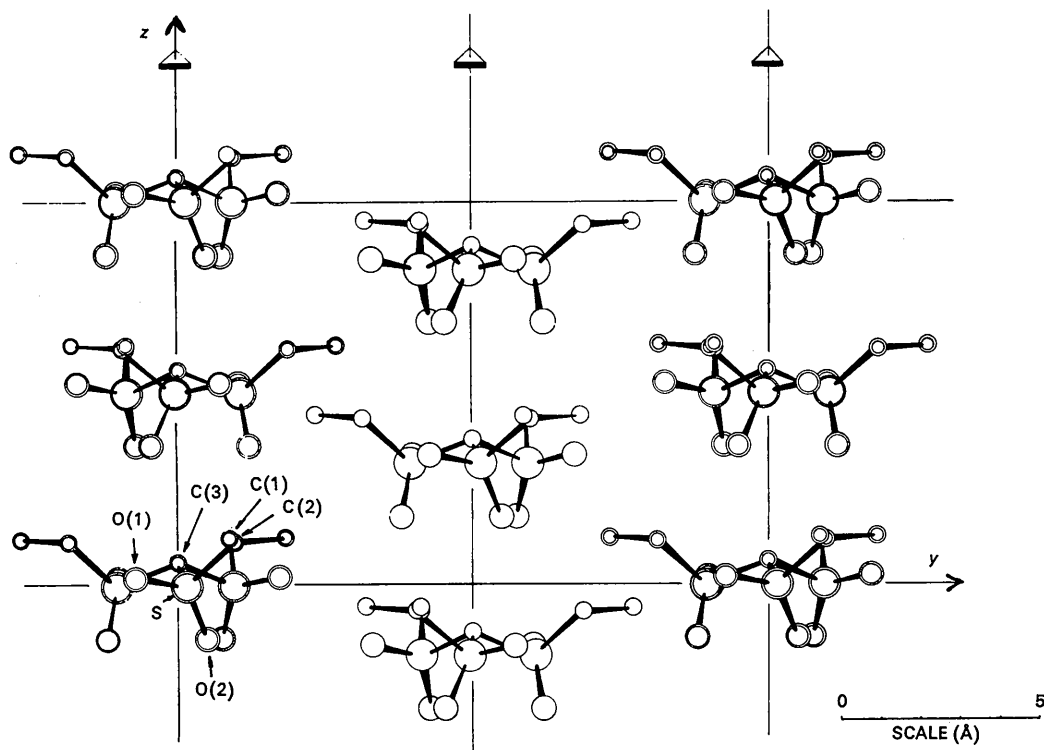


Fig. 2. The crystal structure of TESM seen perpendicularly to the yz plane. The atoms of the CCU are numbered, and only the molecules lying within half the primitive translation a are shown.

dexed as $F(hkl)$ or $F(\bar{h}\bar{k}\bar{l})$. 'The change of indexing was simulated by changing the sign of $\Delta f''$ in the structure-factor calculations' (McGregor, 1967). The choice which gave the lower final R value (0.085, for all observed reflexions, compared with 0.087) was adopted. According to Hamilton's (1965) test, this difference in R is significant at less than the 0.5% level. It also led to closer agreement between the two S-O distances; the bond lying approximately in the c direction was affected by about 0.01 Å, whilst the other, lying roughly perpendicular to c , was changed only marginally.

Results and description of the structure

Figs. 1 and 2 give impressions of the structure in different directions. Final parameters are listed in Tables

2 and 3. Standard deviations, based on the least-squares residuals follow in parentheses, and are expressed in terms of the last figure given. Table 3 also includes principal axes, and their directional cosines, for the ellipsoids representing mean-square amplitudes of vibration of the heavier atoms. Table 4 gives observed and calculated structure amplitudes. The numbering of the S, O and C atoms of the CCU is shown in Figs. 1 and 2: H(1) is the atom attached to C(3), H(2) and H(3) to the methylene C atom, and H(4)–H(6) to the methylic C atom. Other symmetry related units needed in discussing the structure are as follows:

CCU	$x, y, z,$
I	$-y, x-y, z,$
II	$y-x, \bar{x}, z,$
III	$x, y, 1+z.$

Table 2. *Atomic coordinates*

x, y and z are fractional coordinates $\times 10^4$; X', Y and Z are absolute, orthogonal coordinates, expressed as 10^{-3} Å, with X' parallel to a , their standard deviations being included in parentheses.

	x	y	z	X'	Y	Z
S	1329	796	0	1722 (2)	197 (3)	0 (0)
O(1)	1832	206	253	2374 (6)	-1062 (7)	248 (7)
O(2)	1292	1119	-1375	1674 (7)	708 (7)	-1349 (7)
C(1)	3012	2382	1206	3904 (12)	1310 (17)	1183 (13)
C(2)	1864	1888	1109	2416 (9)	1463 (11)	1088 (9)
C(3)	0	0	610	0 (0)	0 (0)	598 (10)
H(1)	0	0	1870			
H(2)	1750	2480	650			
H(3)	1850	1950	1860			
H(4)	3040	2440	740			
H(5)	3070	2960	2020			
H(6)	3160	1750	1730			

Table 3. *Vibrational parameters*

U_{ij} are the tensor components (10^{-4}Å^2) for the ellipsoid representing mean-square vibrational amplitudes, with standard deviations in parentheses.

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
S	302 (9)	339 (10)	215 (0)	41 (15)	90 (11)	288 (14)
O(1)	426 (29)	569 (37)	333 (0)	86 (48)	78 (44)	570 (55)
O(2)	545 (40)	434 (36)	271 (0)	176 (52)	218 (46)	426 (72)
C(1)	493 (54)	806 (89)	431 (0)	-169 (102)	-208 (83)	348 (114)
C(2)	384 (41)	352 (43)	345 (0)	-28 (61)	-59 (60)	183 (66)
C(3)	261 (28)	261 (8)	174 (0)	0 (0)	0 (0)	261 (28)

Principal axes (10^4Å^2) of the vibrational ellipsoids and their directional cosines with respect to the orthogonal axes

	U	D_1	D_2	D_3
S	196	-0.390	-0.006	0.920
	362	0.185	-0.980	0.072
	319	0.902	0.198	0.384
O(1)	577	0.510	0.842	0.175
	319	-0.356	0.021	0.934
	384	0.783	-0.539	0.311
O(2)	219	-0.352	-0.230	0.907
	606	0.885	-0.398	0.242
	468	0.305	0.888	0.344
C(1)	1021	0.150	-0.988	0.037
	344	0.612	0.122	0.781
	566	-0.776	-0.094	0.623
C(2)	556	-0.568	0.819	0.083
	294	0.762	0.485	0.429
	355	0.312	0.307	-0.899
C(3)	261	1.000	0.000	0.000
	261	0.000	1.000	0.000
	174	0.000	0.000	1.000

Table 5. Bond lengths (Å) and bond angles (°)

Standard deviations are added in parentheses			
S—O(1)	1.440 (7)	O(1)—S—O(2)	119.1 (4)
S—O(2)	1.444 (7)	O(1)—S—C(3)	106.0 (3)
S—C(2)	1.785 (10)	O(1)—S—C(2)	108.9 (4)
S—C(3)	1.834 (4)	C(3)—S—O(2)	108.2 (4)
C(1)—C(2)	1.496 (15)	C(3)—S—C(2)	103.9 (4)
C(3)—H(1)	1.240 (210)	O(2)—S—C(2)	110.4 (4)
		S—C(3)—S	109.9 (2)
		S—C(3)—H(1)	109.0 (2)

The principal bond-lengths and angles are given in Table 5, with their standard deviations. They agree reasonably with the corresponding dimensions of the TMSM molecule where, however, the accuracy is less owing to the disorder and the use of less complete data. Viewed along the C(2)—S bond, the dihedral angle from C(2)—C(1) to S—C(3) is about 157°.

Though its position is not precisely determined, the acidic atom, H(1), lies on the threefold axis, with C(3)—H(1) \approx 1.0 Å. It is about 3.9 Å from the central C(1) atom of the next molecule along *c*. It is also equidistant from three O(2) atoms, with H(1) \cdots O(2^{III}) = 3.2 Å. No significant hydrogen bonding seems to exist. No other intermolecular contacts call for special mention.

The relationship between the crystal structures of TMSM and TESM

The standard molecule of TESM consists of the CCU with units I and II. Figs. 3(a) and (b) show the posi-

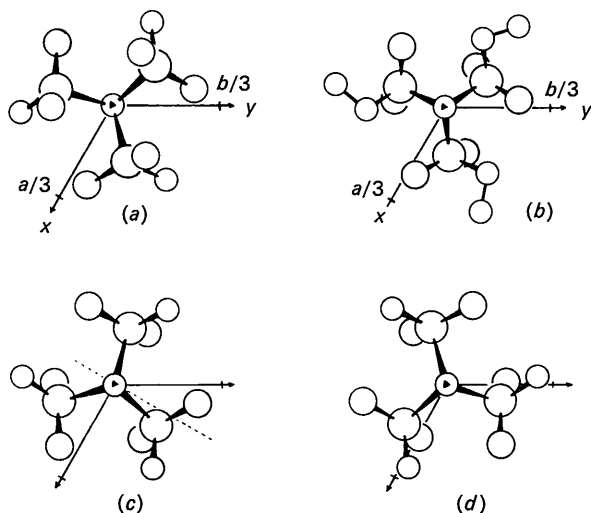


Fig. 3. Relationship between the structure of TESM and TMSM.

tions of standard molecules of TMSM and TESM. For the former we have here chosen the major *A* structure. Seen thus, the aspects of the two appear almost identical, except that the CS₃-pyramid points down the *c* axis in one case and up *c* in the other. At first sight this seemed to be a trivial difference, and to support our presupposition that the crystals were isostructural. However, by no operation of *R3c*, nor by inversion, can the difference between (*a*) and (*b*) be bridged. The crystal structures of TMSM and TESM are qualitatively different.

We now seek to illuminate this difference. Since the *A* and *B* structures of TMSM are related by the operation, $x y z \rightarrow \bar{x} \bar{y} \bar{z}$,* they are equivalent for our present purpose. We therefore concentrate attention on the (minor) *B* structure, which is shown in Fig. 3(c). This has the CS₃-pyramid pointing in the same direction as that of TESM. Operation of the *c*-glide on the molecule shown in (c) gives the antimeric molecule at $z + \frac{1}{2}$ shown in (d). Comparison of this with (b) shows that the two molecules, apart from the extra C atom in TESM, whilst presenting almost identical aspects, differ by a rotation of 55° about the *c* axis (which is a triad, not a hexad).

Figs. 4(a) and (b) represent, in each case, the pair of molecules, lying within the *c*-translation related by the *c*-glide. They differ quantitatively in that the azimuthal angle between members of the pair is 23° for TMSM and only 11½° for TESM. But, when cognisance is taken of their environments, the stacks differ qualitatively: the line bisecting the 23 degree angle between TMSM molecules points towards an equivalent stack at *c*/6, whilst that bisecting the 11½ degree angle between TESM molecules points towards a stack at $-c/6$.

The lateral packing of stacks is therefore different in the two structures. Our understanding of intermolecular forces is perhaps insufficiently detailed to warrant speculation on the factors which cause these very similar molecules to adopt different ways of packing of their stacks. If we did understand these factors, we should be in a better position to explain why TMSM adopts a disordered stacking which gives rise to such dramatic diffuse reflexions.

We wish to record our indebtedness to the Science Research Council for a grant which enabled D. R. McGregor to take part in this work. We have had a valuable correspondence with Drs Silverton and Abra-

* The operation to convert *A* to *B* given by Silverton *et al.* (1965) is $x y z \rightarrow y, x, \frac{1}{2} - z$; when applied to $\bar{y}, \bar{x}, \frac{1}{2} - z$, the space-group equivalent of $x y z$, it yields $\bar{x} \bar{y} \bar{z}$.

Table 6. Structure-factor analysis

Range of $ F_o $	0-10	10-20	20-30	30-40	40-50	50-60	60-70	> 70
No. in batch	116	204	133	76	45	20	20	23
Average Δ	2.3	1.6	1.7	1.6	1.4	2.0	1.5	1.9
R	0.46	0.107	0.068	0.046	0.031	0.036	0.023	0.022

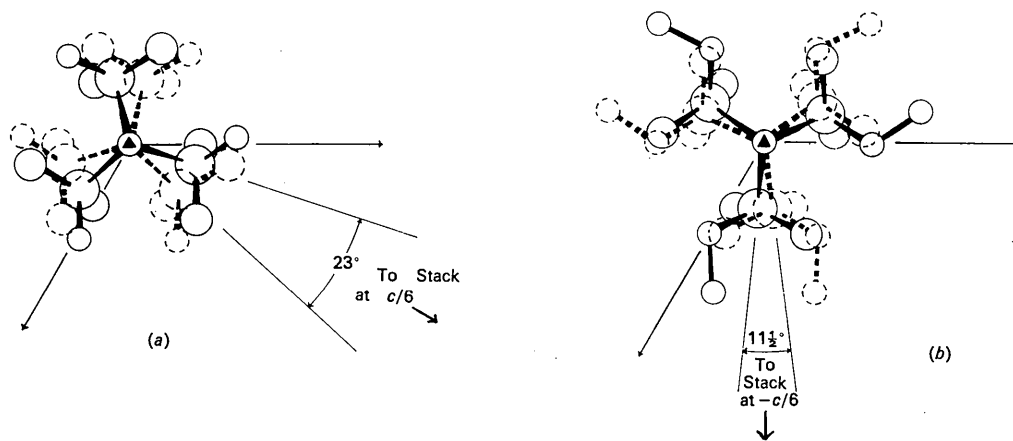


Fig. 4. Relationship between the stacking of molecules in TMSM-B and in TESM.

hams concerning the relationship between the structures of TMSM and TESM. We also wish to thank Dr D. T. Gibson (1931) who prepared these compounds, and whose enthusiasm for them stimulated us to undertake such interesting studies.

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La Liaison Hydrogène Bifide

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(Reçu le 18 mars 1968)

Bifurcated hydrogen bonds exist in all naphthoquinonic compounds which have a hydroxyl or amino group in the β position. There are chelation and intermolecular bonds, the existence of which is proved by crystallographic and infrared analysis. Sokolov's hydrogen bond theory explains the geometry of bonds distributed about the hydrogen atom.

L'existence de la liaison hydrogène bifide est admise depuis longtemps par les structurographes (Marsh, 1958). Mais elle ne fut mise en évidence de façon certaine que récemment par Craven & Takei (1964) dans le cristal d'acide violurique monohydraté.

La persistance de la liaison hydrogène bifide en solution a été démontrée par Dyll & Kemp (1966); l'étude des effets des solvants sur le dérivé orthonitré de la *N*-méthylaniline a amené ces auteurs à conclure que '... l'hydrogène amine peut simultanément former des liaisons hydrogène et avec le groupement NO_2 en *ortho* et avec le solvant'.

