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The Crystal Structure of 1,3,5-Trithiane: A Refinement*

By G. VALLE, V. BUSETTI AND M. MAMMI

Centri di Strutturistica e di Chimica delle Macromolecole del CNR, Istituto di Chimica Organica dell'Università, 35100 Padova, Italy

AND G. CARAZZOLO

Centro Ricerche Resine, Montecatini-Edison, 21053 Castellanza (Varese), Italy

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The crystal structure of 1,3,5-trithiane (orthorhombic, space group $Pmn2_1$, $a=7.668$, $b=7.003$, $c=5.285$ Å; $Z=2$) has been refined by the full-matrix least-squares method with photographic three-dimensional data. Final values of the molecular parameters are: C-S = 1.814 ± 0.009 Å, C-S-C = $98.9 \pm 0.6^\circ$, S-C-S = $114.7 \pm 0.7^\circ$. R index, 6.9%. The crystal packing is discussed also in connexion with the observed anisotropic thermal vibrations.

Introduction

A knowledge of the structure of trithiane was a basic requirement for the investigation of the solid-state polymerization of trithiane (Lando & Stannett, 1964; Carazzolo & Mammi, 1964) and for the correlation of the crystallographic features of the polymer and the monomer (Mammi, Carazzolo & Valle, 1965; Mammi, Valle & Carazzolo, 1968 and references therein). The structure, first determined by Moerman & Wiebenga (1937) and later confirmed by Valle, Carazzolo &

Mammi (1965), has now been refined by three-dimensional data.

Experimental

The single crystals of trithiane used in the analysis were obtained by sublimation at 180°C in the form of long transparent prisms elongated along the c axis and with nearly square cross-sections. Cell parameters were determined on Weissenberg and precession photographs, with Cu $K\alpha$ and Mo $K\alpha$ radiations.

Crystal data

Trithiane, $\text{C}_3\text{H}_6\text{S}_3$, F.W. 138.3, m.p. 215°C . Orthorhombic, space group $Pmn2_1-C_{2v}^7$. $a=7.668 \pm 0.005$, $b=7.003 \pm 0.005$, $c=5.285 \pm 0.005$ Å,

* Work carried out with CNR aid. A report has been given at the VIIth International Congress of I.U.Cr., Moscow, 1966, paper 8-66.

Refinement and discussion

The cyclic molecules are in the special position m , so that half a ring corresponds to the asymmetric unit.

The atomic coordinates of the two-dimensional determination (Valle *et al.*, 1965) were first refined by four cycles of differential synthesis (Nardelli, Musatti, Domiano & Andreotti, 1965), which gave shifts as large as 0.05 Å in z and less than 0.01 Å in the x and y coordinates, the isotropic thermal parameters being kept constant. The residual R decreased from 12.4 to 8.6%.

A fixed contribution for the hydrogen atoms, with coordinates calculated from a model and $B=2.5 \text{ \AA}^2$, was then introduced in two cycles of full-matrix least-squares refinement of the anisotropic thermal parameters. The Cruickshank (1961) weighting scheme was used in the Busing, Martin & Levy *ORFLS* program (1962), as adapted in the *X-ray 63 Program System for X-ray Crystallography* (1965), on an IBM 7094/7040 DCS computer. The refinement fully converged without significant changes in the atomic coordinates and reduced the residual to 6.9% (7.1% without the H atom contribution or 8.2% without accounting for anisotropic vibrations).

The final coordinates, anisotropic thermal parameters and estimated standard deviations so obtained are given in Table 1 and the observed and calculated structure factors in Table 2. Atomic scattering factors by Forsyth & Wells (1959) were used.

Intramolecular distances and angles are listed in Table 3. Their standard deviations were calculated according to Ahmed & Cruickshank (1953) and Darlow (1960), respectively. The values do not deviate significantly from symmetry $3m$, the averages being C-S, 1.814 Å; C-S-C, 98.9°; S-C-S, 114.7° (the previous corresponding values of the two-dimensional analysis were 1.812 Å, 100.6° and 115.7°).

Table 3. *Intramolecular distances (Å) and angles (°), with e.s.d.'s (in parentheses)*

The asterisk denotes the atoms related by mirror plane, at \bar{x}, y, z .

S(1)-C(2)	1.814 (8)	C(2)-S(1)-C(1)	98.9 (5)
S(1)-C(1)	1.816 (8)	C(1)-S(2)-C(1*)	98.9 (6)
S(2)-C(1)	1.811 (10)	S(2)-C(1)-S(1)	114.6 (5)
		S(1)-C(2)-S(1*)	114.9 (8)
S(1)-S(1*)	3.058 (5)	S(2)-S(1)-S(1*)	59.9 (1)
S(1)-S(2)	3.052 (6)	S(1)-S(2)-S(1*)	60.1 (1)
C(1)-C(1*)	2.751 (22)	C(2)-C(1)-C(1*)	60.1 (4)
C(1)-C(2)	2.759 (24)	C(1)-C(2)-C(1*)	59.8 (4)

The value of the carbon valence angle, larger than the tetrahedral, is not unusual for this type of cyclic molecule; *e.g.* 114.5° has been found in 1,3,5-trithioacetaldehyde (Hassel & Viervoll, 1947), 112.5° in 1,4-dithiane (Marsh, 1955), and 114.5° in the isostruc-

tural 1,3,5-triselenane (Mammi, Carazzolo, Valle & Del Pra, 1968).

The plane of the three sulphur atoms and that of the three carbon atoms in the chair molecule are nearly parallel to each other (0.3°) at a distance of 0.67 Å. The molecular plane is tilted by ~33° from the ab plane. The internal rotation angles of the bonds C(2)-S(1), S(1)-C(1) and C(1)-S(2) are 66.1°, 66.5°, 66.9° respectively. The same value (66.0°) was also found in the corresponding polymer chain, where conformational constraints are much less than in the cyclic structure (Carazzolo & Valle, 1966).

Table 4 gives the principal axes of the ellipsoids: although a detailed analysis for rigid body motion has not been carried out, a large translational tensor component in the direction normal to the molecular plane is quite evident (Fig. 1). Moreover, the minimum thermal vibration axis of each atom lies nearly in the plane of its two ring-bonds and is not directed along any of its C---S intermolecular contacts.

Table 4. *Principal axes of the vibration ellipsoids*

Root mean square displacements U_i and angles θ with the crystallographic axes.

	Axis(i)	U_i	θ_{ia}	θ_{ib}	θ_{ic}
S(1)	1	0.1255 Å	31.7°	77.1°	61.6°
	2	0.1666	68.9	155.2	102.5
	3	0.1811	112.6	110.8	31.5
S(2)	1	0.1289	90.0	36.4	53.6
	2	0.1572	180.0	90.0	90.0
	3	0.1849	90.0	126.4	36.4
C(1)	1	0.0759	95.6	53.6	37.0
	2	0.1560	131.6	129.5	66.9
	3	0.2168	42.2	119.5	62.9
C(2)	1	0.1469	90.0	12.9	77.1
	2	0.1741	180.0	90.0	90.0
	3	0.2143	90.0	102.9	12.9

In fact, five C---S contacts are observed for each C and each S atom, in the range from 3.7 to 4.0 Å (Table 5 and Fig. 2). Their correlation with the polymerization geometry in the crystalline state has been already discussed (Valle *et al.*, 1965; Mammi, Valle & Carazzolo, 1968). The crystal packing also shows contacts between like atoms, shorter than 3.8 Å; all the other non-hydrogen distances are longer than 4.6 Å, so that a total number of 46 contacts results for each molecule. Further, there are a large number of distances involving hydrogen atoms (46 per molecule) in the range from 2.9 to 3.4 Å (see Table 5). Intermolecular contacts between hydrogen atoms are not observed, the H---H distances being longer than 2.8 Å. The S---S contacts of 3.478 Å are rather short and must be noted; their occurrence in the crystal is in agreement with the directions of the lowest thermal vibration of the S atoms.

Table 5. Shortest intermolecular distances from atoms of the asymmetric unit to neighbouring molecules numbered as indicated below

3.704 Å	C(2)S(1 ^{VIII})	C(2)S(1 ^{II})	S(1)C(2 ^I)
3.788	C(1)S(1 ^{IV})	S(1)C(1 ^{III})	
3.793	C(1)S(2 ^{IV})	S(2)C(1 ^{III})	S(2)C(1 ^V)
3.822	S(1)C(1 ^I)	C(1)S(1 ^{II})	
3.857	C(1)S(2 ^{III})	S(2)C(1 ^{IV})	S(2)C(1 ^{VI})
3.942	C(2)S(1 ^{VII})	C(2)S(1 ^I)	S(1)C(2 ^{II})
3.947	S(1)C(1 ^X)	C(1)S(1 ^X)	
4.028	C(2)S(2 ^{XI})	S(2)C(2 ^{XII})	
3.478	S(2)S(1 ^{IV})	S(2)S(1 ^{VI})	S(1)S(2 ^{III})
3.706	S(1)S(1 ^I)	S(1)S(1 ^{II})	
3.758	C(1)C(1 ^{III})	C(1)C(1 ^{IV})	
3.790	C(1)C(2 ^{II})	C(2)C(1 ^I)	C(2)C(1 ^{VII})

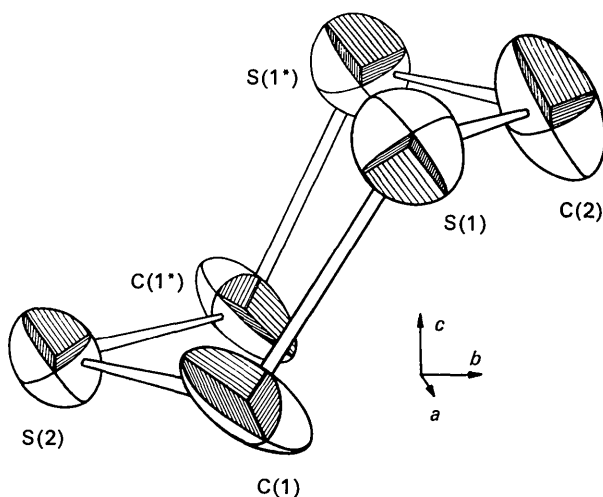


Fig. 1. Vibrational ellipsoids in the trithiane molecule viewed perpendicularly to the *c* axis and nearly along the *a* axis. The asterisk denotes atoms related by a mirror plane.

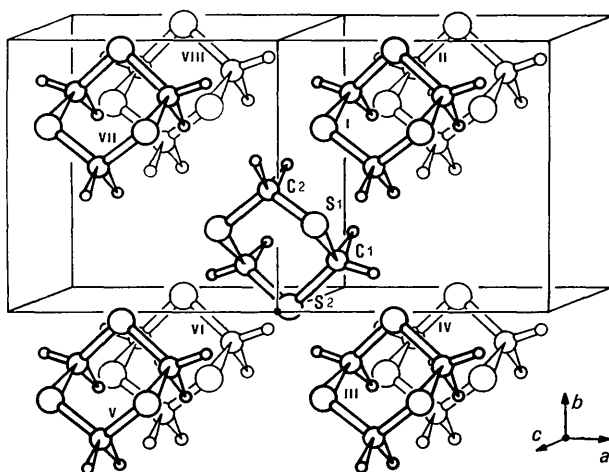


Fig. 2. View of the trithiane molecule (with atoms at *x*, *y*, *z*) and of the eight surrounding molecules in the alternative orientation. The numbers I to VIII indicate the half-molecules whose equivalent positions are listed in Table 5.

Table 5 (cont.)

Distances involving hydrogen atoms.

2.95 Å	S(1)H(4 ^I)	H(4)S(1 ^{II})	H(4)S(1 ^{VIII})
3.00	S(1)H(2 ^X)	H(2)S(1 ^{IX})	
3.01	S(2)H(1 ^{III})	S(2)H(1 ^V)	H(1)S(2 ^{IV})
3.09	S(1)H(2 ^I)	H(2)S(1 ^{II})	
3.10	C(1)H(3 ^{II})	H(3)C(1 ^I)	H(3)C(1 ^{VII})
3.11	S(1)H(1 ^{III})	H(1)S(1 ^{IV})	
3.16	C(1)H(1 ^{III})	H(1)C(1 ^{IV})	
3.18	S(1)H(3 ^{II})	H(3)S(1 ^I)	H(3)S(1 ^{VII})
3.27	C(2)H(2 ^I)	C(2)H(2 ^{VII})	H(2)C(2 ^{II})
3.28	S(2)H(1 ^{IV})	S(2)H(1 ^{VI})	H(1)S(2 ^{III})
3.34	C(1)H(1 ^{IV})	H(1)C(1 ^{III})	
3.38	S(2)H(4 ^{XII})	H(4)S(2 ^{XI})	

I	$\frac{1}{2}-x$,	$1-y$,	$\frac{1}{2}+z$
II	$\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}+z$
III	$\frac{1}{2}-x$,	$-y$,	$\frac{1}{2}+z$
IV	$\frac{1}{2}-x$,	$-y$,	$-\frac{1}{2}+z$
V	$-\frac{1}{2}+x$,	$-y$,	$\frac{1}{2}+z$
VI	$-\frac{1}{2}+x$,	$-y$,	$-\frac{1}{2}+z$
VII	$-\frac{1}{2}+x$,	$1-y$,	$\frac{1}{2}+z$
VIII	$-\frac{1}{2}+x$,	$1-y$,	$-\frac{1}{2}+z$
IX	x ,	y ,	$-1+z$
X	x ,	y ,	$1+z$
XI	x ,	$1+y$,	z
XII	x ,	$-1+y$,	z

The above considerations of the approach between molecules, the high value (0.80) of the packing coefficient (Kitaigorodskii, 1961) and the remarkably low thermal vibration are supporting evidence for a very rigid structure in the trithiane crystals.

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The Crystal Structure of (\pm)-Elaeocarpine Hydrobromide

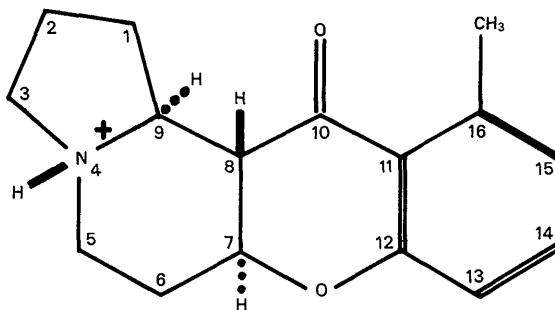
BY J. A. WUNDERLICH

Division of Applied Chemistry, C.S.I.R.O., Chemical Research Laboratories, Box 4331, G.P.O., Melbourne, Victoria 3001, Australia

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The structure of elaeocarpine ($C_{16}H_{19}NO_2$), the first member of a new class of indolizidine alkaloids, has been determined as its hydrobromide salt. The crystals are triclinic with $a=12.46$, $b=7.38$, $c=8.05$ Å; $\alpha=96.1$, $\beta=92.8$, $\gamma=94.0^\circ$. Since the space group, determined by the $N(z)$ versus z test, is $P\bar{1}$ the base is a racemate. The bromine, carbon, nitrogen and oxygen and fifteen hydrogen atom sites were determined from the Patterson, electron density and difference maps respectively and refinement was carried out by full-matrix least-squares methods to a final R value of 0.131.

The structure and relative stereochemistry are shown below:



The two *trans* ring junctions result in a roughly flat molecule. Steric interaction between the carbonyl and methyl groups results in an out-of-plane distortion of the carbonyl group as well as an in-plane angular distortion of the bond between the methyl group and the aromatic ring.

Introduction

Several *Elaeocarpus* species, large trees of the rain forests of New Guinea, have been found to contain as many as five different alkaloids (Johns, Lambertson & Sioumis, 1968a). Preliminary chemical studies indicated that these alkaloids were closely related structurally and represented the first members of a new class of

indolizidine alkaloids. It was therefore decided to determine the structure of one base by X-ray crystallography in the hope that the structures of the other bases could be established from their relationship to the known alkaloid, with the use of standard chemical and spectroscopic, especially nuclear magnetic resonance, techniques. The base chosen for the crystal structure analysis, named elaeocarpine, was extracted from