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THE CRYSTAL AND MOLECULAR STRUCTURE OF 3,3,6,6-TETRAMETHYL-S-TETRATHIANE, $[(CH_3)_2CS_2]_2$

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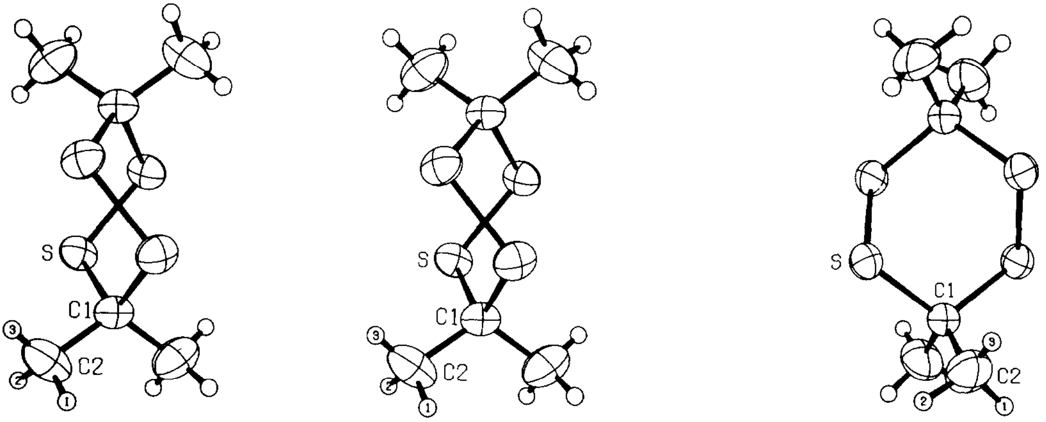
The X-ray crystal structure of 3,3,6,6-tetramethyl-s-tetrathiane ("duplodithioacetone") confirms earlier nmr studies predicting the molecule to adopt a twist-boat conformation.

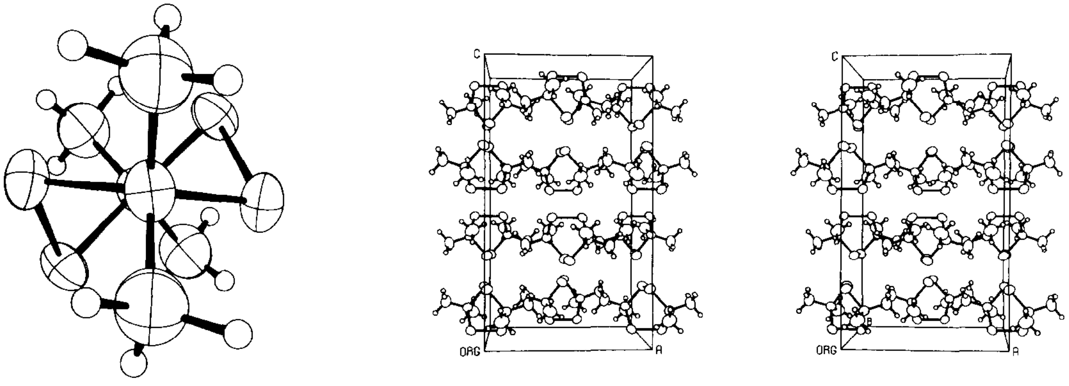
The title compound (I), also known as "duplodithioacetone," was prepared in 1887 by Willgerodt, who correctly assumed that $(CH_3)_2CS_2$ was actually a dimer.[1] This and related substances were investigated by Fredga,[2] who indicated an X-ray study was in progress at that time (1958) which seemed to show a "boat" conformation.[3] We have, however, been unable to locate any structural report in the literature and assume the project was abandoned.

In 1969, Bushweller published a solution nmr study of this molecule which indicated that the twist-boat conformation is favored over the "chair" conformer.[4] Curiously, the predominant form for the corresponding oxygen heterocycle (acetone diperoxide) has been shown to be a "chair" in solution[5] and crystalline bis(C_5H_{10})-s-tetrathiane is also chair.[6] A recent report by MacNicol and Murphy[7] shows that the question of conformation and interconversion in this system is still a lively one and prompts us to, herein, report the final results of our X-ray study of (I) <u>in the solid state</u>.

Crystals of (I) are tetragonal, space group $I4_1/acd$, with a = 10.565(2), c = 18.344(3) Å, and z = 8. The origin was positioned at $\bar{1}$, in compliance with restrictions imposed by the SHELX least-squares program.[8] A total of 409 unique reflections was collected using MoKα radiation, to a limit of 54°(2θ). The phase problem was solved by MULTAN[9] and the molecule was found to lie along the diagonal two-fold axis (C1 at special position x, 1/4+x, 1/8) centered about a crystallographic 222 position. With 36 independent variables, the least-squares refinement converged to $R = R_w = 0.026$. Final atomic coordinates are given in Table 1, along with other pertinent structural parameters. Figures 1-3 show the molecule as viewed down each of the mutually orthogonal two-fold axes inherent to the D_2 point symmetry. Figure 1 especially shows the twist-boat geometry, which can be thought of as two tetrahedra fused at an angle of 50° to each other. The coordination around C1 is not exactly tetrahedral (see Table 1D; Fig. 3), a phenomenon seen in compounds such as dimethylsulphane and attributed to methyl-sulfur repulsions.[10] Although the solid state structure of the



Figures 1 and 2. Two views of the molecule approximately along the two-fold axes demanded by crystallographic symmetry. Figure 1 is a stereo pair. Only those atoms which are crystallographically unique are labelled.



Figures 3 and 4. A view approximately along the third two-fold axis, which coincides with the C--C vector across the ring. Note the staggering (by 50°) of the two tetrahedra centered on the methylene carbons. Figure 4 is a packing diagram, in stereo.

oxygen analogue is unknown, several derivatives have been studied (e.g., dimeric cyclohexanone peroxide[11]) and have been found to be in the chair conformation. These too show an asymmetric environment at the spiro carbon due to H...0 contacts.

The S--S bond length of 2.015 Å is among the shorter values reported in the literature, and is significantly smaller than the value of 2.08 Å usually assumed for a single bond. This suggests some degree of multiple bonding via the sulfur d orbitals and, as noted much earlier by Hordvik,[12] there is a definite relationship between the S--S distance and the C-S-S-C angle. The bond length is greatest when the lone pairs produce maximum repulsion (torsion angle = 0°) and least when the d_π - p_π overlap is maximized (90°). We have recently studied several compounds having angles at one of the extremes (0° or 90°)[13] and some intermediate,[14] all of which serve to confirm this relationship. The present results are quite close to those found in orthorhombic sulfur (S_8; 2.037 Å, 80.7°)[15] but different from those in the S_6 chair (2.06 Å, 74°).[16] The S--C bond length of 1.843 Å is indicative of a pure single bond, and the average endocyclic torsion angle (51°) is only slightly less than that of cyclohexane itself (54°). Figure 4 shows the layered packing of the molecules, and the near perfect alignment of the S--S vectors with the a and b axes accounts for the difficulty found in attempting to interpret the Patterson map.

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TABLE 1

A. Atomic Coordinates

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
S	0.49052(6)	0.65511(5)	0.19979(2)	H1	0.335(3)	0.474(3)	0.067(1)
C1	0.3774(2)	0.6274(2)	0.1250	H2	0.406(3)	0.428(4)	0.142(2)
C2	0.4006(4)	0.4925(3)	0.1006(2)	H3	0.478(3)	0.489(3)	0.079(1)

B. Bond Lengths(Å) and Angles(°)

Bond	Length	Angle	Value
S - S'	2.015(1)	S - C1 - C2	105.4(2)
S - C1	1.843(2)	S - C1 - S"	110.3(1)
C1 - C2	1.514(3)	S - C1 - C2"	111.4(1)
C2 - H1	0.95(3)	C2 - C1 - C2"	113.1(3)
C2 - H2	1.03(3)	S' - S - C1	102.9(1)
C2 - H3	0.91(3)		

C. Torsional Angles(°)

C1 - S - S' - C1'	-80.41	S' - S - C1 - C2"	-80.59
S' - S - C1 - C2	156.44	S' - S - C1 - S"	36.08

D. Dihedral Angles (See Figure 3)

Plane S-C1-S" vs. Plane C2-C1-C2" = 85.8°

Plane S-C1-S" vs. Plane S'-C1'-S"' = 49.9°

E. Ring Puckering Parameters

q_2 = 1.276 ϕ_2 = 30.0 θ = 90.0

q_3 = 0.0 Q = 1.276

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