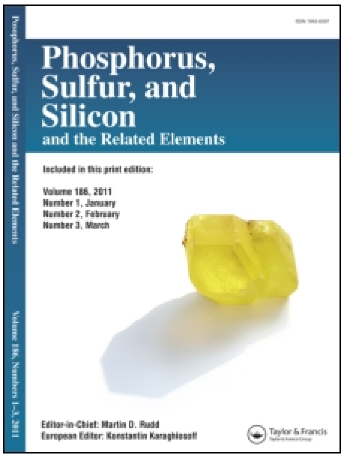

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CONFIGURATION OF OCTADECYL TETRASULFIDE

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Open-chain organic tetrasulfides can exist in three distinct conformations known as *cis-cis*, *cis-trans*, and *trans-trans* forms. Previously, the structure of only one other open chain organic tetrasulfide, benzylidenimine tetrasulfide, has been established and this compound has a *cis-cis* configuration. Now we can report that octadecyl tetrasulfide crystallizes in the *trans-trans* form, is nonbranched, nonplanar, and has two different sulfur-sulfur bondings. Its central S-S bond (2.060A°) is longer than the terminal S-S bond (2.018A°). The central bond length of 2.060A° is close to the average value of 2.08A° selected by Pauling as a normal S-S single bond. Terminal bond lengths of 2.018A° represent another type of S-S bonding that displays some double bond character. A central torsion angle (dihedral angle) is 65.3 (±2)° and this is considerably less than the optimum value of 90° postulated by Pauling. Octadecyl tetrasulfide crystallizes in the monoclinic space group C2/c with $a = 5.44$A°, $b = 9.43$A°, $c = 78.3$A°, $\beta = 90.6$°, and $z = 4$. The compound is stable at ordinary laboratory temperatures under indirect lighting.

We wish to report the characterization of octadecyl tetrasulfide (19, 20, 21, 22-tetrathiatetracontane) and to establish that its crystals consist of right- and left-handed *trans,trans* conformers. Symmetric organic tetrasulfides can exist in three distinct conformations known as the *cis,cis*, *cis, trans*, and *trans,trans* forms (Figure 1). Since each of these is chiral, it may exist in a right- or left-handed configuration. A tetrasulfide contains two successive SSS planes. Thus, four conformers are possible; but if the terminal groups are identical, the *cis,trans* and *trans,cis* forms are indistinguishable. The *cis,trans* nomenclature in these compounds refers to the steric relationship of the two groups bonded to the ends of each trisulfide grouping in the molecule. The nature of S—S bonding is such that these two groups will be rotated appreciably out of the trisulfide plane. Torsion angles reported are in accord with the definition of Klyne,[1] see Figure 1.

Conversion of a polysulfide molecule from one form to another requires large (ca. 180°) rotations about nominally single S—S bonds, but no inversion or bond breaking. Thus, it is likely

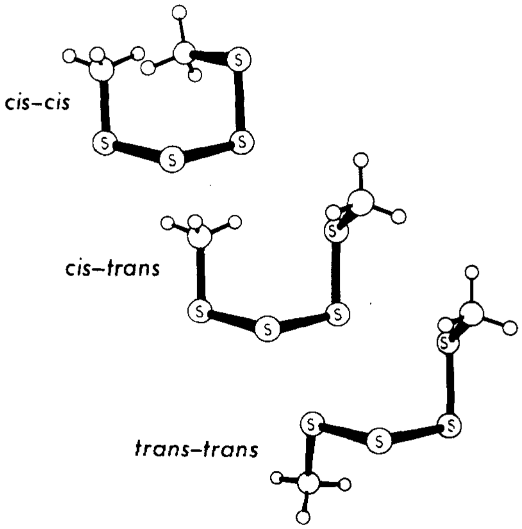

FIGURE 1 Schematic representation of the three rotational isomers of a symmetrically substituted tetrasulfide.

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that solutions will contain an equilibrium mixture of several of these forms. However, crystallization usually leads to one pure conformer depending upon energies of the various forms from a solution mixture. Tsurugi[2] isolated two different cyrstalline forms of dibenzhydryl tetrasulfide and concluded that the two forms are rotational isomers, but they did not characterize their structures. Sulfur itself crystallizes in *cis,cis* forms (S_6, S_8 rings) and *trans,trans* forms (the helical polymers of fibrous sulfur). In inorganic crystals, the *cis,cis* grouping is most often found in tetrasulfides which are part of rings. However, the acyclic hexathionate ion $(O_3S{-}S_4{-}SO_3)^{-2}$ exists in the *cis,cis* form in one crystal, $K_2Ba(S_6S_6)_2$,[3] and in the *trans,trans* form in another, $[Co(en)_2Cl_2]_2S_6O_6 \cdot H_2O$.[4] A review of the structural reports on organic polysulfides revealed only one other open-chain tetrasulfide. The crystallographic analysis of benzylidenimine tetrasulfide[5] showed that it is in the *cis,cis* form despite the absence of ring closure constraints.

Dialkyltetrasulfides can be prepared by reacting mercaptans with sulfur monochloride.[6] A 0.025 M hexane solution of sulfur monochloride was added dropwise with cooling to a 0.05 M hexane solution of octadecyl mercaptan. Hydrogen chloride evolved during addition. The solution was refluxed for 1 h and then cooled to room temperature, admixed with dry acetone, and refrigerated at 5°C. After filtration, crystals were vacuum dried at 25°C. Yield: 15.1 g; mp 44–45°C; calcd. for $C_{36}H_{74}S_4$: C, 68.07; H, 11.74; S. 20.19; Found: C, 67.86; H, 11.04; S, 19.31. Very thin plates of octadecyl tetrasulfide were crystallized by slowly evaporating *n*-octanol solutions.

A mass spectrum[7] showed a parent ion of 634 along with a 318 fragment resulting from symmetric cleavage and rearrangement. Besides the usual hydrocarbon carbon fragments, peaks were observed at 285, 256, 224, 192, 160, 128, 96, 64, and 32. High resolution peak matching identified the fragments at 128, 160, 192, and 256 as sulfur species. A literature search failed to show mass spectra of similar dialkyltetrasulfides. The mass spectrum though is consistent for one expected of an organic tetrasulfide. Polysulfides are reported to have weak S—S bonds,[8] and the appearance of sulfur species in the mass spectrum is not too surprising.

Nuclear magnetic resonance measurements showed a chemical shift of 2.91 ppm [relative to external $Si(CH_3)_4$] downfield for the α-methylene protons. This shift is attributed to the electronegativity of the sulfur moiety and is similar to a shift reported for dibutyl tetrasulfide.[9] The *d* orbitals of sulfur have been used in explanations of the electron rich and polar characteristics of sulfur-sulfur bonds.[10] One of the objectives of our current studies is to acquire additional information on sulfur-sulfur bonding.

Raman spectroscopy has been used in demonstrating rotational isomerism in disulfides.[11] We obtained spectra[7] on the tetrasulfide by the 180° angle technique on crystals at 1° and on the melt at 58°. A very strong peak at 488 cm^{-1} and a strong peak at 432 cm^{-1} were observed for the solid state; but a reversal was noted in the liquid state, a very strong peak occurred at 437 cm^{-1} and a strong peak at 488 cm^{-1} (Figure 4). The band at 437 cm^{-1} is attributed to a rotamer such as a *cis,trans* or *cis,cis* enantiomer. The peak at 488 cm^{-1} can be attributed to a *trans,trans* isomer. Table I lists vibrational frequencies (cm^{-1}) for solid sodium tetrasulfide[12] in comparison with our values on solid octadecyl tetrasulfide. Identical numbers of 123, 213, and 278 cm^{-1} were common to both specimens and these bands are assigned to S—S bending and torsion. The S—S stretching vibrations at 410, 432, and 488 cm^{-1} for octadecyl tetrasulfide vary from values of 424, 448, and 481 cm^{-1} reported by Daly on sodium tetrasulfide. Since Raman spectra are not unequivocal for a structure assigned of octadecyl tetrasulfide, we used single crystal analysis by X-ray diffraction.[13]

Analysis of diffraction data from a single crystal showed that octadecyl tetrasulfide crystallizes in the monoclinic space group $C2/_c$ with $a = 5.44A$, $b = 9.43A$, $c = 78.3A$, $\beta = 90.6°$, and

TABLE I

Raman shift wave numbers for solid and liquid octadecyl tetrasulfide compared with data for sodium tetrasulfide[a]

Wave numbers			
Octadecyl tetrasulfide		Sodium tetrasulfide[a]	
Solid (1°C)	Liquid (58°C)	Solid	Aqueous solution
123		123	115
213		209	191
278		278	245
410		424	414
432 (0.19)[b]	437	448	448
488 (0.07)[b]	488	481	497

[a] F. P. Daly and C. W. Brown, *J. Phys. Chem.*, **79**, 350 (1975).

[b] Obtained in benzene solution.

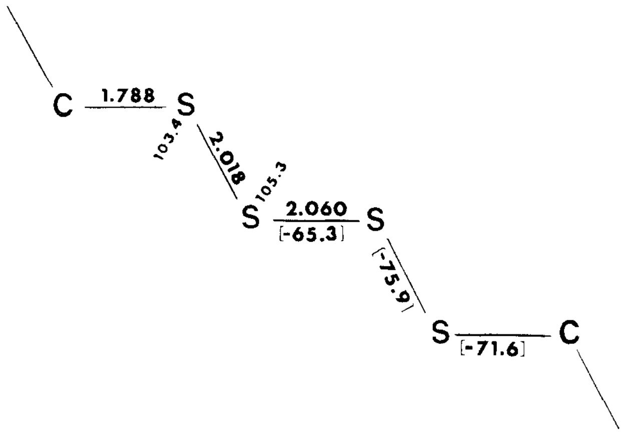

FIGURE 2 Structural parameters of the tetrasulfide linkage; right and left halves are related by a two-fold axis. Torsion angles are given in brackets.

$Z = 4$. Since this space group contains a center of symmetry, the crystal must be composed of an equal number of right- and left-handed versions of the molecule. Structure of octadecyl tetrasulfide was solved by the symbolic addition procedure for centrosymmetric crystals.[14] The structure was refined, using a full-matrix least-squares program, to a crystallographic R-factor of 1.1% for the full set of 1789 observed X-ray intensities. X-ray results showed that the molecule has a *trans,trans* configuration and a two-fold axis of rotation that passes through the central S—S bond. Distances and angles describing the tetrasulfide moiety are given in Figure 2. Figure 3 is a computer-generated[15] perspective drawing of octadecyl tetrasulfide showing the *trans,trans* geometry.

Discrete rotational isomers exist in polysulfide chains because of restricted rotation about the S—S bonds and the existence of two low-energy minima for the torsion angle about each S—S bond. The optimal values for this torsion angle are said to be near ±90°,[16,17] although observed magnitudes commonly vary over a wide range from 70° to 110°. However, there are occasional reports of even larger variations. Torsion magnitudes range from 5° to 135° in the cyclic octasulfur cation, S_8^{2+},[18] and from 0° to 108° in cycloheptasulfur ($\delta - S_7$).[19] The value reported here for the central torsion of octadecyl tetrasulfide, 65.3(±2)°, is exceptionally small, especially considering the apparent lack of intramolecular constraints that might cause torsional strain. It is possible that crystal packing forces combine to produce a net torsional strain that reduces the S—S torsions far below optimal values. Further studies of organic sulfides in various environments may show that this is so, or may alternatively lead to a lowering of the optimal value for saturated organic sulfides.

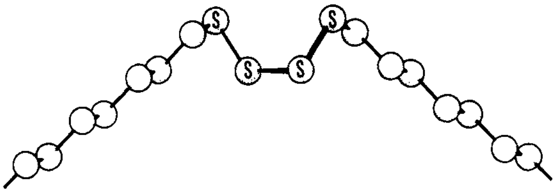

FIGURE 3 A computer-generated[14] representation of the atomic coordinates derived from analysis of X-ray diffraction data.

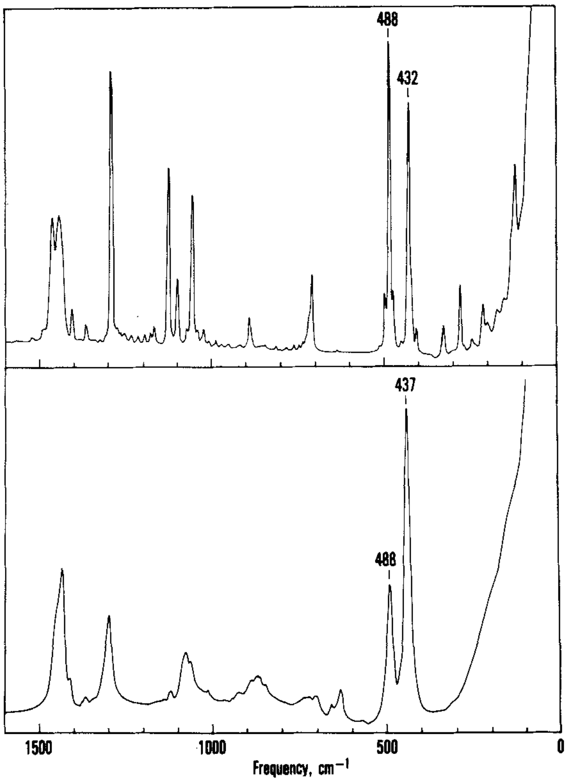

FIGURE 4 Raman spectra of solid octadecyl tetrasulfide (top) and liquid octadecyl tetrasulfide (bottom).

Our results show a longer central S—S bond (2.06 Å) than the terminal S—S bond (2.018 Å). The central bond length of 2.060 Å is close to the average value of 2.08 Å selected by Pauling as a normal S—S single bond. Terminal bond lengths of 2.018 Å represent another type of S—S bonding that displays some double bond character. Questions on bonding and torsional strain cannot be considered settled yet. Our value for C-S distance of 1.788 Å is only slightly less than the normal C-S single bond length of 1.82 to 1.83 Å and considerably more than the 1.61 Å value chosen by Abrahams as the best value for carbon-sulfur double bond.

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