

# Synthesis and Structure of a Novel Macrocyclic Polydisulfide<sup>1</sup>

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**Abstract:** A new 16-membered ring compound, 1,1,5,5,9,9,13,13-octamethyl-3,4,7,8,11,12,15,16-octathiacyclohexadecane (I), was synthesized by reaction of ethanolic sodium hydrosulfide with an isobutylene-sulfur monochloride adduct, with 2-chloro-2-methylpropyl disulfide, with methallyl disulfide, or with sodium methallylthiosulfate. The high-melting acicular and tabular crystals are in the triclinic space group  $P\bar{1}(C_i^1)$  with lattice parameters  $a = 9.590 \pm 0.004 \text{ \AA}$ ,  $b = 10.319 \pm 0.003 \text{ \AA}$ ,  $c = 6.328 \pm 0.001 \text{ \AA}$ ,  $\alpha = 102.48 \pm 0.02^\circ$ ,  $\beta = 90.25 \pm 0.02^\circ$ , and  $\gamma = 101.92 \pm 0.02^\circ$ .

There has been considerable recent interest in macrocyclic sulfur analogues of the crown ethers.<sup>2-7</sup> Most of the work has been directed to sulfides and little is known of macroheterocyclic disulfides or polydisulfides.

The novel 16-membered ring polydisulfide 1,1,5,5,9,9,13,13-octamethyl-3,4,7,8,11,12,15,16-octathiacyclohexadecane (I) has been synthesized by reaction of an isobutylene-sulfur monochloride adduct with ethanolic sodium hydrosulfide. The same product is obtained from reaction of sodium hydrosulfide with 2-chloro-2-methylpropyl disulfide derived from addition of hydrogen chloride to methallyl disulfide or sodium hydrosulfide directly with methallyl disulfide in the presence of hydrogen sulfide. Also, the Bunte salt, sodium methallylthiosulfate, provides I in low yield by reaction with sodium hydrosulfide in ethanol.

Chemical and spectroscopic methods characterized this material as a cyclic compound  $[-SCH_2C(CH_3)_2S-]_n$ . Thus, reduction with lithium aluminum hydride produced 2,2-dimethyl-1,2-ethanedithiol. Owing to its unusually high symmetry, however, neither the value of  $n$  nor the sequence of  $-CH_2-$  and  $>C(CH_3)_2$  groups around the ring could be determined unambiguously. Unusual lubricant antiwear and antioxidant properties which this thermally stable compound was found to have prompted us to initiate a single-crystal X-ray diffraction study to determine its molecular stereochemistry and to establish its structural elements.

X-ray crystallography shows I in the crystalline phase to be a symmetrical 16-membered cyclic tetramer with  $C_i$  symmetry, as illustrated in Figures 1 and 2. The crystals are triclinic, space group  $P\bar{1}(C_i^1)$ , with lattice parameters at  $21 \pm 2^\circ \text{ C}$  of  $a = 9.590 (4) \text{ \AA}$ ,  $b = 10.319 (3) \text{ \AA}$ ,  $c = 6.328 (1) \text{ \AA}$ ,  $\alpha = 102.48 (2)^\circ$ ,  $\beta = 90.25 (2)^\circ$ ,  $\gamma = 101.92 (2)^\circ$ ; observed and calculated densities were 1.31 and 1.337 (4)  $\text{g/cm}^3$ , respectively, for one molecule/unit cell. A total of 1763 reflections with  $F_o \geq 2\sigma(F_o)$  ( $\sin \theta/\lambda \leq 0.650 \text{ \AA}^{-1}$ ) were collected from a single crystal measuring  $0.14 \times 0.16 \times 0.21 \text{ mm}$  using Mo  $K\alpha$  radiation. Full-matrix anisotropic-isotropic least-squares refinement led to final reliability values of  $R = 0.125$  and  $wR = 0.098$  for convergence at  $\Delta/\sigma < 0.05$ . Full details of the structure and its determination will be published elsewhere.<sup>8</sup>

The unique feature is a 16-membered ring consisting of four nearly planar S-C-C-S units linked through sulfur atoms. Such a linkage gives an alternating sequence of S-S and C-C bonds. The two sulfur atoms in the planar S-C-C-S units are trans to one another and the  $CH_2$  and  $C(CH_3)_2$  groups across two linked units, viz.,  $-CH_2SSC(CH_3)_2-$ , adopt gauche positions.

The  $CH_2$  carbon atom deviates the most from the  $SC_2S$  least-squares plane. The hydrogen atoms point inward toward the center of the ring and their distances of approach range from 2.7 to 2.8  $\text{\AA}$ . These values are just slightly greater than

the hydrogen van der Waals radius sum of 2.4  $\text{\AA}$ .<sup>9</sup> Accordingly, the molecule is relatively free of the steric strain which may be present in the lower order homologues.

Interatomic distances are summarized in Figure 2. The ring contains four types of bonds, S-S, S- $CH_2$ , S- $C(CH_3)_2$ , and  $CH_2-C(CH_3)_2$ , there being four of each within a ring. By virtue of the crystallographic  $C_i$  symmetry, two of each are equivalent.

While the single crystal of the polydisulfide used in this investigation was found to comprise molecules having structure I, other isomers such as II and III should also be possible reaction products. X-ray diffraction demonstrates that isomer I is, in fact, the only structure obtained in this reaction. The computed powder pattern<sup>10</sup> for the derived model (isomer I) agrees within experimental error with both the simulated powder pattern<sup>11</sup> derived from the observed single crystal data and the observed powder pattern of the synthesized material. These patterns are compared in Figure 3 and tabulated in Table I. All the lines in the observed powder pattern are accounted for indicating that only lines due to isomer I were observed.

The predominant isomer obtained from the addition of sulfur monochloride to isobutylene has been found by infrared and nuclear magnetic resonance spectroscopic analysis<sup>12</sup> to be 2-chloro-2-methylpropyl disulfide.

An attractive pathway which accounts for the rearrangement to the mixed primary and tertiary alkyl disulfide structure in I involves nucleophilic attack by  $^-SH$  on sulfur accompanied by base-catalyzed elimination of hydrogen chloride to produce methallyl hydrogen disulfide (attack on carbon with subsequent proton transfer cannot be excluded). The hydrodisulfide group then adds in intermolecular reactions to the double bond to give the tetramer which undergoes an intramolecular addition cyclization favored by steric considerations.

In addition to the interest in I as a dithio analogue of the crown ethers, the compound shows unusual antiwear characteristics in a variety of greases and in lubricating oils and possesses unpredicted antioxidant properties in hydrocarbons.<sup>7,8</sup>

## Experimental Section

**A. Preparation of I from the Adduct of Sulfur Monochloride and Isobutylene.** In a typical preparation, sulfur monochloride (10.3 g, 75 mmol) was stirred while keeping the temperature between 45 and 50  $^\circ \text{C}$ , and isobutylene was passed over 60 g of methanol into the reaction flask through a subsurface gas sparger over an 8-h period, during which 716 g (12.8 mol) of isobutylene was absorbed. The reaction mixture was then vacuum stripped at 40  $^\circ \text{C}$  and filtered to yield 1579 g of a light amber liquid adduct. Sodium hydrosulfide (1200 g) in 1250 mL of ethanol was vigorously stirred to get a good dispersion-solution of solids and 620 g of the isobutylene-sulfur monochloride adduct was then added in 2 h keeping the temperature at 40  $^\circ \text{C}$ . The reaction

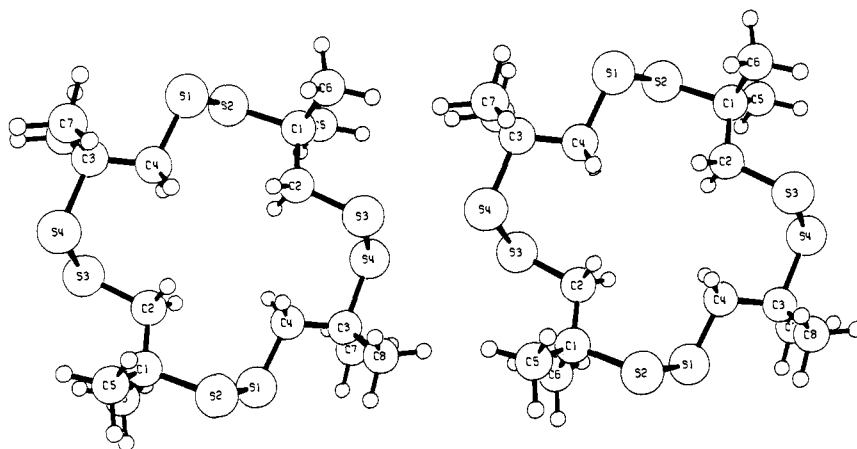
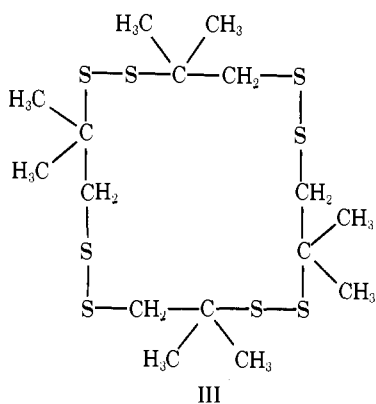
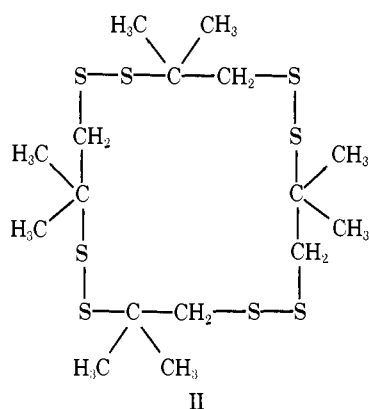
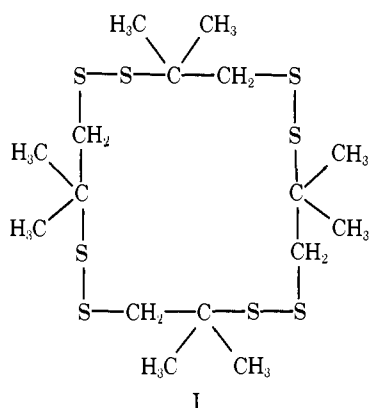


Figure 1. Stereoview of the polydisulfide I molecule. C-H bonds are shown at lengths adjusted to 1.11 Å.



mixture was heated at 45–50 °C for an additional 3 h, cooled, and filtered. The solids were collected and washed with water and ether, leaving an insoluble white product. Some additional solids which precipitated from the filtrate were similarly collected, washed several

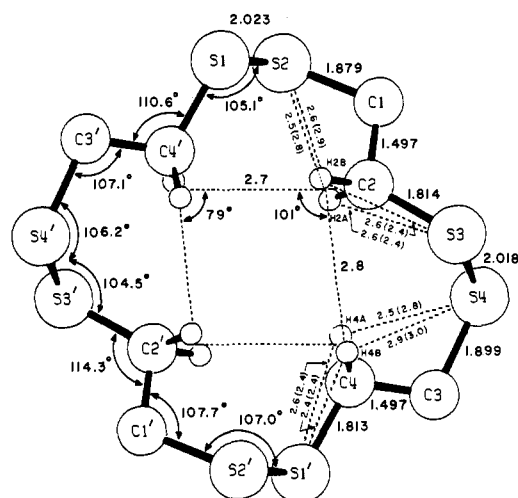


Figure 2. Summary of distances and angles within the 16-membered  $(C_2S_2)_4$  ring. Internal H...H and H...S distances are also shown, based on C-H bonds adjusted to 1.11 Å in length. Numbers in parentheses correspond to theoretical H...S distances when the hydrogens are at tetrahedral positions. Average standard deviations follow: S-S, 0.004 Å; S-C, 0.009 Å; C-C, 0.013 Å; S-S-C, 0.4°; S-C-C, 0.7°; C-C-C, 0.9°.

times with water and ether, and dried. The combined solids were further purified by stirring vigorously in water and a little ether, collected, and dried to yield 250g (45%) of white cyclic polydisulfide, mp 260 °C.

Liquid chromatography showed a single component for the white solid which was soluble in heated dichloromethane, 1,2-dimethoxyethane, and benzene. It had limited solubility in hot *N,N*-dimethylformamide and hot methyl sulfoxide but was very sparingly soluble in other organic solvents.

Elemental analysis corresponding to the empirical composition  $(C_4H_8S_2)_n$  was obtained for the solid product recrystallized from benzene. Anal. Calcd for  $C_4H_8S_2$ : C, 39.96; H, 6.71; S, 53.33. Found: C, 40.04; H, 6.65; S, 53.44. Molecular weight determinations by osmometry were imprecise and unreliable probably owing, in part, to solubility problems in maintaining stable solutions. Three-dimensional X-ray diffraction data determined for I carefully recrystallized from dichloromethane were collected on an automated three-circle diffractometer and used to solve the structure by direct methods. The molecular weight determined from the unit cell volume was 481; thus, the tetramer  $(C_4H_8S_2)_4$  represents the formula of I,  $C_{16}H_{32}S_8$ .

Infrared and  $^1H$  NMR spectra obtained for I were consonant with the tetramer structure established by X-ray crystallography: IR (KBr) 2970 (m), 2960 (m), 2918 (m), 2860 (w), 1450 (s), 1374 (s), 1361 (s), 1257 (s), 1214 (m), 1110 (s), 999 (w), 966 (m), 861 (w), 846 (w), 798 (w), 712 (w), 692 (w), 672 (w), and 615  $cm^{-1}$  (m);  $^1H$  NMR ( $CCl_4$ )  $\delta$  1.30 (s, 3,  $CH_3$ ), 3.18 (s, 1,  $CH_2$ ); UV shows broad band at 250 nm ( $\alpha = 4.05$ ).

Lower yields obtained using other alcohols, methanol, 2-propanol, and ethylene glycol in the isobutylene-S<sub>2</sub>Cl<sub>2</sub> adduct reaction with sodium hydrosulfide were 2, 15, and 4%, respectively.

**B. From 2-Chloro-2-methylpropyl Disulfide.** 2-Chloro-2-methylpropyl disulfide (99 g) (obtained from the addition of hydrogen chloride to methallyl disulfide in ethanol as a pale yellow liquid, bp 100–101 °C at 0.05 mm) was added to sodium hydrosulfide (27 g) in 100 mL of ethanol at 45–47 °C; there was obtained a total of 4.8 g (33%) of white solids not depressed in melting point by admixture with solids of part A and having matching infrared and NMR spectra.

**C. From Methallyl Disulfide.** To 30 g of sodium hydrosulfide in 100 mL of ethanol saturated with hydrogen sulfide was added a solution of 8.7 g of methallyl disulfide in 20 mL of ethanol. From this reaction, there was isolated 3.7 g of the same white solids obtained in A and B above. In addition, 3.5 g of an oil–solids reaction product fraction was estimated to contain about 5% of the same solids (infrared spectrum). In independent experiments, hydrogen sulfide did not add to methallyl disulfide in ethanol and sodium hydrosulfide did not react with methallyl disulfide to form the white solids of A and B in the absence of hydrogen sulfide.

**D. From Sodium Methallylthiosulfate (Bunte Salt).** A mixture of 95 g of sodium methallylthiosulfate (from the reaction of methallyl chloride with sodium thiosulfate) and 135 g of sodium hydrosulfide in 500 mL of ethanol was stirred and heated at 45–50 °C for 3 h while passing hydrogen sulfide into the reaction mixture. The reaction mixture was filtered; the filtrate was taken up in benzene, refiltered, dried, and concentrated by evaporation of solvents. From the residue there was obtained by direct precipitation and column chromatography over neutral alumina (elution by benzene and dichloromethane and trituration of the solvent-free eluent fractions with 30–60 °C petroleum ether) a total of 4.5 g of I.

**Reduction of I to 2,2-Dimethyl-1,2-ethanedithiol.** Thirty grams of I in 1 L of tetrahydrofuran was stirred at reflux with 10 g of LiAlH<sub>4</sub> for 4 h. The solution was treated with water and 15% sulfuric acid and

dried over anhydrous MgSO<sub>4</sub> and the solvent was removed. The residue was distilled to afford 20 g of foul-smelling, oily liquid, bp 134–135 °C, which was identified by elemental analysis and <sup>1</sup>H NMR and infrared spectroscopy as 2,2-dimethyl-1,2-ethanedithiol. Anal. Calcd for C<sub>4</sub>H<sub>10</sub>S<sub>2</sub>: C, 39.34; H, 8.24. Found: C, 40.05; H, 8.22. <sup>1</sup>H NMR (CS<sub>2</sub>): δ 1.42 (s, 3, CH<sub>3</sub>), 2.69 (d, 2, CH<sub>2</sub>), 1.98 (s, 1, CSH), 1.68 (t, 1, CH<sub>2</sub>SH). IR (neat, KBr optics): 2960 (s), 2922 (s), 2862 (s), 2545 (m), 1460 (s), 1445 (m), 1435 (m), 1412 (m), 1380 (s), 1275 (m), 1238 (w), 1200 (m), 1146 (w), 1115 (s), 1012 (w), 975 (w), 920 (w), 862 (w), 832 (w), 812 (w), 720 (m), 692 (m), 622 (m), 575 cm<sup>-1</sup> (m).

**Supplementary Material Available:** Table I, observed and calculated powder data for polydisulfide I, and Figure 3, comparison of the computed and experimental X-ray diffraction patterns (λ = Cu Kα) of polydisulfide I (3 pages). Ordering information is given on any current masthead page.

## References and Notes

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- (12) Nuclear magnetic resonance studies on this and related sulfide and disulfide systems to be reported by Dr. R. F. Bridger.

## Stopped-Flow Kinetics of Proton Transfer Involving Cyclopentadiene Derivatives

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**Abstract:** Rates of protonation of cyclopentadienide ions and deprotonation of cyclopentadienes in aqueous solution have been measured by the stopped-flow method at 30 °C. Substrates investigated include 1-nitro-, 1-formyl-, 1-acetyl-, 1-methoxycarbonyl-, and 1,2-bis(methoxycarbonyl)cyclopentadienes, whose pK<sub>a</sub>s were found to be 3.25, 7.40, 8.84, 10.35, and 5.00, respectively. Plots of the logarithms of the rate constants against pK<sub>a</sub> were found to be roughly linear, falling in the range of scattering of those found previously with nonconjugated nitro and carbonyl compounds. General acid–base catalyses obeyed the Brønsted law with substantial downward deviations of the H<sub>3</sub>O<sup>+</sup>, H<sub>2</sub>O, and OH<sup>-</sup> plots. The reasons for the reduction in rate of proton transfer to and from carbon have been discussed.

Proton transfers between electronegative atoms such as N and O are very fast and diffusion controlled if the process is thermodynamically favorable, whereas those involving carbon are usually quite slow.<sup>1</sup> Numerous examples of such slow proton transfers have been known ever since the first discovery by Hantzsch<sup>2</sup> with nitromethane. Reasons for the reduction in rate of proton transfer involving carbon acids have been discussed by a number of investigators.<sup>1,3–6</sup> The reasons considered include (1) the small hydrogen-bonding ability of carbon acid, (2) the electronic and structural reorganization on going from the acid to its conjugate base (carbanion), and (3) the accompanying reorientation of solvent molecules. The second one is established to be important and the electronic

delocalization in carbanions is often emphasized as a crucial factor to retard the proton transfer. If this is in fact the case, the process involving a carbanion of electronic structure quite different from the others may exhibit some anomalies in its rate.

As a class of carbon acids with such a possibility, we here choose cyclopentadiene derivatives, **1a–5a**. Their conjugate bases, **1b–5b**, are cyclopentadienide ions of 6π aromatic electron delocalization. The rates of proton transfers involving these compounds were directly measured by means of stopped-flow spectrophotometry. Most of the rate measurements so far made with carbon acids have been indirect and limited to nitro alkanes and carbonyl compounds. Cyano and