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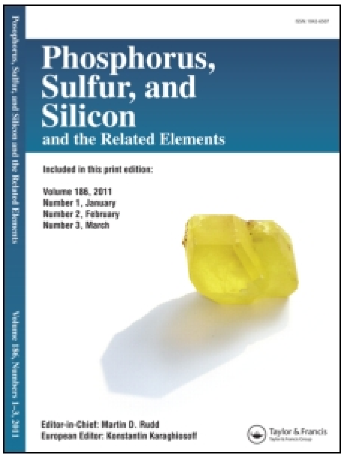

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PREPARATION AND X-RAY CRYSTAL STRUCTURE OF THE CYCLIC DIMER OF 1,2-DITHIOLANE: 1,2,6,7-TETRATHIACYCLODECANE

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PREPARATION AND X-RAY CRYSTAL STRUCTURE OF THE CYCLIC DIMER OF 1,2-DITHIOLANE: 1,2,6,7-TETRATHIACYCLODECANE

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The synthesis and characterization by X-ray crystallography of 1,2,6,7-tetrathiacyclodecane is described. Two routes to the compound are given: (A) Treatment of 1,3-propanethiol with I_2/triethylamine in $CHCl_3$ under titrimetric high dilution conditions and (B) Oxidative cyclization of 1,5,6,10-tetrathiadecane. Recrystallization from hexane yields crystals (mp 131–132°C) belonging to space group $P2_1/n$, with cell dimensions (at 140 K) of $a = 5.195(1)$, $b = 12.446(3)$, $c = 7.427(2)$ Å, $\beta = 106.45(2)°$, $Z = 2$, ρ_{exptl} (298 K) $= 1.50$ g cm^{-3}. Solution and refinement of the structure gave a final R value of 0.033 using 70 parameters and 947 unique observed reflections.

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INTRODUCTION

Oxidized lipoic acid contains a stable 1,2-dithiolane ring, but the unsubstituted 1,2-dithiolane ring is unstable out of solution and polymerizes when attempts are made to isolate it.[1] The cyclic dimer of lipoic acid containing a substituted 1,2,6,7-tetrathiacyclodecane ring is reported to form when lipoic acid is treated with X-rays, but it too was never isolated. Evidence for its existence was based on the lack of recognizable end groups and on the molecular weight (320 in acetone) of a "somewhat rubbery" substance.[2] Likewise numerous reports of the unsubstituted 1,2,6,7-tetrathiacyclodecane ring can be found in the literature but here again definitive evidence for the existence of the molecule is lacking.[3-9] The molecule has at various times been described as a white powder or crystalline material insoluble in water, ethanol, ether (and most organic solvents) but soluble in chloroform, benzene and pyridine. Although analytical data confirmed the stoichiometry, and molecular weight determinations suggested a dimer, the solubility characteristics and low melting point (71 to 77.5°) suggested that the material was a mixture of acyclic oligomers rather than a cyclic dimer. Because of the unusual reported properties, we wondered whether the 1,2,6,7-tetrathiacyclodecane ring system had ever been prepared or whether it, like the substituted 1,2-dithiolane ring system, spontaneously decomposed or disproportionated to monomer and polymer. We have now prepared and characterized for the first time, 1,2,6,7-tetrathiacyclodecane **1** (mp 131–132°C). Since the melting point was appreciably different from that reported previously, an X-ray crystal structure was required to confirm the existence of this ring system.

RESULTS AND DISCUSSION

The conformation of the ten-membered ring is of point symmetry $2/m$ (C_{2h}). This conformation is the same as that found for all crystal structures of derivatives of cyclodecane that have been determined to date,[14,15] except for cyclodecasulfur, which crystallizes in a conformation having D_2 symmetry.[16] Bond distances and angles are normal and agree well with those found for the structure of 1,2,5,6-tetrathiacyclooctane.[17]

Considerable attention has been directed to the effect on conformation and transannular interactions upon substituting a S atom for a CH_2 group. In general, it is found that the smaller C—S—C angles than C—C—C angles will have the effect of increasing the puckering in the medium ring system.[15] For example, torsion angles in 1,6-dithiacyclodecane[15] average 4.2° larger than in those computed for cyclodecane. The same trend is seen in 1,2,6,7-tetrathiacyclodecane, with torsion angles an average of 3.0° larger than in 1,6-dithiacyclodecane. The positions occupied by the sulfur atoms in the ring can be expected to be those that most efficiently remove transannular steric interactions while also avoiding sulfur atom lone pair-lone pair interactions. It is not surprising, therefore, that the S(1) atom in 1,2,6,7-tetrathiacyclodecane occupies the same ring position as the S atom in 1,6-dithiacyclodecane. Upon careful examination, it can also be seen that the S(1)—S(2) group of 1,2,6,7-tetrathiacyclodecane has replaced the CH_2CH_2 group of cyclodecane that exhibits the most severe transannular H—H interactions.[14] The shortest transannular distance is 2.41(1) Å between H(2A) and H(1A)′, close to the sum of their van der Waals radii. However, the H(2A) ··· S(1) contact of 2.70(1) Å is notably less than the sum of the hydrogen and sulfur radii[17] (3.05 Å).

The mass spectrum of 1,2,6,7-tetrathiacyclodecane reveals a base peak at (m/z = 106) which is due to the 1,2-dithiolane cation radical. This peak is often the base peak when two sulfur atoms are separated by three methylene groups and a strong intramolecular interaction can occur.[10,17,19]

As expected 1,2,6,7-tetrathiacyclodecane is soluble in most organic solvents, slightly soluble in ethanol and cold hexane but insoluble in water. Its melting point is appreciably higher (131–132°C) than that reported earlier for this compound.

One nagging question we have been unable to answer is "What is the material that melts near 75° and has a molecular weight of ~ 210?". We have never isolated a pure substance with these characteristics. The TLC of the reaction mixture always exhibits a series of spots which converge at the origin.

EXPERIMENTAL

Synthesis of 1,2,6,7-tetrathiacyclodecane, 1

A. From 1,3-propanedithiol. Employing the procedure previously reported,[10] solutions of 10.8 g (0.100 mol) of 1,3-propanedithiol in 250 ml of $CHCl_3$ and 25.4 g (0.100 mol) of I_2 in 750 ml of $CHCl_3$ were added simultaneously to a vigorously stirred solution of 20.2 g (0.220 mol) of triethylamine in 500 ml of $CHCl_3$ over a 6 h period. After about 5% of the reagents were added, the reaction mixture retained a permanent yellow color due to the formation of the yellow 1,2-dithiolane,[1] hence metering of the reactants in at 1 : 1 mole ratio was not precise. The reaction mixture was washed thoroughly with water, followed by 0.1 N HCl, water, and dried. Removal of solvent at reduced pressure provided 10.6 g (0.050 mol, 100%) of a viscous yellow oil which slowly solidified to a hard mass. Thin layer chromatography on silica plates (pre-coated silica gel 60 F-254, E. Merck) with 4% tetrahydrofuran in hexane as eluant showed a multicomponent mixture with components having R_f's of 0.62, 0.53 (**1**), 0.37, 0.28 and 0.00 (major component). The solid was powdered and refluxed several hours with hexane. The crude product, mp 128–130°C, could be obtained on evaporation of the hexane-soluble fraction. However, purification was more easily accomplished by column chromatography on silica gel. The fractions eluting with 10%

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CH_2Cl_2 in hexane contained the desired compound admixed with small amounts of two impurities. Recrystallization of the combined fraction from hexane provided crystals of **1**, mp 132.5–133.5°C. TLC $R_f = 0.58$ eluted with 4% tetrahydrofuran in hexane. ^1H NMR ($CDCl_3$/TMS) δ 3.03 [t, 3 H, CH_2S], 2.14 [p, 4 H, CH_2]. UV (anhydrous ethanol) λ 254 (ε 690), 209 nm (ε 1700). Raman 502 cm^{-1}. MS (70 eV) *m/z* (relative intensity) 214 (8, M + 2), 213 (4, M + 1), 212 (35, $C_6H_{12}S_4$), 106 (100, $C_3H_6S_2$), 73 (50, C_3H_5S). Compound **1** was insoluble in water, very soluble in acetone, ether, benzene and $CHCl_3$, and moderately soluble in ethanol and hexane.

B. From 1,5,6,10-tetrathiadecane. 1,5,6,10-tetrathiadecane was prepared using the procedure of Frank and Smith.[11] A mixture of 5.3 g (0.029 mol) of 4,5-dithiaoctane-1,8-diol,[12] 5.0 g (0.066 mol) of thiourea and 31 g (0.19 mol) of 48% aqueous HBr was heated under reflux for 9 h. The intermediate isothiouronium salt was decomposed by addition of 7.2 g of sodium hydroxide and 50 ml of water followed by a 2 h reflux. Dilute HCl was used to bring the solution to pH 2. The solution was extracted with ether (4 × 50 ml portions) and dried (Na_2SO_4). After the solvent was removed at reduced pressure 1.65 g (7.7 mmol, 27%) of crude 1,5,6,10-tetrathiadecane was obtained as a yellow oil. ^1H NMR ($CDCl_3$/TMS) δ 2.7 [m, CH_2S], 2.0 [m, CH_2], 1.37 [t, 5 H]. Employing the procedure previously reported,[10] the tetrathiadecane was oxidatively cyclized with I_2 in $CHCl_3$ in the presence of triethylamine. Work up in the same manner gave 1.65 g of a viscous yellow oil which consisted of a multicomponent mixture of compounds by TLC. Column chromatography on silica gel with 10% $CHCl_3$/hexane provided several fractions enriched in **1**. Combination of these fractions (78 mg) and recrystallization from hexane gave 16 mg of **1**, mp 131.5–132.0°C.

X-Ray data collection and structure solution. Crystals of 1,2,6,7-tetrathiacyclodecane, M = 212.42, are colorless, monoclinic, space group $P2_1/n$, with cell dimensions (at 140 K) of $a = 5.195(1)$, $b = 12.446(3)$, $c = 7.427(2)$ Å, $\beta = 106.45(2)°$, $V = 460.5(1)$ Å^3, $Z = 2$, ρ_{exptl} (298 K) = 1.50 g cm^{-3}, ρ_{calcd} (140 K) = 1.53 g cm^{-3}; Mo K_α radiation, $\lambda = 0.71069$ Å, μ(Mo K_α) = 9.2 cm^{-1}. Intensity data were collected on a Syntex $P2_1$ diffractometer at 140 K and corrected for Lorentz and polarization effects but not for absorption. Of the 1054 unique data, 947 with $F > 3\sigma(F)$ were retained for solution and

TABLE I

Atom coordinates (× 10^4)

Atom	*z*	*y*	*z*
S(1)	−370(1)	3150(1)	3764(1)
S(2)	−2217(1)	4139(1)	1600(1)
C(1)	−1135(5)	5521(2)	2288(3)
C(2)	1777(5)	5662(2)	3422(3)
C(3)	2255(5)	6719(2)	4508(4)
H(1A)	−2314(50)	5840(18)	2900(31)
H(1B)	−1428(47)	5893(19)	1097(32)
H(2A)	2397(44)	5014(18)	4275(29)
H(2B)	2971(50)	5616(19)	2565(33)
H(3A)	4178(52)	6812(20)	5108(34)
H(3B)	1667(40)	7406(20)	3724(31)

TABLE II

Bond lengths (Å), Bond angles (deg.) and torsion angles (deg.)

S(1)—S(2)	2.036(1)	S(2)—S(1)—C(3)′	105.9(1)
S(1)—C(3)′	1.829(3)	S(1)—S(2)—C(1)	107.9(1)
S(2)—C(1)	1.836(3)	S(2)—C(1)—C(2)	116.1(2)
C(1)—C(2)	1.519(3)	C(1)—C(2)—C(3)	112.3(2)
C(2)—C(3)	1.526(4)	C(2)—C(3)—S(1)′	114.1(2)
C(3)′—S(1)—S(2)—C(1)	78.6(1)	C(1)—C(2)—C(3)—S(1)′	61.5(2)
S(1)—S(2)—C(1)—C(2)	37.6(2)	C(2)—C(3)—S(1)′—S(2)′	73.7(2)
S(2)—C(1)—C(2)—C(3)	−159.5(2)		

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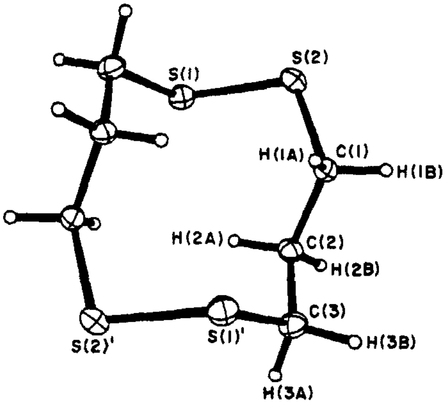

FIGURE 1 A perspective drawing of 1,2,6,7-tetrathiacyclodecane showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level except for those for hydrogen atoms, which have been given an arbitrary size.

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refinement of the structure. The structure was solved by direct methods and Fourier techniques and refined by full-matrix least-squares to a final R value of 0.033. Hydrogen atoms were included in the refinement with isotropic thermal parameters. Non-hydrogen atoms were assigned anisotropic thermal parameters. Atom coordinates, bond lengths, bond angles and torsion angles have been summarized in Tables I and II.[13] A perspective view of the molecule is shown in Figure 1.

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