Tetrahedron Letters,Vol.23,No.32,pp 3231-3234,1982 0040-4039/82/323231-04$03.00/0
Printed in Great Britain

PREPARATION, PROPERTIES AND CRYSTAL STRUCTURE OF 1,2,5,6-TETRATHIACYCLOOCTANE

THE ELUSIVE MESOCYCLIC BIS-DISULFIDE

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Summary: The synthesis of the eight-membered ring containing two disulfides, 1,2,5,6-tetrathiacyclooctane, is described. It is characterized by x-ray crystallography as well as by mass, IR, Raman, 'H-NMR and UV spectroscopy.

In 1887, Fasbender[1] reported that he had synthesized an eight-membered ring containing two disulfides, 1,2,5,6-tetrathiacyclooctane, by treating benzilidineethylenedisulfide with Br_2 in $CHCl_3$. Later, he reported[2] that the same material had formed when 1,2-ethanedithiol was treated with hydroxylamine. Otto and Heydecke[3] synthesized the same substance and agreed that the melting point ranged between 150 and 154°C. Each investigator found that the material was rather insoluble in most organic solvents. Although these properties are cited in many references,[4-11] subsequent investigators[12-14] were skeptical of the ring structure of the compound and considered that the material reported by Fasbender might actually be a polymer. When 1,2-ethanedithiol was treated with chloramine a different polymer melting at 248° was obtained.[12] It was then suggested that Fasbender's polymer was linear whereas the polymer which melted at 248° was highly cross linked. Nevertheless, many investigators still cite Fasbender's erroneous data for the bis-disulfide.

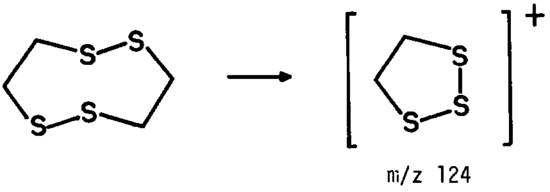
After our recent report[15] of the facile formation of mesocyclic disulfides by titration of dithiols with I_2 in $CHCl_3$, we decided to oxidize 1,2-ethanedithiol under these conditions. The crude solid product melted at 52-80°C, well below all of the melting ranges previously reported. When the solid was chromatographed on silica gel, a number of components were observed. The first few fractions, which were enriched in the oligomers of lowest molecular weight, were redissolved in chloroform. As the chloroform evaporated a colorless crystalline solid deposited above the level of the chloroform. These needles melted at 63-64.5°C and were ideally suited to an X-ray crystal structure determination. The results confirmed that this low melting substance is actually the elusive 1,2,5,6-tetrathiacyclooctane. The rather low melting point for 1,2,5,6-tetrathiacyclooctane is not unexpected. In the series of mesocyclic dithioethers having from 7 to 10 membered rings only the dithiacyclooctanes are liquids.[16]

EXPERIMENTAL

1,2,5,6-Tetrathiacyclooctane(I). Employing the procedure previously reported,[15] solutions of 9.4 g (0.10 mol) of 1,2-ethanedithiol in 250 mL chloroform and 26.6 g (0.105 mol) of iodine in 850 mL of chloroform were added simultaneously to a vigorously stirred solution of 22.2 g (0.220 mol) of triethylamine in 500 mL of chloroform over 5 h. The resulting solution was washed with water (2 x 200 mL) followed by a 0.1 M sulfuric acid wash (200 mL) and again with water. After drying (Na_2SO_4) and removing the solvent at reduced pressure there remained 9.0 g of a yellow solid. Most of the solid melted over the range of 52-80°C but some non-melting solid remained in the melt up to 200°C. Thin layer chromatography on silica plates[17] with 4% tetrahydrofuran in hexane as eluent showed at least seven components with the major components having R_f's of 0.62 (I), 0.49, 0.39, and 0.26. Sublimation of 1.0 g of the mixture at 60° and 0.05 Torr gave 0.517 g (2.80 mmol, 51%), of white solid, mp 63.0-64.5°, showing only a trace of a component less mobile than I by TLC. Slow recrystallization from hexane gave pure I, mp 63.5-65.0°, shown to be free from impurity by TLC; ^{1}H-NMR ($CDCl_3$/TMS) δ 3.15 ppm (s, CH_2S); mass spectrum, m/z, (rel intensity) 186(18), 185(8), 184(100, $C_4H_8S_4$), 156(10, $C_2H_4S_4$), 128(56, S_4), 124(82, $C_2H_4S_3$), 92(37, $C_2H_4S_2$), 64(11, S_2); IR (KBr) 2960(m), 2930(m), 2985(m), 1408(m), 1385(s), 1287(m), 1269(s), 1113(w), 903(s), 819(vs), 809(s), 664(w) cm^{-1}; UV max (C_2H_5OH) 239 nm (ε 811), 208 (ε 1670).

Structure of 1,2,5,6-tetrathiacyclooctane (I).

The mass spectrum shows only one important fragment other than the parent peak at m/z 184. This fragment which appears at m/z 124 corresponds to $C_2H_4S_3$ and is presumably analogous to the intense m/z 106 peak observed during fragmentation of 1,5-dithiacyclooctane.[18] These five-membered ring fragment result from an intramolecular S-S coupling reaction and are always observed when a series of methylene groups separate two sulfur atoms in a mesocyclic system. We have previously observed[15] the m/z 124 fragment as 36% of the base fragment C_2H_4S (m/z 60) from 1,2,5-trithiacycloheptane. As might be expected 1,2,6-trithiacyclooctane produced the exceptionally stable 106 base peak at the expense of the 124 fragment which was only 10% of the base peak. The 124 fragment was absent in compounds containing three or more methylene groups separating the thioether and disulfide groups, i.e. 1,2,6-trithiacyclononane and 1,2,6-trithiacyclodecane.



The crystal selected for data collection was a colorless needle of dimensions 0.08 x 0.125 x 0.25 mm. The determination of the cell dimensions and data collection were carried out with the crystal cooled to 140°K on a Syntex $P2_1$ diffractometer using MoKα radiation and a graphite monochromator. Crystal data are: space group $P2_1/n$; a = 6.470(1), b = 13.760(3), c = 8.706 (1)Å. β = 103.60(1)°, Z = 4, ρ exptl (298K) = 1.54 g cm^{-3} (in $ZnCl_2$(aq)). A total of 1338 unique reflections with 2θ = 0-50° were measured using a variable speed ω scan technique. The data were corrected for Lorenz, polarization and absorption effects. There were 1144 reflections with I > 2.5 σ(I) that were used in the subsequent solution and refinement of the structure. The structure was solved by direct methods. The R value with anisotropic non-hydrogen atoms was 0.030. Tables of positional and thermal parameters and structure factors are available.[19]

A drawing of the molecular structure of 1,2,5,6-tetrathiacyclooctane and torsion angles is given in Figure 1. The S–S, S–C and C–C bond distances are normal and are listed in Table I. Non-bonded sulfur-sulfur distances across the eight membered ring range from 3.488(2) to 4.034 (2) Å and are comparable to the sulfur-sulfur contacts between neighboring molecules. For example, S(1) has intermolecular contacts of 3.548(2), 3.605(2) and 3.995(2) Å. The conformation of the eight-membered ring can best be described as twist-boat-chair[20] and corresponds to that found in the alkaloid cassipourine, the only other similar ring system which has been studied by X-ray crystallography.[21] This conformation allows one of the C–S–S–C torsion angles to be close to the ideal value of 90° at the expense of the second torsion angle. Our results show a S(1)-S(2) distance of 2.049(1) Å (C–S–S–C of 117.4(1)°) and S(3)-S(4) distance of 2.039(1) Å (C–S–S–C of -86.3(1)°). A similar trend is found in cassipourine, although the data are of lower accuracy. As a consequence of the two different disulfide groups in the crystal, we expect two different S–S bands in the Raman spectrum of 1,2,5,6-tetrathiacyclooctane, and these are observed at 504(w) and 521(s) cm^{-1}. Low temperature studies on this compound and related ring disulfides are underway.

FIGURE 1.

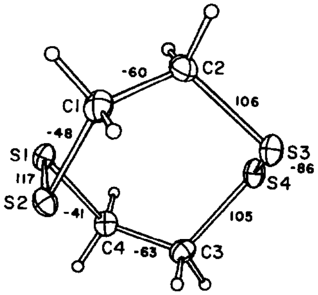
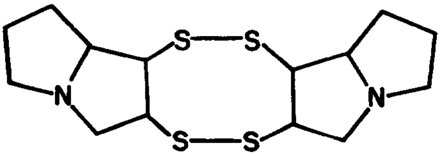


TABLE I. BOND LENGTHS (Å) AND BOND ANGLES (DEG.)

S(1)-S(2)	2.049(1)	S(1)-C(4)	1.824(3)
S(2)-C(1)	1.826(3)	S(3)-S(4)	2.039(1)
S(3)-C(2)	1.820(3)	S(4)-C(3)	1.820(3)
C(1)-C(2)	1.520(4)	C(3)-C(4)	1.521(4)
S(2)-S(1)-C(4)	103.4(1)	S(1)-S(2)-C(1)	103.3(1)
S(4)-S(3)-C(2)	104.4(1)	S(3)-S(4)-C(3)	105.2(1)
S(2)-C(1)-C(2)	116.7(2)	S(3)-C(2)-C(1)	113.9(2)
S(4)-C(3)-C(4)	114.7(2)	S(1)-C(4)-C(3)	117.5(2)

Cassipourine



ACKNOWLEDGEMENT: We thank the National Institutes of Health for support of this research and Modesto Junior College for a sabbatical leave (MHG). We also appreciate the help of Dr. Brenda Kimble for the mass spectra and Dr. Charles P. Nash for the Raman spectra.

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(Received in USA 10 May 1982)