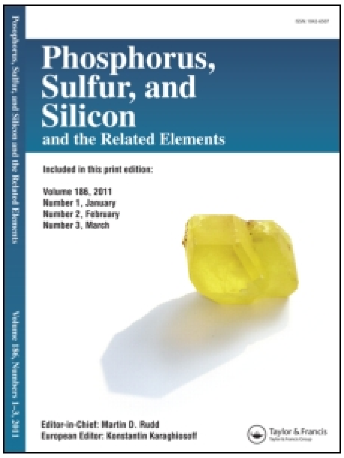

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THE CRYSTAL AND MOLECULAR STRUCTURE OF 1,4,7,11,14,17-HEXATHIACYCLOEICOSAN-9,19-DIONE-SOLID-STATE CONFORMATION OF A MACROCYCLIC DIKETOHEXATHIOETHER[1]

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THE CRYSTAL AND MOLECULAR STRUCTURE OF 1,4,7,11,14,17-HEXATHIACYCLOEICOSAN-9,19-DIONE—SOLID-STATE CONFORMATION OF A MACROCYCLIC DIKETOHEXATHIOETHER[1]

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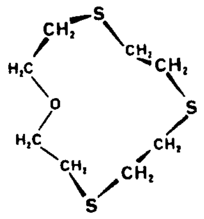
The macrocyclic hexathioether, 1,4,7,11,14,17-hexathiacycloeicosan-9,19-dione (diketo-20-ane-S_6) has been synthesized and the crystal and molecular structure of the compound determined from a single-crystal X-ray study. The compound crystallizes in the monoclinic space group $P2_1/c$ with two molecules per unit cell of dimensions $a = 10.361(3)$ A, $b = 9.370(3)$ A, $c = 11.132(2)$ A, and $\beta = 108.25(2)°$. The observed and calculated densities are 1.37(1) and 1.35 g cm^{-3}, respectively. Full-matrix least-squares refinement using 1342 unique reflections having $4° \leq 2\theta \leq 50°$ and $I \geq 3\sigma(I)$ converged at $R = 0.039$ and $R_w = 0.049$. The compound exists, in the crystalline state, in a conformation such that the sulfur atoms point away from the cavity of the ring, (*exodentate*), and the two ketone functionalities point above and below the plane of the ring, away from each other (*anti*), but toward the cavity of the ring (*endodentate*).

Key words: X-ray; crystal; structure; conformation; macrocycle; thioether.

INTRODUCTION

There is considerable current interest in conformational analysis of mesocyclic (medium-sized ring) and macrocyclic polythioethers.[3–5] Replacement of methylene groups in cycloalkanes with sulfur may have important consequences in the preferred conformations of these compounds as well as conformational equilibria involved. If such heterocycles contain more than one heteroatom or other functional groups, the geometrical disposition of the sulfur atoms may have important consequences in the chemistry of these compounds, e.g., transition metal complexation.

X-ray crystal structural analyses have been done on a number of saturated macrocyclic polythioethers, including 1-oxa-4,7,10-trithiacyclododecane, **1**,[6] 1,4,8,11-tetrathiacyclotetradecane, **2**,[7] 1,4,7-trioxa-10,13-dithiacyclopentadecane, **3**,[6] 1,4,7,10,13-pentaoxa-16-thiacyclooctadecane, **4**,[8] 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane, **5**,[6] 1,4,10,13-tetraoxa-7,16-dithiacycyclooctadecane, **6**,[6] 1,4,7,10-tetrathiacyclododecane, **7**,[9] 1,4,7,10,13-pentathiacyclopentadecane, **8**,[9] 1,4,7,10,13,16-hexathiacyclooctadecane, **9**,[9,10] and the 1,10-diaza-4,7,13,16-tetrathiacyclooctadecane derivative, **10**.[11] All of these macrocycles adopt conformations such that the C—C—S—C dihedral angles are gauche (none are anti), and, with the exceptions of **9** and **10**, all of the sulfur atoms are directed out of the cavity of the ring (exodentate).



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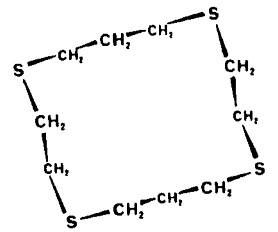

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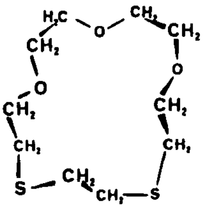

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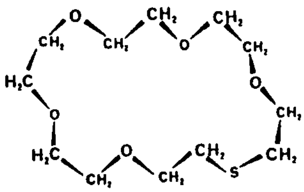

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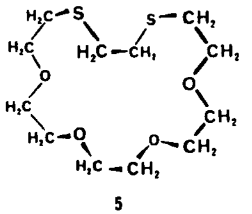

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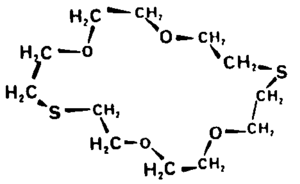

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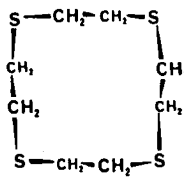

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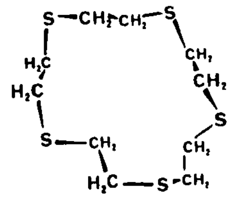

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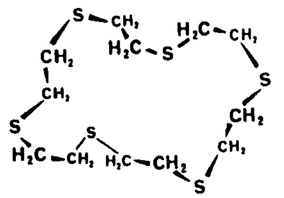

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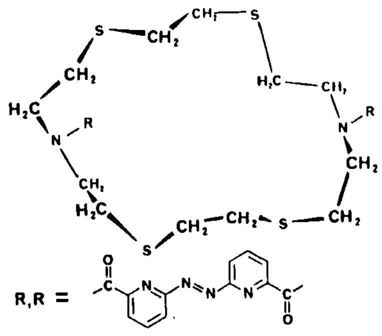

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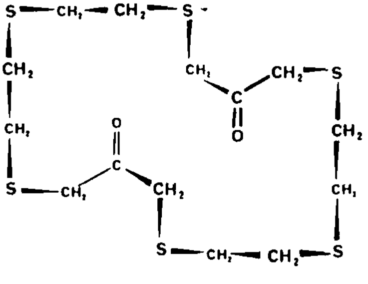
In this paper we report the synthesis and the crystal and molecular structure of the macrocyclic hexathioether diketone, 1,4,7,11,14,17-hexathiacycloeicosan-9,19-dione (diketo-20-ane-S_6).



Diketo-20-ane-S_6

RESULTS AND DISCUSSION

A perspective view of the diketo-20-ane-S_6 molecule is shown in Figure 1. A summary of the crystallographic data for the molecule is listed in Table I while the final atomic parameters are listed in Table II. Geometrical parameters for the molecule are compiled in Table III.[12] The bond lengths and bond angles for diketo-20-ane-S_6 appear to be completely regular. The S—C and C—C bond lengths average 1.814 A and 1.510 A, respectively. The average of the C—S—C bond angles is 101.4° while the S—C—C bond angles average 111.5°. The C=O bond length of 1.204 A and bond angles around the carbonyl carbon (sum = 360.0°) show the carbonyl group to be completely regular.

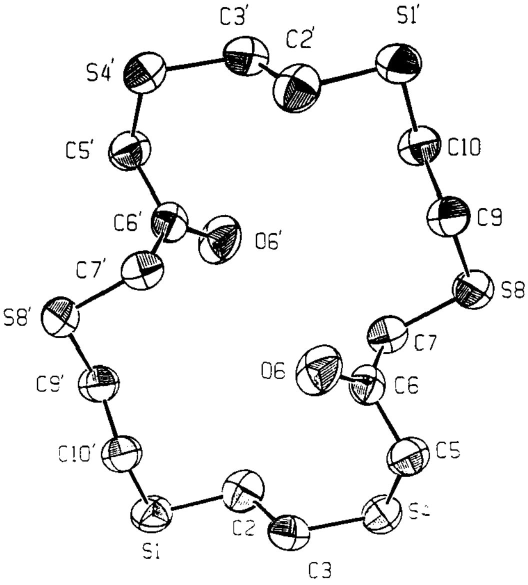


FIGURE 1 ORTEP perspective drawing of diketo-20-ane-S_6.

TABLE I

Summary of crystallographic data for diketo-20-ane-S_6

Molecular formula	$C_{14}H_{24}O_2S_6$
Molecular weight	416.73
Crystal dimensions, mm	0.25 × 0.40 × 0.50
Space group	monoclinic, $P2_1/c$
Cell dimensions	
a, A	10.361(3)
b, A	9.370(3)
c, A	11.132(2)
β, deg	108.25(2)
V, A^3	1026.3
Z	2
d_{calcd}, g/cm^3	1.35
d_{exptl}, g/cm^3	1.37(1)
$F(000)$, e$^-$	440
No. of unique data	1821
No. of observed data	1342
Absorption coeff. (μ_λ), cm^{-1}	6.4
Final residuals	
R	0.039
R_w	0.049

The conformation adopted by this macrocycle is such that the sulfur atoms occupy the corners of each "quadrangular" substructure. Such a conformation is a consequence of the all-gauche orientation about the C—S—C—C bonds while the S—C—C—S bonds are all trans. The structure can be visualized as two —S—CH_2—CH_2—S—CH_2—CH_2—S— "bracket" units[9] connected by the two ketone units. The conformation about each ketone group is also gauche with one of the carbonyl groups pointing above the plane of the heterocyclic ring and the other carbonyl pointing below. Both ketone groups point *toward* the cavity of the ring, however. The ketone functionalities are best described, then, as *endodentate*

TABLE II

Final atomic parameters for diketo-20-ane-S_6

Atom	x	y	z	B(Å^2)
S1	0.22083(8)	−0.07289(9)	0.57303(7)	4.98(2)
S4	0.03505(7)	0.0618(1)	0.86303(7)	4.93(2)
S8	0.33327(7)	0.0289(1)	1.25902(7)	5.38(2)
O6	0.3881(2)	0.1517(2)	0.9817(2)	5.79(5)
C2	0.1679(3)	−0.0732(3)	0.7139(3)	4.87(7)
C3	0.1003(3)	0.0645(3)	0.7291(3)	4.79(7)
C5	0.1589(3)	0.1697(3)	0.9765(3)	4.51(7)
C6	0.2985(3)	0.1016(3)	1.0161(2)	3.73(6)
C7	0.3203(3)	−0.0270(3)	1.1000(3)	4.23(6)
C9	0.5031(3)	0.1048(3)	1.3128(3)	4.45(7)
C10	0.6119(3)	−0.0079(3)	1.3659(3)	4.32(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)*[a2*B(1, 1) + b2*B(2, 2) + c2*B(3, 3) + ab(cos gamma)*B(1, 2) + ac(cos beta)*B(1, 3) + bc(cos alpha)*B(2, 3)].

TABLE III

Geometrical parameters for diketo-20-ane-S_6

Bond Lengths (A)			
S1—C2	1.816(3)	O6—C6	1.204(3)
S1—C10	1.817(2)	C2—C3	1.503(4)
S4—C3	1.819(3)	C5—C6	1.515(3)
S8—C7	1.810(3)	C6—C7	1.498(3)
S8—C9	1.817(3)		
Bond Angles (deg)			
C2—S1—C10	100.8(1)	O6—C6—C5	120.3(2)
C3—S4—C5	101.6(1)	O6—C6—C7	122.1(2)
C7—S8—C9	101.7(1)	C5—C6—C7	117.6(2)
S1—C2—C3	111.9(2)	S8—C7—C6	109.1(2)
S4—C3—C2	112.7(2)	S8—C9—C10	112.3(2)
S4—C5—C6	111.9(2)	S1—C10—C9	111.1(2)
Torsion Angles (deg)			
S1—C2—C3—S4	175.7(2)	C5—C6—C7—S8	−75.0(3)
C2—C3—S4—C5	104.7(2)	C6—C7—S8—C9	−75.3(2)
C3—S4—C5—C6	−64.1(2)	C7—S8—C9—C10	−85.0(2)
S4—C5—C6—C7	−72.1(3)	S8—C9—C10—S1′	−176.8(1)
S4—C5—C6—O6	108.7(3)	C9—C10—S1′—C2′	−88.2(2)

while the thioether groups are *exodentate*. The *anti* orientation of the ketone moieties would provide the structure with a favorable dipole–dipole interaction. Note that the molecule lies on a crystallographic inversion center, imposing C_i symmetry on the compound in this crystal structure.

Examination of this macrocycle and related compounds as potential ligands for complexation of heavy-metal ions is currently underway in our laboratories.

EXPERIMENTAL SECTION

Methods and Materials. Analyses were carried out by Atlantic Microlab, Inc., Atlanta, Georgia. Melting points are uncorrected. Infrared spectra were obtained on a Perkin–Elmer Model 1330 spectrophotometer. ^{1}H NMR spectra were obtained on an IBM/Bruker AF 200 spectrometer, operated in the FT mode.

Preparation of 1,4,7-trithiacyclodecan-9-one and 1,4,7,11,14,17-hexathiacycloeicosan-9,19-dione. A 1000-mL three-necked round-bottom flask, equipped with matching calibrated 200 mL addition funnels, magnetic stir bar, thermometer, and nitrogen inlet–outlet, was charged with freshly distilled dimethylformamide (200 mL) and cesium carbonate (32.6 g, 100 mmol; Aldrich Chemical Company). In one funnel was prepared a solution of *bis*-(2-mercaptoethyl)sulfide (14.5 mL, 17.1 g, 100 mmol; Aldrich Chemical Company) and sufficient anhydrous DMF to dilute to 200 mL. In the other funnel was prepared a solution of 1,3-dichloroacetone (9.7 mL, 13.4 g, 100 mmol; Aldrich Chemical Company) and sufficient anhydrous DMF to dilute to 200 mL. The two solutions were added simultaneously to the rapidly stirred, warm (52°C) DMF/Cs_2CO_3 mixture at a rate of about 15 drops/min. After completion of the addition (9 h), the reaction mixture was heated and stirred for an additional 12 h, allowed to cool to room temperature, and stirred for 24 h more. The CsCl was removed by filtration and the DMF was removed from the filtrate by rotary evaporation. A 10.0 g sample of the crude product was chromatographed on a silica gel gravity column (2.5 cm diameter × 40 cm length), eluting with 20% ethyl acetate in hexane to give 343 mg (5.8% yield) of 1,4,7,11,14,17-hexathiacycloeicosan-9,19-dione as a colorless crystalline solid (parallelepipeds): mp 107–108°C; IR (KBr) 2910, 1665 (C=O), 1395, 1250, 1194, 1145, 1073, 944, 750, 719, 690, 670, 604, 468, 401 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.72 (*s*, 8 H, —SCH_2CH_2S—), 3.53 (*s*, 4 H, —$SCH_2C(O)$—); mass spectrum (CI, methane) m/e (relative intensity) 417 (100%, M + 1), 269(41%), 209(32%), 149(28%), 121(35%), 89(24%), 61(25%). Anal. Calcd. for $C_{14}H_{24}S_6O_2$: C, 40.37; H, 5.81; S, 46.13. Found: C, 40.34; H, 5.85; S, 46.20. Continued chromatography gave 150 mg (2.5% yield) of 1,4,7-trithiacyclodecan-9-one as a colorless crystalline solid (needles): mp 102–104°C; IR (KBr) 2890, 1690 (C=O), 1436, 1413, 1385, 1270, 1200, 1147, 1123, 1068, 940, 923, 891, 858, 826, 810, 755, 719, 688, 649, 540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.92 (*s*, 8 H, —SCH_2CH_2S—), 3.70 (*s*, 4 H, —$SCH_2C(O)$—); mass spectrum (Cl, methane) m/e (relative intensity) 209(75%, M + 1), 181(23%), 149(100%), 121(30%), 89(15%), 61(24%); Anal. Calcd. for $C_7H_{12}S_3O$: C, 40.37; H, 5.81; S, 46.13. Found: C, 40.36; H, 5.86; S, 46.22. The density of diketo-20-ane-S_6 was determined by the flotation method using CCl_4/hexane to be 1.37(1) g cm^{-3}.

X-ray Diffraction Data Collection and Reduction. A colorless irregular crystal of diketo-20-ane-S_6 having approximate dimensions of 0.25 × 0.40 × 0.50 mm was mounted on a glass fiber with its long axis roughly parallel to the phi axis of the goniometer. Preliminary examination and data collection were performed with MoKα radiation ($\lambda = 0.71073$ A) on a Syntex $P2_1$ diffractometer equipped with a graphite crystal incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $7° \le 2\theta \le 28°$. The monclinic cell parameters and calculated volume are: $a = 10.361(3)$, $b = 9.379(3)$, $c = 11.132(2)$ A, $\beta = 108.25(2)°$, $V = 1026.3$ A^3. For Z = 2 and F.W. = 416.73, the calculated density is 1.35 g/cm^3. As a check on crystal quality, omega scans of several intense reflections were measured; the width at half-height was 0.20°, indicating good crystal quality. From the systematic absences of $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, and from subsequent least-squares refinement, the space group was determined to be $P2_1/c$ (No. 14).

The data were collected at a temperature of 23 ± 1° using the θ–2θ scan technique. Data were collected over the range $4° \le 2\theta \le 50°$ of which those with $I \ge 3\sigma(I)$ were considered observed and were used in the calculations. The scan rate varied from 2 to 8°/min. A total of 2061 reflections were collected of which 1821 were unique and not systematically absent. As a check on crystal and electronic stability, 3 check reflections were measured after every 97 data reflections. The intensities of these standards remained constant within experimental error throughout data collection. No decay correction was applied.

The data were reduced to F_0^2 and $\sigma(F_0^2)$ by the following procedures. The integrated intensities were calculated from the relationship $I = [c - (\mathrm{LB} + \mathrm{RB})/\mathrm{rt}]S$, where c is the peak count, LB the left background count, RB the right background count, rt the ratio of the total background time to peak scan time, and S the scan rate. The polarization correction for the parallel–parallel mode of the diffractometer was chosen assuming the monochromator to be 50% perfect and 50% mosaic. Initial standard deviations were calculated by: $\sigma(I) = [c + (\mathrm{LB} + \mathrm{RB})/(\mathrm{rt})^2]^{1/2}S$. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 6.4 cm^{-1} for MoKα radiation; no absorption correction was made.

Solution and Refinement of the Structure. The structure was solved by direct methods. A total of 8 atoms were located from an E-map. the remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded.

The structure was refined by full-matrix least-squares where the function minimized was $\Sigma w(|F_0| - |F_c|)^2$ with the weighting factor $w = 4F_0^2/[\sigma^2(F_0^2) + (pF_0^2)^2]$, where p, the factor to prevent overweighting of strong reflections was set equal to 0.040. Scattering factors were taken from Cromer and Waber.[13] Anomalous dispersion effects were included in F_c;[14] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[15] Only the 1342 reflections having intensities greater than 3.0 times their standard deviation were used in the reflnements. The final cycle of refinement included 100 variable parameters and converged at $R = \Sigma ||F_0| - |F_c||/\Sigma |F_0| = 0.039$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma wF_0^2]^{1/2} = 0.049$. The highest peak in the final difference Fourier had a height of 0.45 e/A^3; the minimum negative peak had a height of −0.36 e/A^3. All calculations were performed on a VAX computer using SPD/VAX.[16]

ACKNOWLEDGMENTS

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