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Conformational Analysis of 1,4,7-Trithiacyclodecane and Related Compounds: Synthesis and Complexation Studies of Mesocyclic and Macrocyclic Polythioethers VI[†]

William N. Setzer,* Qin Guo, and Edward J. Meehan, Jr.

Department of Chemistry, The University of Alabama in Huntsville, Huntsville, Alabama 35899, U.S.A.

Gregory J. Grant

Department of Chemistry, The University of Tennessee at Chattanooga, Chattanooga, Tennessee 37403, U.S.A.

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ABSTRACT

Molecular mechanics (MM2) calculations have been carried out on the ten-membered ring trithioethers, 1,4,7-trithiacyclodecane (10S3) and 1,4,7-trithiacyclodecan-9-one (keto-10S3). The lowest energy conformations according to these calculations are a [1333] and a [2233] conformation, respectively. The crystal and molecular structure of the ketone, 1,4,7-trithiacyclodecan-9-one, has been determined by a single-crystal X-ray study. The compound crystallizes in the monoclinic space group $P2_1$*, with two molecules per unit cell of dimensions* a = *7.176(1) Å,* b = *5.3447(6) Å,* c = *12.0914(6) Å, and* β = *96.486(7)°, and* R = *0.048. The conformation adopted by the compound in the crystalline state is a [2323] or boat-chair-boat conformation with two sulfur atoms endodentate and one sulfur atom exodentate.*

INTRODUCTION

There is considerable current interest in conformational analysis of medium-sized rings and their saturated heterocyclic analogs [2]. We have examined the 1,4,7-trithiacyclodecane ring system and other related mesocyclic trithioethers as potential ligands for complexation of transition metal and heavy metal ions [1]. In order to gain insight into complexation of transition metal ions by mesocyclic polythioethers, we have undertaken conformational studies of medium-sized rings containing both carbon and sulfur atoms. As part of this program the crystal and molecular structure of 1,4,7-trithiacyclodecan-9-one (keto-10S3) has been determined by X-ray crystallographic techniques. In addition, we have carried out molecular mechanics calculations to determine the preferred conformations of 1,4,7-trithiacyclodecane (10S3) as well as keto-10S3.

The preferred conformation of cyclodecane is the [2323] conformation. It is found in a number of crystalline derivatives including 1,6-dithiacyclodecane and 1,2,6,7-tetrathiacyclodecane [3]. Force-field calculations indicate a [2323] conformation to be the preferred conformation for cyclodecanone [4]. Cyclodecasulfur, on the other hand, has been calculated to adopt a "crown" conformation (D_{5d} symmetry) [5], but it actually crystallizes in a conformation having D_2 symmetry [6].

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*To whom correspondence should be addressed.

†Dedicated to Prof. Dr. Paul von Rague' Schleyer on the occasion of his sixtieth birthday. For Parts I–V, see reference [1].

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RESULTS AND DISCUSSION

We have carried out molecular mechanics calculations [7] on the 1,4,7-trithiacyclodecane ring system and its corresponding ketone, 1,4,7-trithiacyclodecan-9-one. The general procedure was to determine the relative energies of all of the conformational possibilities for these two compounds. The conformational possibilities were derived from the conformers of cyclodecane. The relative energies were calculated using the molecular mechanics MM2 program of Allinger [8]. The conformational possibilities (local energy minima) for 1,4,7-trithiacyclodecane (10S3) and 1,4,7-trithiacyclodecan-9-one (keto-10S3) are shown in Figures 1 and 2, respectively, along with their relative calculated (MM2) energies.

The molecular mechanics (MM2) calculations for 10S3 indicate a [1333] conformation, not a [2323] conformation, to be the one of lowest energy. All of the [2323] conformations are about 4 kcal/mol higher in energy than the lowest energy [1333] conformation. MM2 calculations on this heterocycle indicate that the D_2 conformations are not energy minima, but rather these conformations optimize to lower symmetry [2233] conformations. Similarly, D_{5d} conformations reduce to [1414] conformations upon geometry optimization in these calculations.

Note that the lowest-energy conformation of 1,4,7-trithiacyclodecane is not suitable for complexation of metal ions in tridentate fashion. Facial tridentate coordination would require a conformation in which all three of the sulfur atoms are syn endodentate. There are four conformations that meet this requirement, [2323]A, [2233]A, [1333]A, and [1324]A, but all of them are relatively high in energy according to the MM2 calculations (≥ 4 kcal/mol than conformation [1333]D). These calculations indicate, then, that a conformational change must take place in 10S3 in order for tridentate complexation of metal ions to occur.

The conformation adopted by the 1,4,7-trithiacyclodecane ligand in $Fe(10S3)_2(ClO_4)_2$ is [2323]A (a boat-chair-boat conformation) [1c] while the conformation adopted by the 1,4,7-trithiacyclodecan-9-one ligand in $Ni(keto\text{-}10S3)_2(BF_4)_2$ is the [2233]A conformation [1c]. A consequence of both of these conformations is that the six-membered chelate ring in the metal complex is a chair. Curiously, the conformation adopted by 10S3 in $Mo(0)(10S3)(CO)_3$ is the [1333]A conformation [1b]. This conformation of the ten-membered-ring ligand results in a boat conformation of the six-membered chelate ring in the resulting complex. Note that complexation of 10S3 or a derivative thereof involving a [1324] conformation would also result in a boat conformation of the six-membered chelate ring.

Perspective views of keto-10S3 from the X-ray crystal structure are shown in Figure 3. A summary of the crystallographic data for the molecule is listed in Table 1 while the final atomic parameters are listed in Table 2. Geometrical parameters for the molecule are compiled in Table 3. The bond lengths and bond angles for keto-10S3 reflect the transannular strain inherent in this medium-sized ring. The S–C and C–C bond lengths range from 1.807(5) Å to 1.850(8) Å and 1.511(7) Å to 1.530(8) Å, respectively. It is curious that the S–C bonds are somewhat longer and the C–C bonds are somewhat shorter, on the average, than those typically observed in mesocyclic thioethers (S–C average 1.81 Å, C–C average 1.53 Å) [9]. The C–S–C bond angles in keto-10S3 range from 100.0(3) to 102.8(3)°, whereas the S–C–C bond angles range from 112.0(4)° to 117.9(5)°. The S–C–C bond angles are opened up compared to the dimeric compound, diketo-20S6 (111.5°) [1a]. The C=O bond length of 1.220(7) Å and the bond angles around the carbonyl carbon (sum = 359.9°) show the carbonyl group to be regular.

The conformation adopted by keto-10S3 in the crystalline state is [2323]C, a boat-chair-boat conformation analogous to that calculated for cyclodecanone [4]. In this conformation, two of the sulfur atoms are endodentate while the third sulfur is exodentate. Note that 10S3 is a liquid at room temperature. We have thus far been unsuccessful in growing suitable crystals at low temperature.

The molecular mechanics calculations for keto-10S3 indicate [2233]A, the same conformation observed for that ligand in $[Ni(keto\text{-}10S3)_2](BF_4)_2$ [1c], to be the lowest energy conformation. The conformation observed in the crystalline state for the free ligand, [2323]C, is calculated to be 1.6 kcal/mol higher in energy than [2233]A. It is interesting that the conformation observed in the crystalline state is not the calculated lowest energy conformation. It may be that crystal packing forces are enough to overcome the small energy difference, resulting in the [2323]C rather than the [2233]A conformation. The results of the MM2 calculations for conformation [2323]C seem to reflect the geometrical parameters observed in the X-ray crystal structure (Table 4). Thus, the unusually long C–S bonds observed in the crystal structure [S(3)–C(4), S(6)–C(5), and S(9)–C(8)] are also elongated in the MM2 calculations, albeit not to so great an extent. The bond angles show analogous trends: for the C–S–C bond angles, C(7)–S(6)–C(5) < C(2)–S(3)–C(4) < C(8)–S(9)–C(10) in both the X-ray and the MM2 results. The C–C–S bond angles are also comparable.

EXPERIMENTAL

Preparation of 1,4,7-Trithiacyclodecan-9-one (Keto-10-ane-S_3)

The compound was prepared using the cesium dithiolate technique [1c,e].

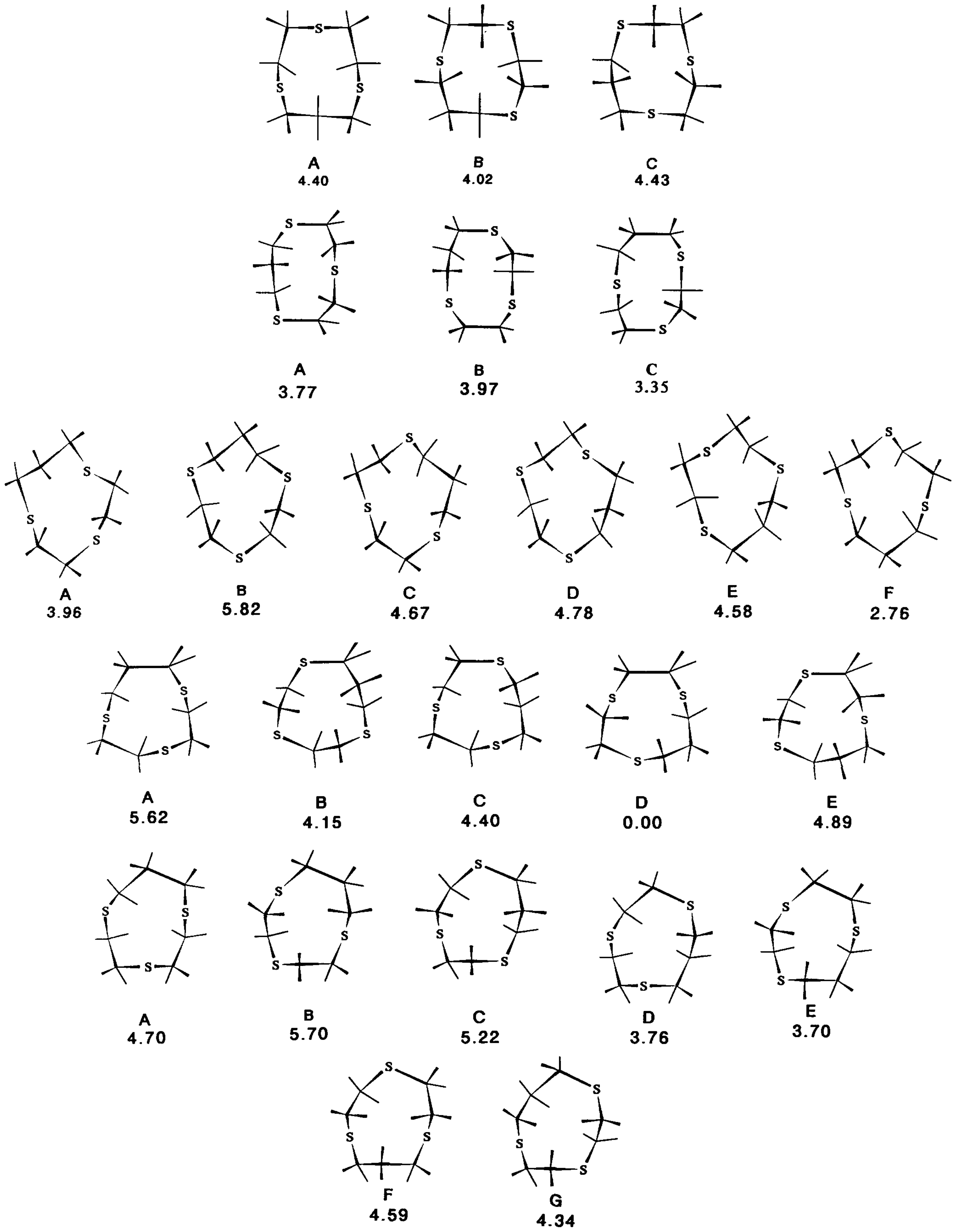

FIGURE 1 Conformational Possibilities of 1,4,7-Trithiacyclodecane.

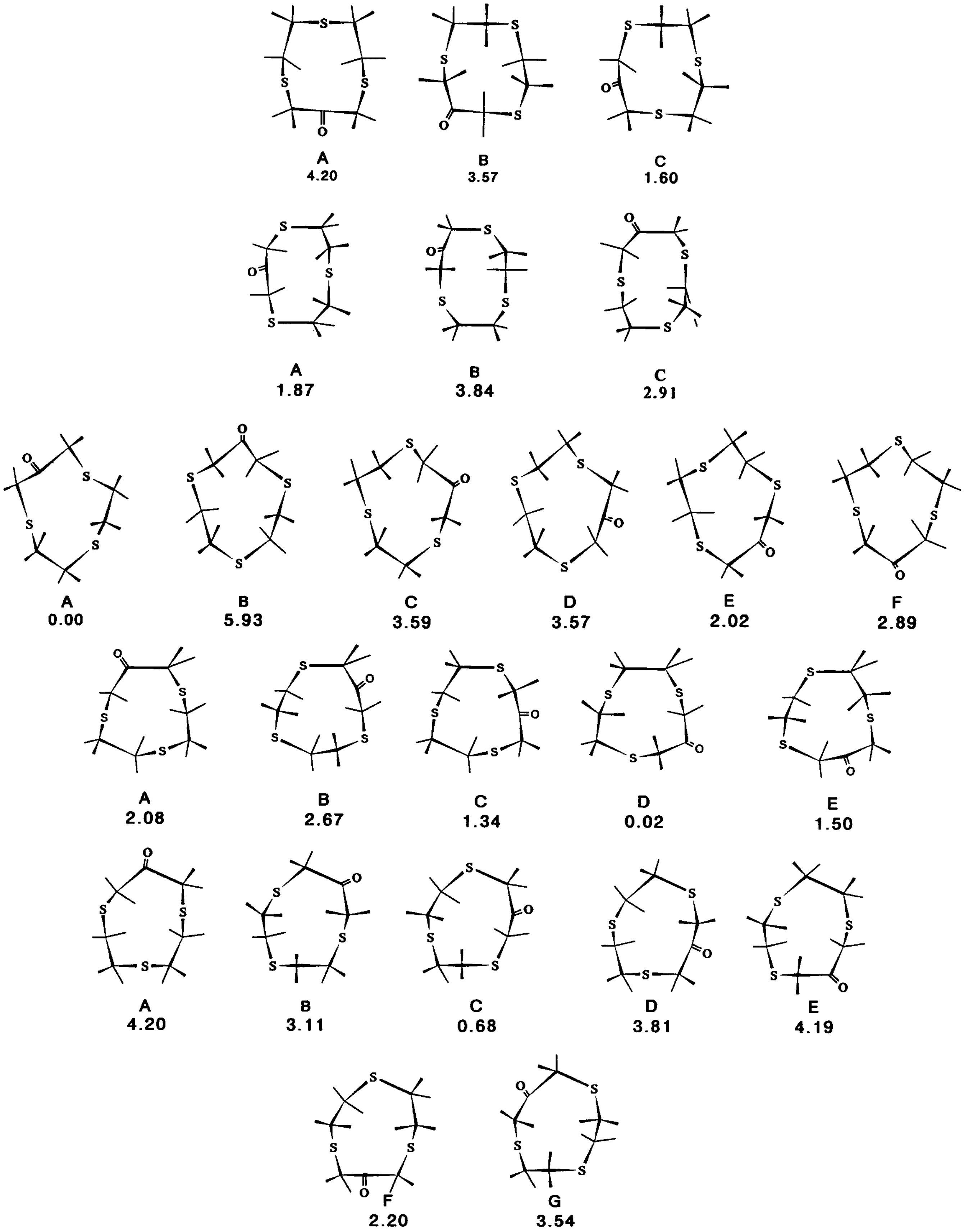

FIGURE 2 Conformational Possibilities of 1,4,7-Trithiacyclodecan-9-one.

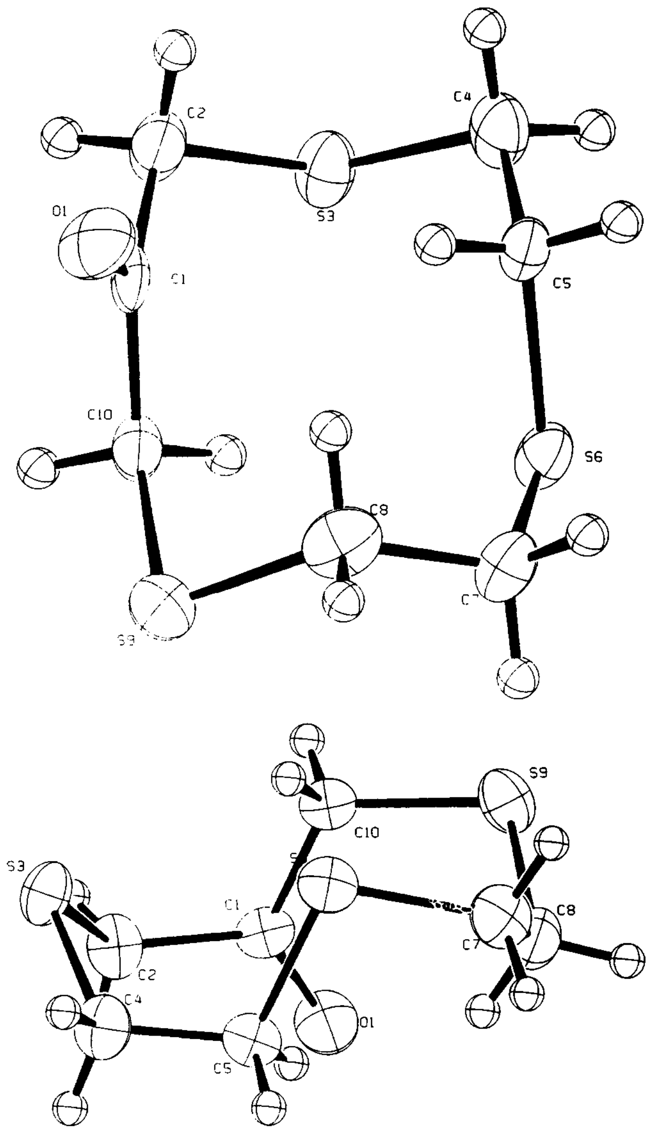

FIGURE 3 Two ORTEP Perspective Views of Keto-10S3.

TABLE 1 Crystallographic Data for Keto-10S3

Molecular formula	$C_7H_{12}S_3O$
Molecular weight	208.35
Crystal system	Monoclinic
Space group	$P2_1$ (No. 4)
Cell dimensions	
a, A	7.176(1)
b, A	5.3447(6)
c, A	12.0914(6)
β, deg	96.486(7)
V, A^3	460.75(9)
Z	2
$F(000)$, e^-	220
No. of obsd. data	751
No. variables	99
Final residuals	
R	0.048
R_w	0.061

X-ray Single Crystal Structure Study of Keto-10S3 [*10*]

Clear colorless crystals of keto-10S3 were obtained by vapor diffusion of a solution of the compound in ethyl acetate with pentane. A well-formed crystal was mounted in a Rigaku AFC5R diffractometer equipped with scintillation counter and CuKα radiation (λ = 1.54178 Å, Rigaku rotating anode generator run at 50 kV and 100 mA). The θ-2θ technique was used to collect the data ($2\theta \leq 120.0°$); those with $I \geq 3\sigma(I)$ were considered observed and were used in the calculations.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. The hydrogen atoms were added to the model in geometrically ideal positions and were not refined. Anisotropic refinement converged at R = 0.048, R_w = 0.061, and GOF = 3.09. The largest peak in the final difference map was 0.35 e^-/A^3.

TABLE 2 Final Atomic Parameters for Keto-10S3

Atom	*x*	*y*	*z*	*B*(Å²)
S(3)	1.0045(2)	0.2984(5)	0.6079(1)	2.56(6)
S(6)	0.9473(2)	0.2564(5)	0.8832(1)	2.47(6)
S(9)	0.4810(2)	0.0177(5)	0.7947(1)	2.93(7)
O(1)	0.4822(5)	0.450(1)	0.6226(4)	3.2(2)
C(1)	0.6112(7)	0.302(1)	0.6207(4)	2.0(2)
C(2)	0.7662(8)	0.361(2)	0.5486(5)	2.6(2)
C(4)	1.0455(7)	0.556(2)	0.7099(5)	2.7(2)
C(5)	0.9258(7)	0.554(1)	0.8050(4)	2.2(2)
C(7)	0.7406(8)	0.276(2)	0.9556(4)	2.9(2)
C(8)	0.5511(8)	0.288(2)	0.8837(5)	3.0(3)
C(10)	0.6207(7)	0.055(1)	0.6805(4)	2.2(2)

TABLE 3 Geometrical Parameters for Keto-10S3

Bond Lengths (Å)			
S(3)–C(2)	1.809(6)	O(1)–C(1)	1.220(7)
S(3)–C(4)	1.850(8)	C(1)–C(10)	1.50(1)
S(6)–C(7)	1.808(6)	C(1)–C(2)	1.521(8)
S(6)–C(5)	1.846(7)	C(4)–C(5)	1.511(7)
S(9)–C(10)	1.807(5)	C(7)–C(8)	1.530(8)
S(9)–C(8)	1.836(8)		
Bond Angles (*deg*)			
C(2)–S(3)–C(4)	101.5(3)	C(1)–C(2)–S(3)	117.0(4)
C(7)–S(6)–C(5)	100.0(3)	C(5)–C(4)–S(3)	116.1(5)
C(8)–S(9)–C(10)	102.8(3)	C(4)–C(5)–S(6)	112.0(4)
O(1)–C(1)–C(10)	123.6(5)	C(8)–C(7)–S(6)	116.9(4)
O(1)–C(1)–C(2)	118.9(6)	C(7)–C(8)–S(9)	117.9(6)
C(2)–C(1)–C(10)	117.4(5)	C(1)–C(10)–S(9)	117.8(4)
Torsion Angles (*deg*)			
S(3)–C(2)–C(1)–O(1)	137.8(5)	C(1)–C(10)–S(9)–C(8)	-53.1(5)
S(3)–C(2)–C(1)–C(10)	-45.9(7)	C(1)–C(2)–S(3)–C(4)	-73.4(6)
S(3)–C(4)–C(5)–S(6)	56.0(5)	C(2)–S(3)–C(4)–C(5)	64.6(5)
S(6)–C(7)–C(8)–S(9)	63.3(7)	C(4)–C(5)–S(6)–C(7)	-162.5(4)
S(9)–C(10)–C(1)–O(1)	-20.9(7)	C(5)–S(6)–C(7)–C(8)	61.3(6)
S(9)–C(10)–C(1)–C(2)	163.0(4)	C(7)–C(8)–S(9)–C(10)	-76.7(5)

TABLE 4 MM2 Calculated Geometrical Parameters for Keto-10S3

Bond Lengths (Å)			
S(3)–C(2)	1.816	O(1)–C(1)	1.212
S(3)–C(4)	1.823	C(1)–C(10)	1.526
S(6)–C(7)	1.818	C(1)–C(2)	1.527
S(6)–C(5)	1.822	C(4)–C(5)	1.541
S(9)–C(10)	1.818	C(7)–C(8)	1.541
S(9)–C(8)	1.821		
Bond Angles (*deg*)			
C(2)–S(3)–C(4)	102.7	C(1)–C(2)–S(3)	115.2
C(7)–S(6)–C(5)	101.6	C(5)–C(4)–S(3)	113.9
C(8)–S(9)–C(10)	104.8	C(4)–C(5)–S(6)	110.7
O(1)–C(1)–C(10)	121.9	C(8)–C(7)–S(6)	114.7
O(1)–C(1)–C(2)	118.6	C(7)–C(8)–S(9)	114.9
C(2)–C(1)–C(10)	119.4	C(1)–C(10)–S(9)	116.5
Torsion Angles (*deg*)			
S(3)–C(2)–C(1)–O(1)	132.4	C(1)–C(10)–S(9)–C(8)	-46.2
S(3)–C(2)–C(1)–C(10)	-51.6	C(1)–C(2)–S(3)–C(4)	-75.0
S(3)–C(4)–C(5)–S(6)	52.2	C(2)–S(3)–C(4)–C(5)	65.7
S(6)–C(7)–C(8)–S(9)	66.9	C(4)–C(5)–S(6)–C(7)	-164.6
S(9)–C(10)–C(1)–O(1)	-23.4	C(5)–S(6)–C(7)–C(8)	62.1
S(9)–C(10)–C(1)–C(2)	160.8	C(7)–C(8)–S(9)–C(10)	-78.6

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SUPPLEMENTARY MATERIAL AVAILABLE

A complete description of the X-ray crystallographic determination on keto 10S3 has been deposited with the Cambridge Crystallographic Data Centre.

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