Cesium Dithiolate Based Syntheses of Keto-Functionalized Thio-Crown Ethers Employing the Novel Building Block 1,3-Dimercaptoacetone. Molecular Structures of 2,5,9,12-Tetrathia-7-oxo-(13)-*m*-benzenophane and 1,4,7,10,13-Pentathiacyclohexadecan-15-one

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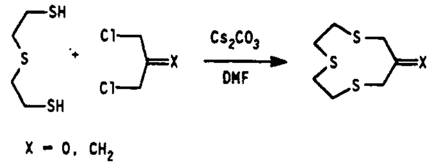
Cyclization of the bis cesium thiolate (generated *in situ*) of 1,3-dimercaptoacetone (1) with α,ω-dihalides in DMF affords the corresponding cyclic thioethers in good yields, providing an efficient alternative route to keto-functionalized thio-crown ethers. A previously suggested dimeric structure for 1 is supported by NMR spectra, which also allow distinction between cis and trans isomers of 1. Equilibration between the isomers can also be followed by NMR. The molecular structures of two specific thio-crown ethers have been determined by X-ray crystallography. Crystal data for 2,5,9,12-tetrathia-7-oxo-(13)-*m*-benzenophane (8) at 130 K: triclinic, space group P-1; a = 7.230(1) Å, b = 8.690(1) Å, c = 13.253(1) Å, α = 83.153(7)°, β = 84.257(6)°, γ = 85.575(6)°, Z = 2, μ(Mo Kα) = 5.5 cm^{-1}, R = 0.029 (R_w = 0.041) for 3082 reflections ($I \geq 2.5\sigma(I)$). Crystal data for 1,4,7,10,13-pentathiacyclohexadecan-15-one (9) at 140 K: monoclinic, space group $P2_1/a$; a = 16.558(1) Å, b = 5.399(1) Å, c = 16.734(1) Å, β = 90.28(5)°, Z = 4, μ(Mo Kα) = 7.3 cm^{-1}, R = 0.048 (R_w = 0.66) for 3021 reflections ($I \geq 3\sigma(I)$).

Introduction

Macrocyclic thio-crown ethers are of particular interest, among other reasons, as potential heavy-metal receptors[1-5] and could be useful for treatment of heavy-metal poisoning.[6] Especially during the past two decades an increase in interest in these ligand systems has prompted several research groups to develop practical synthetic strategies.[1-3] The incorporation of functional groups or functionalizable building blocks[7-10] into the macromolecular framework has been of special importance with a view toward preparation of specific receptor molecules.

In previous reports, the use of keto building blocks in the assembly of the molecular periphery of the (macro)-cycle has been described using 1,3-dichloro-2-propanone, 1,4-dichloro-2-butanone, and 1,5-dichloro-3-pentanone.[8,9] However, a serious drawback of this method, illustrated for a specific case in eq 1, can be the need for the appropriate dithiol in the final ring-closure step. The often cumbersome and laborious purification, especially of the longer-chain dithiols, gives rise to practical problems.



(1)

Results and Discussion

In this paper we describe an alternative procedure for the introduction of 2-propanone groups by use of 1,3-

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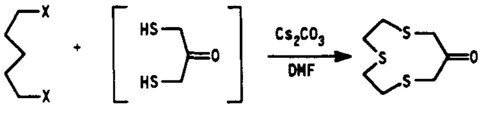
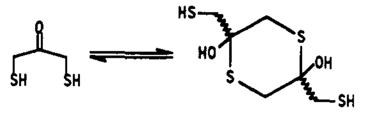
dimercaptoacetone (1) as a synthon. In this approach (eq 2) the positions of sulfide nucleophile and of the leaving group in the chain components are reversed relative to eq 1.



1 4 (2)

Free 1,3-dimercaptoacetone (1) does not occur as such. The molecule dimerizes spontaneously in solution to form the thioacetal 2 (see eq 3). Schotte[11a,b] apparently first



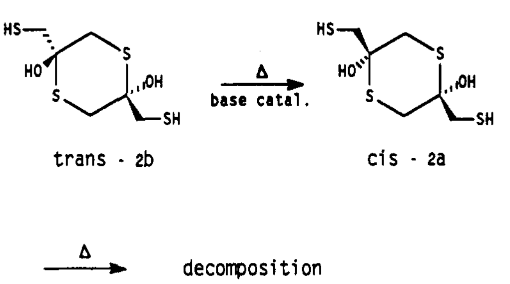
1 2 (3)

suggested the structure of dimer (2) although he was unable to provide any stereochemical assignment.

On the basis of ^1H-NMR and ^{13}C-NMR spectra we are able both to suggest the stereochemistry and to follow the course of the dimerization. For further discussion we will restrict ourselves to the ^{13}C-NMR spectra, which are the most informative. Quick workup (<1 h) of the reaction mixture (see Experimental Section for details) led to a very clean decoupled ^{13}C-NMR spectrum (CD_3SOCD_3) with lines at 34.4, 37.7, and 76.7 ppm. No absorption in the carbonyl region was detectable. On treatment of this material in CD_3SOCD_3 with NaOD or $(C_2H_5)_3N$ at 80–100 °C for several hours the intensity of the original lines decreased and new absorptions grew in slowly at 32.0, 34.2, 36.7, and 78.6 ppm. The same change occurred when 2 was allowed to stand a number of days; this behavior led initially to considerable confusion. The ratio of original to new lines was roughly 1:8. The further chemical reactions of 2 were not observably dependent on the time used for synthesis or other history of the material except that observable deterioration occurred over a period of months.

These observations are consistent with formation of two stereoisomers of dimeric 2, the isomers being in equilibrium. The stereochemical assignment is straightforward. The special problem represented in 2 is well known. *trans*-2 is a meso compound that does not have a plane of symmetry but rather a 4-fold alternating axis.[12] *cis*-2 is a racemate. The CH_2SH groups in *trans*-2 are equivalent as are the ring CH_2's. These give rise to two absorptions at 34.4 and 37.7 ppm (absolute assignment has not been done). The absorption at 76.7 ppm is that of the quaternary carbon. These assignments were verified by coupled ^{13}C spectra (two triplets and a singlet). For *cis*-2 the CH_2SH groups are not equivalent. The ring CH_2's are averaged to a single signal. This gives rise to three absorptions for the methylene groups. The 78.6 ppm absorption is that of the quaternary carbon.

We conclude therefore on the basis of these observations that *trans*-2 is the kinetic product of dimerization of 1 and that *cis*-2, which has lower symmetry, is the thermodynamic product (eq 4).



(4)

These two stereoisomers are in equilibrium, and there is no detectable amount of free dimercaptoacetone (1). Dimercaptoacetone (1/2), preferably reasonably freshly prepared, consumes 1 mol of Cs_2CO_3 for each equivalent of 1. The dicesium salt of 1 that presumably is formed reacts smoothly with long-chain dihalides.

In Scheme I, some examples are illustrated of keto thio-crown ethers that have been prepared using the above-mentioned method. Compounds 4–8 have also been prepared according to the method illustrated in eq 1 and have been discussed in a preliminary paper.[10a–d] Compound 4 has also been reported recently by the group of Setzer et. al.[10e]

The dihalides 10–15 used in this study are illustrated in Scheme II. All were prepared according to a literature method.[10d] *CAUTION: these compounds must be handled with extreme care owing to their vesicant properties.* In our hands the purification of the longer chain dihalides, despite the vesicant properties, proceeds more readily than of the dithiols derived by nucleophilic substitution of chloride.

These results demonstrate clearly that the dimer 2 is a precursor of (the otherwise unstable) 1 as the dithiolate. The 2-propanone unit can be neatly introduced in thio-crown ethers (as well other systems) by this expedient.

The molecular structure of the xylyl derivative 8 is slightly bent with respect to the molecular S-4 plane. The angle between the least-squares planes of the aromatic unit and the 16-atom ring is 63.97(6)°. Also, the propanone moiety is not coplanar and assumes a rather wide angle with respect to the 16-atom least-squares ring (58.21(7)°) and points inward into the cavity. It is remarkable that the carbonyl moiety is directed into the macrocycle. Although a short intramolecular O···H distance is present (O1···H91 = 2.60(2) Å), it is unlikely that the geometry is imposed by significant hydrogen bonding, although an additional short intermolecular H-bridge may be present (O1···H92 = 2.44(2) Å). A directing effect of the residual portion of the molecule seems more probable. The sulfur atoms are oriented anti, the ligating sites pointing away from the molecular cavity (S1–C8–C9–S2 = −173.15(8)°, S3–C13–C14–S4 = −177.73(8)°). This phenomenon is quite common and is found in many larger thio-crown ethers possessing ethylene bridges[1,13] and rigid xylylene building blocks[14] (see Table II for selected bond distances and angles).

The large macrocycle 9 has been prepared in only 25% yield, in contrast to the smaller thio-crown ethers. Ap-

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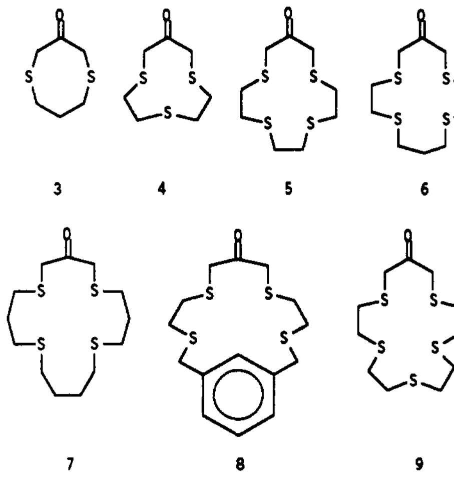
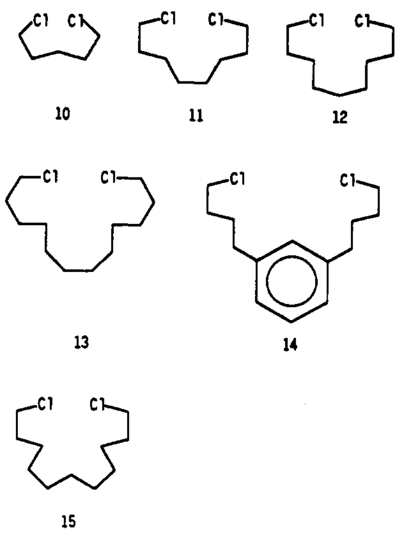
Scheme I



Scheme II



plication of the reversed methodology employing[10] the readily available 1,3-dichloroacetone and dithiol gives in this case a significant improvement in yield (60–80%).[13]

The molecular structure of 9 was determined by X-ray diffraction methods. The molecule is heavily twisted as a result of the all-anti orientation of the sulfur atoms. The dihedral angles do not significantly deviate from 180° (see Table II for selected bond distances and angles).

The propanone moiety points inward into the molecular cavity. This orientation is most probably imposed by the sulfur atoms; weak hydrogen bonding is unlikely since no significantly short O···H contacts are observed that may account for the overall orientation of the carbonyl moiety. However, as already mentioned, weak hydrogen bonding may be present in 8 as is suggested by the short H···O contacts.

Experimental Section

All reactions were carried out under an inert atmosphere (N_2). Solvents were dried and distilled prior to use according to standard procedures. Dihalides were purchased from Aldrich and used as received or prepared according to methods described in Beilstein.[1]

A general procedure for the preparation of the thio dihalides 10–15 as reported by Cooper and co-workers has been followed.[10d]

Preparation of 1,3-Dimercaptoacetone.[11] A well-stirred solution of NaOH (4.0 g, 0.1 mol) in 150 mL of H_2O was saturated with gaseous H_2S. The solution was cooled to 0–5 °C. A solution of 6.3 g (0.05 mol) 1,3-dichloroacetone in 96% EtOH (75 mL) was added dropwise to the solution. Care was taken to keep the temperature below 5 °C. During the addition, a flaky greyish-white precipitate formed. After the addition was complete, the stirring was continued for 45 min. The precipitate was collected and washed with three portions (50 mL) of cold (0 °C) water to remove inorganic salts and dried in vacuo (0.5 mmHg) at 50 °C. Yield 4.9 g (0.04 mol, 79%).

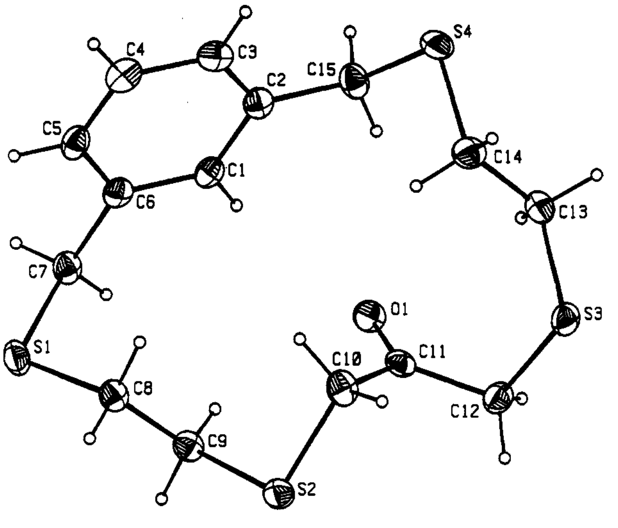


Figure 1. ORTEP (50% thermal ellipsoids) plot of 8.

Table I. Crystal Data and Structural Analysis Results

compd	8	9
formula	$C_{15}H_{20}S_4O$	$C_{11}H_{20}S_5O$
M_w	344.56	328.60
space grp	P-1	$P2_1/a$
crystal syst	triclinic	monoclinic
Z	2	4
a (Å)	7.230 (1)	16.558 (1)
b (Å)	8.690 (1)	5.399 (1)
c (Å)	13.253 (1)	16.734 (1)
α (deg)	83.153 (7)	
β (deg)	84.257 (6)	90.28 (5)
γ (deg)	85.575 (6)	
V (Å^3)	820.79 (16)	1495.9 (5)
D_c (g cm^{-3})	1.394 (4)	1.46
μ (cm^{-1})	5.5	7.3
radiatn (Mo Kα, Å)	0.71073	0.71073
T (K)	130	140
R_f[a]	0.029	0.048
R[b]	0.041	0.066

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table II. Selected Bond Distances (Å) and Angles (deg) for 8 and 9

8	9
O1–C11 = 1.213(2)	O(17)–C3 = 1.206(6)
O1–C11–C12–S3 = 99.65(15)	O(17)–C3–C2 = 120.7 (4)
S2–C10–C11–O1 = 86.53 (16)	O(17)–C3–C4 = 120.3 (4)
S1–C8–C9–S2 = 173.15(8)	S1–C2–C3–O17 = 107.0 (4)
S3–C13–C14–S4 = −177.73(8)	O17–C3–C4–S5 = 88.3(5)
	S5–C6–C7–C8 = 171.1(2)
	S8–C9–C10–S11 = 171.3(2)
	S11–C12–C14–C14 = 160.7(2)
	S14–C15–C16–S1 = 179.6(2)

General Procedure for the Synthesis of Thio-Crown Ethers via 1,3-Dimercaptoacetone. A DMF solution of both dithiol and (*in situ* prepared) dihalide (generally 10^{-2} M) was added dropwise onto a well-stirred, warm (50–65 °C) suspension of Cs_2CO_3 in DMF during a period of 10–18 h. After the reaction had ceased, the mixture was filtered to remove the insoluble and unreacted Cs_2CO_3 and CsCl. The DMF was evaporated under reduced pressure (0.5–1 mmHg) leaving an oily residue. This residue was taken up in a minimum amount of CH_2Cl_2 and chromatographed over silica gel using CH_2Cl_2–hexane (10:1) as eluent. On evaporation of the organic layer, the thio-crown ether was obtained.

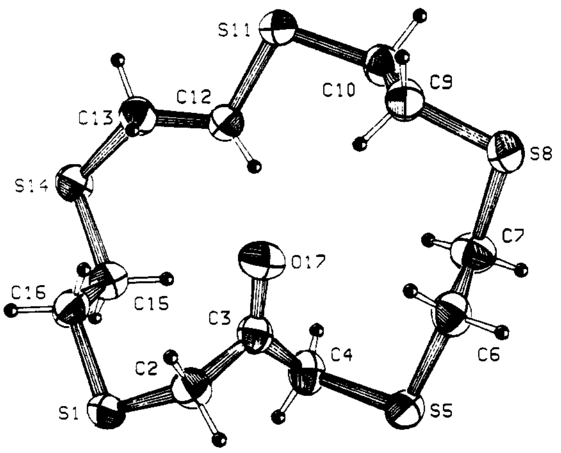


Figure 2. ORTEP (50% thermal ellipsoids) plot of **9**.

1,5-Dithiacyclooctan-3-one (3): mp 48.8-49.7 °C; yield 68%; ^{1}H-NMR ($CDCl_3$) 1.90 (quint, 2H), 2.94 (t, 4H), 3.49 (s, 4H); ^{13}C-NMR ($CDCl_3$) 29.1 (t), 33.3 (t), 41.5 (t), 205.9 (s); IR (KBr, cm^{-1}) 2960 s, 2926 m, 1700 s, 1424 s, 1407 s, 1346 s, 1309 s, 1256 s, 1065 s, 905 s; HRMS $m/z^+ = 162.271$ (calcd for $C_6H_{10}S_2O$ 162.271). Anal. Calcd. (found) for $C_6H_{10}S_2O$: C 44.41 (44.40) H 6.21 (6.17) S 39.52 (39.53).

1,4,7-Trithiacyclodecan-9-one (4): yield 72%; mp 105.1–107.2 °C; ^{1}H-NMR ($CDCl_3$) 2.87 (s), 3.65 (s); ^{13}C-NMR ($CDCl_3$) 32.1 (t), 33.1 (t), 41.1 (t), 202.3 (s); IR (KBr, cm^{-1}) 2950 m, 1710 s, 1650 s, 1400 s, 1280 s, 1210 m, 1080 s, 920 w; HRMS $m/z^+ =$ 208.031 (calcd for $C_7H_{12}S_3O$ 208.032). Anal. Calcd (found) for $C_7H_{12}S_3O$: C, 40.35 (39.99); H, 5.81 (5.78); S, 46.17 (46.29).

1,4,7,10-Tetrathiacyclotridecan-12-one (5): yield 73%; mp 162.1–164.2 °C; ^{1}H-NMR ($CDCl_3$) 3.21 (s, 12H), 4.17 (s, 4H); ^{13}C-NMR ($CDCl_3$) 30.4 (t), 30.7 (t), 32.5 (t), 39.9 (t), 200.6 (s); IR (KBr, cm^{-1}) 2950 s, 1720 s, 1440 s, 1380 s, 1040 s, 920 m; HRMS $m/z^+ = 268.487$ (calcd 268.487 for $C_9H_{16}S_4O$). Anal. Calcd (found) for $C_9H_{16}S_4O$: C, 40.26 (40.09); H, 6.01 (5.98); S, 47.77 (47.74).

1,4,8,11-Tetrathiacyclotetradecan-13-one (6): yield 67%; mp 124.2–125.7 °C; ^{1}H-NMR ($CDCl_3$) 1.85 (q, 2H), 2.60 (t, 4H), 2.88 (m, 8H), 3.51 (s, 4H); ^{13}C-NMR ($CDCl_3$) 30.4 (t), 30.5 (t), 31.6 (t), 33.1 (t), 200.4 (s); IR (KBr, cm^{-1}) 2950 s, 1710 s, 1440 s, 1380 s, 1280 s, 1200 s, 1030 s, 920 m; mass spectrum (m/z^+) 282, 133, 106, 105, 73; HRMS $m/z^+ = 282.487$ (calcd 282.487 for $C_{10}H_{22}S_4O$). Anal. Calcd (found) for $C_{10}H_{22}S_4O$: C, 42.52 (42.43); H, 6.42 (6.36); S, 45.40 (45.39).

1,5,9,14-Tetrathiacycloheptadecan-3-one (7): yield 68%; mp 96.1–99.3 °C; ^{1}H-NMR ($CDCl_3$) 1.72 (m, 4H), 1.88 (q, 4H), 2.57 (m, 4H), 2.64 (m, 12H), 3.46 (s, 4H); ^{13}C-NMR ($CDCl_3$) 27.8 (t), 29.1 (t), 30.5 (t), 31.1 (t), 31.5 (t), 39.8 (t), 200.3 (s); IR (KBr, cm^{-1}) 2982 s, 2959 s, 2924 s, 1697 s, 1664 s, 1614 m, 1456 s, 1433 s, 1414 s, 1377 s, 1362 m, 1339 m, 1292 s, 1257 s, 1244 s, 1214 s, 1201 m, 1185 s, 1157 s, 1116 m, 1069 s, 1055 s, 1037 s, 1016 s, 996 s, 970 m, 881 m; mass spectrum (m/z^+) 324, 161, 130, 106, 88; HRMS $m/z^+ = 324.071$ (calcd 324.071 for $C_{13}H_{24}S_4O$). Anal. Calcd (found) for $C_{13}H_{24}S_4O$: C, 48.10 (48.33); H, 7.45 (7.53); S, 39.51 (38.80).

2,5,9,12-Tetrathia-7-oxo-(13)-*m*-benzenophane (8): yield 76%; mp 115.2–116.5 °C; ^{1}H-NMR ($CDCl_3$) 2.60 (br s, 8H), 3.32 (s, 4H), 3.70 (s, 4H), 7.20 (m, 4 H); ^{13}C-NMR ($CDCl_3$) 29.7 (t), 31.3 (t), 37.2 (t), 39.1 (t), 127.9 (d), 129.5 (d), 139.1 (s), 200.2 (s); IR (KBr, cm^{-1}) 3000 m, 2950 s, 1705 s, 1600 s, 1520 s, 1500 s; HRMS $m/z^+ = 344.040$ (calcd 344.040 for $C_{15}H_{20}S_4O$). Anal. Calcd (found) for $C_{15}H_{20}S_4O$: C, 52.29 (52.11); H, 5.85 (5.73); S, 37.22 (37.17).

1,4,7,10,13-Pentathiacyclohexadecan-15-one (9): yield 25%; mp 119.8–110.7 °C; ^{1}-NMR ($CDCl_3$) 2.82 (s, 8H), 2.84 (m, ABXY-system, 8H), 3.20 (s, 4H); ^{13}C-NMR ($CDCl_3$) 30.2 (t), 32.1 (t), 32.4 (t), 32.6 (t), 37.8 (t), 197.8 (s); IR (KBr, cm^{-1}) 2950 s, 1705 s, 1430 s, 1400 s, 1280 s, 1200 m, 1100 s, 910 s, 740 s; exact mass $m/z^+ = 328.012$ (calcd 328.012 for $C_{11}H_{20}S_5O$). Anal. Calcd (found) for $C_{11}H_{20}S_5O$: C, 40.21 (40.18); H, 6.14 (6.12); S, 48.79 (48.78).

X-ray Data Collection and Refinement of 8. All calculations were performed on a VAX-11/730 system. Scattering factors were taken from Cromer and Mann,[15] and data were corrected for anomalous dispersion (Cromer and Liberman[16]). Illustrations were done with PLATON.[17,18] A polyfacial transparent crystal of approximate dimensions 0.25 × 0.30 × 0.45 mm was mounted on a glass fiber in a random orientation on an ENRAF-NONIUS CAD4F four-circle diffractometer interfaced with a VAX-11/730 computer. From the setting angles of 22 independent reflections in the range $13.29 \leq \theta \leq 20.63°$, the space group was determined to be P-1: the E-statistics showed unambiguously a centric space group.[19] This choice was confirmed by the solution and the successful refinement in this space group. Reduced cell calculations did not indicate any higher metric lattice symmetry,[20] and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[21,22]

From a total of 4276 reflections (3554 unique data, $\omega/2\theta$ scan, T = 130 K, Mo Kα-radiation graphite-monochromated, $\lambda =$ 0.710 73 Å), 3082 ($I \geq 2.5\sigma(I)$) were used in the refinements. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86).[17] Final full-matrix least-squares refinements based on F_o converged satisfactorily to $R =$ 0.029 and $R_w = 0.041$. A final Fourier map showed no peaks outside ±0.040 eA^{-3}. Further details on data collection and refinement are listed in Table I.

X-ray Data Collection and Refinement of 9. A crystal of **9** of approximate dimensions 0.12 × 0.52 × 0.40 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation ($\lambda =$ 0.710 73 Å) on an Enraf-Nonius CAD4F diffractometer equipped with a graphite crystal, incident beam monochromator and interfaced to a VAX-11/730. Cell constants and an orientation matrix for the data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $13° \leq \theta \leq 17.1°$. Due to systematic absences the space group was determined to be $P2_1/a$. The data collection was performed at 140 K using the $\theta - 2\theta$ scan technique. The intensities of three standard reflections, measured every 3 h, were used to control drift in the primary beam and counting system and also a decrease in the crystal quality.

From a total of 3582 reflections in the range $1° \leq \theta \leq 28°$, a number of 3021 reflections satisfied the criterion of observability ($I \geq 3\sigma(I)$). Scaling factors based on the fluctuations of the standard reflections, Lorentz and polarization corrections, and empirical absorption corrections were applied to the data. The linear absorption coefficient is 7.3 cm^{-1} (minimum transmission coefficient 0.905, maximum transmission coefficient 0.997).

The structure was partly solved by direct methods. The remaining atoms were located from succeeding Fourier difference syntheses. Block diagonal least-squares of F converged satisfactorily to a final $R = 0.048$ ($R_w = 0.066$, $w = 1$) including 190 parameters, using anisotropic temperature factors for the non-H atoms and isotropic fixed temperature factors (B = 4.0 Å^2) for the H-atoms. A final Fourier map showed no peaks outside ±0.043 eÅ^{-3}. Further details on data collection and refinement are listed in Table I.[23]

Supplementary Material Available: Spectra of **3–9** and **2a,b** and structure diagrams of **8** and **9** (30 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(23) The author has deposited atomic coordinates for the structures 8,9 with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.