sodium thiosulfate. Preparative tlc using the above solvent gave 490 mg (51%) of **11** as a homogeneous syrup: λ_{max}^{MeOH} 282 mμ (ε 7500), 215 (9700); ν_{max}^{KBr} 2120 cm^{-1} (N_3); nmr ($CDCl_3$) 2.21 and 2.25 (s, 3, OAc), 4.33 (q, 1, $J_{1',2'}$ = 4 Hz, $J_{2',3'}$ = 6 Hz, $C_{2'}H$), 4.41 (m, 3, $C_{4'}H$ and $C_{5'}H_2$), 5.23 (m, 1, $C_{3'}H$), 5.93 (d, 1, $J_{1',2'}$ = 4 Hz, $C_{1'}H$), 7.97 ppm (s, 1, C_6H); mass spectrum (70 eV) *m/e* 479 (M^+), 451 (M − N_2), 409 (M − N_2 − C_2H_2O), 391 (M − AcOH), 242 (M − base), 238 (base + H), 214 (sugar − N_2), 172 (sugar − N_2 − C_2H_2O).

Anal. Calcd for $C_{13}H_{14}N_5O_7I$: C, 32.58; H, 2.94. Found: C, 32.95; H, 3.11.

2′-Amino-2′-deoxy-5-iodouridine (**11b**).—A solution of **11a** (420 mg, 0.87 mmol) and sodium borohydride (300 mg) in 2-propanol (60 ml) was heated under reflux for 3 days. After evaporation of the solvent the residue was dissolved in water, brought to pH 6 with acetic acid, evaporated, and repeatedly coevaporated with methanol. The final residue was dissolved in water and passed through a column containing Dowex 50 (H^+) resin (60 ml). The eluate and washings contained 2250 optical density units (262 mμ) of 2′-azidonucleosides. Elution with 1 *N* ammonium hydroxide gave 2000 optical density units (273 mμ) of 2′-aminonucleosides. After evaporation to dryness, this material (200 mg) was purified by preparative tlc using acetone giving two main bands. The slower band (70 mg) consisted of 2′-amino-2′-deoxyuridine, while the faster band contained 60 mg (18%) of **12** which was crystallized from methanol with mp 204.5–205.5°: $\lambda_{max}^{H_2O}$ 287 mμ (ε 7200), 216 (11,900); $\lambda_{max}^{pH\ 13}$ 277 mμ (ε 5500); ORD (H_2O) multiple Cotton effect with a peak at 280 mμ (Φ +3700°) a trough at 250 mμ (Φ +3200°), a peak at 217 mμ (Φ 14,400°), and crossover at 205 mμ; nmr (pyridine-d_5) 4.01 (q, 1, $J_{1',2'}$ = 6.5 Hz, $J_{2',3'}$ = 5 Hz, $C_{2'}H$), 4.07 (AB of ABM, 2, J_{gem} = 14 Hz, $C_{5'}H_2$), 4.62 (br q, 1, $J_{4',5'a}$ = $J_{4',5'b}$ = $J_{3',4'}$ = 3 Hz, $C_{4'}H$), 4.77 (q, 1, $J_{2',3'}$ = 5 Hz, $J_{3',4'}$ = 3 Hz, $C_{3'}H$), 6.52 (d, 1, $J_{1',2'}$ = 6.5 Hz, $C_{1'}H$), 9.10 ppm (s, 1, C_6H).

Anal. Calcd for $C_9H_{12}N_3O_5I$: C, 29.28; H, 3.28; N, 11.38. Found: C, 28.86; H, 3.33; N, 11.29.

2′-Azido-3′,5′-di-*O*-benzoyl-2′-deoxyuridine (**9b**).—A solution of **2** (950 mg, 3.5 mmol) and benzoyl chloride (1.4 g, 10 mmol) in pyridine (10 ml) was kept for 16 hr at 23°. After addition of water, the solution was diluted with ethyl acetate, extracted with sodium bicarbonate, dried, and evaporated leaving a brown syrup. Purification by preparative tlc using benzene–ethyl acetate (9:1) gave 1.22 g (60%) of the N^2,3′-*O*,5′-*O*-tribenzoate (**9b**) as a homogeneous foam with λ_{max} 250 mμ (sh), 232, and unchanged in alkali: nmr ($CDCl_3$) 4.4–4.8 (m, 4, $C_{2'}$, $C_{3'}$, and $C_{5'}H$'s), 5.60 (t, 1, $J_{2',3'}$ = $J_{3',4'}$ = 5.5 Hz, $C_{3'}H$), 5.66 (d, 1, $J_{5,6}$ = 8 Hz, C_5H), 5.97 (d, 1, $J_{1',2'}$ = 4 Hz, $C_{1'}H$), 7.4–7.7 and 7.9–8.2 ppm (m, 16, aromatic and C_6H).

This compound (1.2 g) was dissolved in pyridine (10 ml) containing 2% water and heated under reflux for 1 hr. Evaporation to dryness, preparative tlc using ether–hexane (85:15) and crystallization from chloroform–hexane gave 735 mg (75%) of **9b** with mp 153–154°: λ_{max}^{MeOH} 256 mμ (ε 11,900), 231 (28,800); nmr ($CDCl_3$) 4.49 (q, 1, $J_{1',2'}$ = 4 Hz, $J_{2',3'}$ = 6 Hz, $C_{2'}H$), 4.6–4.8 (m, 3, $C_{4'}H$ and $C_{5'}H_2$), 5.63 (t, 1, $J_{2',3'}$ = $J_{3',4'}$ = 6 Hz, $C_{3'}H$), 5.64 (d, 1, $J_{5,6}$ = 8 Hz, C_5H), 6.04 (d, 1, $J_{1',2'}$ = 4 Hz, $C_{1'}H$), 7.4–7.7 and 8.0–8.2 ppm (m, 11, aromatic and C_6H).

Anal. Calcd for $C_{23}H_{19}N_5O_7$: C, 57.86; H, 4.01; N, 14.66. Found: C, 57.77; H, 4.06; N, 14.80.

Registry No.—**2**, 26929-65-7; **3**, 26889-39-4; **5**, 26889-40-7; **6**, 26889-41-8; **7**, 26929-67-9; **8**, 26889-42-9; **9a**, 26889-43-0; **9b**, 26889-44-1; **10**, 26889-45-2; **11a**, 26889-46-3; **11b**, 26889-47-4.

Macrocyclic Polyether Sulfides

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Macrocyclic polyether sulfides have been synthesized and some of their properties have been determined. These compounds contain two to four oxygen atoms and two to four sulfur atoms in the polyether–polysulfide ring. Formation of complexes of the macrocyclic polyether sulfides with alkali, alkaline earth, and silver cations is reported.

The preparation and properties of a number of macrocyclic polyethers derived from aromatic vicinal diols have been previously reported.[1] It was shown that certain of these compounds, particularly those containing five to ten oxygen atoms in the polyether ring, form stable complexes with cations including those of the alkali and alkaline earth metals and silver. In a continuation of this work, some macrocyclic polyethers in which two to four –O– linkages are replaced by –S– linkages were synthesized in order to determine the effects of this change on the complexing of cations. Differences were to be expected because oxygen is a smaller atom than sulfur, the C–O–C bond angle is greater than the C–S–C bond angle, and the electronegativity of oxygen is higher than that of sulfur which makes the C–S bond less ionic than the C–O bond. It is the purpose of this paper to report on the preparation of the macrocyclic polyether sulfides and to give a brief description of some of their properties.

4,7,10-Trioxa-1-thiacyclododecane, 4,10-dioxa-1,7-dithiacyclododecane, 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane, and 4,7,10,16,19,22-hexaoxa-1,13-dithiacyclotetracosane,[2] 1,3,5,7,9-oxatetrathiacyclodecane, and 1,3,5,7,9,11-oxapentathiacyclododecane[3] have been previously described, but their tendency to form complexes with cations is not mentioned.

The code letters and the structural formulas of the compounds described in this paper are shown in Figure 1. The digits within the diagrams indicate the total number of atoms in the polyether ring. The full names of the compounds and their preparation are given in the Experimental Section.

Results and Discussion

In general, the compounds were prepared by refluxing in 1-butanol under nitrogen cyclic vicinal mercaptophenol or dithiols with equivalent proportions of terminally substituted ether dichlorides and sodium hydroxide. The yields, melting points, and analytical data are shown in Table I. No attempt was made to maximize the yields or develop methods of recovery.

The infrared spectra of the compounds showed the

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[1] C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); C. J. Pedersen, *Fed. Proc. Fed. Amer. Soc. Exp. Biol.*, **27**, 1305 (1968).

[2] J. R. Dann, P. P. Chiesa, and J. W. Gates, Jr., *J. Org. Chem.*, **26**, 1991 (1961).

[3] L. Mortillaro, M. Russo, L. Credali, and C. DeChecchi, *J. Chem. Soc. C*, 428 (1966).

absence of OH and the presence of the appropriate ether linkages. The nmr spectra were consistent with the proposed structures. The ultraviolet spectra of the compounds which absorb in the region of 220–400 $m\mu$ are summarized in Table II, as well as the changes induced in them by the addition of excess silver nitrate.

The ultraviolet spectra of the macrocyclic polyethers in methanol show a single absorption peak at about 275 $m\mu$ with an extinction coefficient approximately 2100–2600 per aromatic ring.[1] The spectra of the aromatic macrocyclic polyether sulfides having at least one sulfur atom attached to the aromatic ring have a strong peak at about 255 $m\mu$ and another, often evident as a shoulder, in the region of 280–300 $m\mu$. The spectra of such compounds, B, C, E, F, and G, are profoundly affected by the addition of silver nitrate. The aromatic macrocyclic polyether sulfide, D, and sulfite, J, with no sulfur attached to the aromatic ring have spectra like those of the aromatic cyclic polyethers, and the effect of silver nitrate is also similar.

The ultraviolet spectra of all these compounds are little affected by the addition of an excess of the salts of the alkali and alkaline earth elements, suggesting that the interaction between the compounds and the cations of these salts in methanol is not strong.[1]

Crystalline complexes of silver nitrate with E and H were obtained. However, no crystalline complex of potassium thiocyanate and E was formed when an attempt was made to prepare it by the method which gave the crystalline complex of potassium thiocyanate with the macrocyclic polyether dibenzo-18-crown-6.[1]

The extraction method described below is a convenient way of comparing the relative complexing powers of organic compounds for different cations. This method has these advantages over the previously employed spectral method[1]: complexing efficiencies can be ranked numerically, and saturated compounds which do not absorb in the region of 220–400 $m\mu$ can also be evaluated.

When an aqueous solution of an alkali metal hydroxide or salt containing a very low concentration of the picrate of the same cation is mixed with an equal volume of an immiscible organic solvent, nearly all the picrate is present in the yellow aqueous phase and the organic phase remains substantially colorless. If a complexing agent is added to the system (by dissolving in the organic solvent), the complexed picrate transfers to the organic phase, the extent depending on the effectiveness of the polyether as a complexing agent for the cation (assuming no complication due to lack of solubility). If the additive is ineffective, the organic phase will be colorless; if the complexing agent is very powerful, most of the color will be in the organic phase, the intensity of which can be quantitatively determined spectrophotometrically by means of the picrate absorption band. The efficiencies of the complexing agents will lie between these two limits and can be expressed as percentage extracted. The stoichiometry of the extractable complex is 1:1 in respect to a univalent cation and picrate anion, hence, the maximum extraction is limited by the component present at the lowest concentration. For this reason, per cent extraction always means per cent of the extractable maximum.

The results obtained with some of the macrocyclic polyether sulfides are shown in Table III. For the pur-

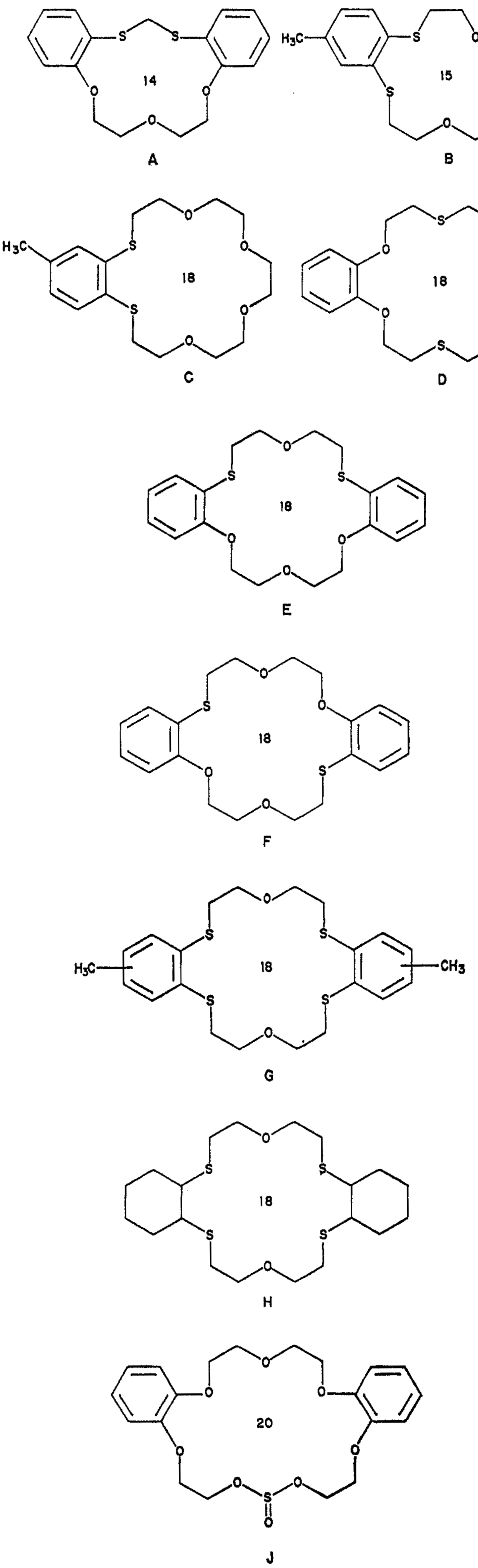

Figure 1.—Structural formulas and codes.

TABLE I

YIELDS AND ANALYTICAL DATA

Compd	Formula	Yield, %	Mp, °C[a]	Carbon, %		Hydrogen, %		Sulfur, %		Mol wt	
				Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
A	$C_{17}H_{18}O_3S_2$	3	150–153	60.9	61.0	5.4	5.4	19.7	19.2		334
B	$C_{15}H_{22}O_3S_2$	30	Viscous oil	57.0	57.3	7.1	7.0	19.8	20.4	333	314
C	$C_{17}H_{26}O_4S_2$	56	Viscous oil	56.5	57.0	7.3	7.3	17.9	17.9	382	358
D	$C_{16}H_{24}O_4S_2$	1	91	55.0	55.8	7.1	7.0	17.4	18.6		344
E	$C_{20}H_{24}O_4S_2$	15	143–144	61.3	61.2	6.1	6.1	16.3	16.3	384	392
F	$C_{20}H_{24}O_4S_2$	5	114–115	61.3	61.2	6.0	6.1	16.3	16.3	357	392
G	$C_{22}H_{28}O_2S_4$	6	147	58.7	58.4	6.0	6.2	27.6	28.3	462	452
H	$C_{20}H_{36}O_2S_4$	24	Viscous oil	56.7	55.0	7.8	8.3	28.8	29.4	432	436
J	$C_{20}H_{24}O_8S$	33	133	56.7	56.6	5.8	5.7	7.0	7.5		424

[a] Melting points were determined on a Fisher-Johns apparatus and are uncorrected.

TABLE II

ULTRAVIOLET SPECTRA IN METHANOL

Compd	Without any salt		With silver nitrate[a]	
	Peaks, mμ[b]	Ext coeff	Peaks, mμ[b]	Ext coeff
A	286.5	6,800	*c*	*c*
	292	6,700		
B	256	10,500	249	13,400
	(*ca.* 294)	1,700	(*ca.* 292)	1,200
C	254	11,300	(*ca.* 258)[d]	4,300
	(292)	2,000	(*ca.* 288)	1,900
D	277	3,000	275	3,100
			(280.5)	2,600
E	254	9,600	252	12,400
	282.5	6,100	282	7,400
	288	6,200		
F	255	9,100	(*ca.* 247)[d]	10,000
	282	6,100	282	5,700
	288.5	6,000		
G	256	22,000	(*ca.* 259)[d]	3,800
	(*ca.* 300)	2,300	297	1,400
J	276	4,600	...[c]	...[c]

[a] Silver nitrate was added in about 50-fold excess, and its effects on the spectra of the compounds (without any salt) are indicated by the changed values of the peaks and the extinction coefficients. [b] Parentheses indicate shoulders rather than peaks. [c] Little change on addition of silver nitrate. [d] The peak nearly disappears on addition of silver nitrate and is replaced by a slight shoulder on the sloping curve with a peak at 224 mμ.

TABLE III

EXTRACTION DATA. WATER–METHYLENE CHLORIDE[a]

Compd	Concn $\times 10^5$ *M*	Salt	Concn, *M*	Extracted, %[b]
B	7.0	KNO_3	0.1	2.4
B	7.0	$AgNO_3$	0.1	52
C	7.0	KNO_3	0.1	3.2
C	7.0	$AgNO_3$	0.1	77
E[c]		KCl		Poor
E[c]		$AgNO_3$		Good
F[c]		KCl		Poor
F[c]		$AgNO_3$		Good
G	7.0	KNO_3	0.1	5.5
G	7.0	$AgNO_3$	0.1	92
H	6.4	NaOH	0.125	2.2
H	6.4	$AgNO_3$	0.059	68
K[d]	25.4	NaOH	0.125	<1
K[d]	25.4	$AgNO_3$	0.059	10
XXXI[e]	7.0	KNO_3	0.1	69
XXXI[e]	7.0	$AgNO_3$	0.1	63

[a] Equal volumes of water and methylene chloride, and picric acid at 7.0×10^{-5} *M*. [b] The cation of the listed salt. [c] Not run quantitatively. [d] Di(*n*-octadecyl) sulfide. [e] Dicyclohexyl-18-crown-6, see ref 1.

pose of comparison, the extraction data for dicyclohexyl-18-crown-6 (XXXI)[1] and di(*n*-octadecyl) sulfide, K, are included. Of the previously studied polyethers, XXXI is the best complexing agent for potassium and also, in general, the most effective for the other cations.

It is evident that, as a group, the macrocyclic polyether sulfides are poorer complexing agents for sodium and potassium than the oxygen analogs (compare H with XXXI), but they are, at least, as good for complexing silver. B, C, G, and H were also tested with the other alkali metal and alkaline earth metal salts with similar results. Cursory tests indicated that the macrocyclic polyether sulfides are good complexing agents for gold, but the valence of the complexed gold was not determined.

A comparison of K with any other sulfur compound suggests that the macrocyclic polyether sulfides are very much better complexing agents for silver than the open-chain sulfide. It does not seem likely, however, that different types of coordination are involved in the two cases, but the great advantage accrues from chelation and the more favorable steric environment in the case of macrocyclic complexing agents.

The strong complexing power of the macrocyclic polyethers for the alkali and alkaline earth cations is destroyed by substituting –S– for –O–, probably because the symmetrical distribution of the negative charge around the "hole" of the polyethers is disturbed due to the larger size of the sulfur atom, its lower electronegativity, and the different bond angles involving the sulfur atom.

Experimental Section

The following instruments were used: Varian Model A-60 for nmr spectra, Perkin-Elmer Infracord Model 137 for infrared spectra, and Perkin-Elmer ultraviolet–visible spectrophotometer Model 202 for ultraviolet spectra. All inorganic compounds were reagent grade, and all solvents and available organic materials were commercial products used without purification.

Preparation of 2,3,7,8-Dibenzo-1,9,12-trioxa-4,6-dithiacyclotetradeca-2,7-diene (A).—To a mixture of 24.7 g (0.0936 mol) of bis(*o*-hydroxyphenylmercapto)methane, 200 ml of 1-butanol, and 7.5 g (0.188 mol) of sodium hydroxide dissolved in 10 ml of water was added dropwise 13.4 g (0.0936 mol) of bis(2-chloroethyl)ether diluted with 50 ml of 1-butanol. The mixture was refluxed overnight.

The solvent was distilled off while the volume was kept constant by the addition of water, and the aqueous mixture was extracted with 200 ml of chloroform and washed twice with 100 ml of aqueous 5% sodium hydroxide. (There was trouble due to emulsion.) The chloroform solution was evaporated and the residue, 20.3 g of very viscous material, was recrystallized from *n*-heptane. The desired compound was obtained as white crystals, 1.0 g.

Preparation of 2,3-(4′-Methylbenzo)-1,4-dithia-7,10,13-trioxacyclopentadeca-2-ene (B).—A mixture of 17.3 g (0.111 mol) of toluene-3,4-dithiol, 400 ml of 1-butanol, 25.6 g (0.111 mol) of

1,11-dichloro-3,6,9-trioxaundecane, and 8.9 g (0.222 mol) of sodium hydroxide dissolved in 10 ml of water was refluxed with good agitation for 6.5 hr (temperature 104°). The warm reaction mixture was filtered, the insoluble material was washed with 100 ml of 1-butanol, and the filtrate and the washing were concentrated. The residue, 17.5 g of viscous oil, was placed on a column (1.75 × 8 in.) of acid-washed, 200 mesh alumina, and the portion which came off with a mixture of 600 ml of benzene and 600 ml of chloroform, 10.5 g of viscous oil, was the desired compound.

Preparation of 2,3-(4′-Methylbenzo)-1,4-dithia-7,10,13,16-tetraoxacyclooctadeca-2-ene (C).—This compound was synthesized in the same way as the previous compound, B. The elution from the alumina column was effected, however, with benzene (20.1 g of product as a viscous oil).

Preparation of 2,3-Benzo-1,4,10,13-tetraoxa-7,16-dithiacyclooctadeca-2-ene (D).—To a boiling mixture of 900 ml of ethyl alcohol, 900 ml of water, and 6.4 g (0.06 mol) of anhydrous sodium carbonate was added dropwise in 1 hr 100 ml of ethyl alcohol containing 14.0 g (0.06 mol) of 1,2-bis(β-chloroethoxy)benzene and 11.0 g (0.06 mol) of 1,2-bis(β-mercaptoethoxy)ethane. The mixture was refluxed overnight, cooled, filtered, and evaporated. The residue, 9.4 g of brownish paste, was placed on a porous plate and 0.16 g of white fibrous crystals was obtained. No attempt was made to recover more product from the residue.

Preparation of 2,3,11,12-Dibenzo-1,7,13,16-tetraoxa-4,10-dithiacyclooctadeca-2,11-diene (E).—To a boiling mixture of 126 g (1 mol) of *o*-mercaptophenol, 1000 ml of 2-butanol, and 40 g (1 mol) of sodium hydroxide was added dropwise in 2 hr 74 g (0.52 mol) of bis(2-chloroethyl) ether diluted with 50 ml of 2-butanol. The mixture was cooled to 87°, 40 g of sodium hydroxide was added, and it was refluxed for 30 min (96°). Bis(2-chloroethyl)ether (74 g) diluted with 50 ml of 2-butanol was then added dropwise in 2 hr and the mixture was refluxed for 16 hr.

The mixture ws acidified with 30 ml of concentrated hydrochloric acid diluted with 200 ml of water, and the solvent was distilled off while making up the volume with water until the vapor temperature had risen to 100°. The pasty solids were filtered off, washed with water, and sucked as dry as possible. It was then mixed with 500 ml of acetone, filtered, and washed with 500 ml of acetone, and dried. The desired product, 60.4 g, was obtained as fibrous crystals.

Preparation of 2,3,11,12-Dibenzo-1,7,10,16-tetraoxa-4,13-dithiacyclooctadeca-2,11-diene (F).—To a mixture of 70.6 g (0.56 mol) of *o*-mercaptophenol, 460 ml of 1-butanol, and 22.4 g (0.56 mol) of sodium hydroxide in 25 ml of water was added rapidly 160 g (1.12 mol) of bis(2-chloroethyl) ether dissolved in 340 ml of 1-butanol and refluxed for 2 hr. The mixture was distilled while 1 l. of water was being added until about 1600 ml of distillate had been removed and the temperature was 104°. To the residue in the flask was added dropwise 22.4 g of sodium hydroxide in 25 ml of water which was then diluted with 400 ml of 1-butanol, and refluxed for 20 hr (97°).

The mixture was cooled, acidified with 29 ml of concentrated hydrochloric acid, and distilled while 1200 ml of water was added until about 1150 ml of distillate had been removed and the temperature was 105°. The mixture was extracted with 500 ml of chloroform and washed twice with 400 ml of water containing 20 g of sodium hydroxide. The chloroform solution was evaporated and gave 29.7 g of yellow oil. This was placed on a column of alumina and eluted with benzene. The residue from the eluate, 23.6 g, was extracted with *n*-hexane and gave the desired compound as white crystals.

Preparation of 2,3,11,12-Bis(4′- and/or 5′-methylbenzo)-1,4,10,13-tetrathia-7,16-dioxacyclooctadeca-2,11-diene (G).—A mixture of 48.8 g (0.313 mol) of toluene-3,4-dithiol, 500 ml of 1-butanol, and 20.7 g (0.313 mol) of 85% potassium hydroxide was heated to reflux temperature (114°) and to it was added dropwise in 2 hr 22.5 g (0.157 mol) of bis(2-chloroethyl) ether diluted with 50 ml of 1-butanol, and refluxed for 1 hr. The temperature was lowered to 76°, potassium hydroxide (20.7 g of 85%) was added, the temperature was raised to reflux, and to the mixture was added dropwise in 1 hr 22.5 g of bis(2-chloroethyl)ether diluted with 50 ml of 1-butanol. Then the refluxing was continued for 4 hr more.

After acidifying with 3 ml of concentrated hydrochloric acid, 1-butanol was distilled off while the volume of the mixture was kept constant by the addition of water. The pinkish paste which separated from the aqueous phase was dissolved in 600 ml of chloroform and extracted with 400 ml of 5% aqueous sodium hydroxide. The chloroform solution was dried with calcium chloride and evaporated. The residue, 67.2 g of very thick, sticky paste, was extracted with *n*-heptane and then with acetone. From these extracts, 4.2 g of white, shiny crystals of the desired compound were recovered. It is probable that the yield of the product was considerably higher, but an efficient method of recovery had not been developed.

Preparation of 2,8,15,21-Tetrathia-5,18-dioxatricyclo[20.4.0.-$0^{9.14}$]hexacosane (H).—To a mixture of 57.4 g (*ca.* 0.37 mol) of crude *trans*-1,2-cyclohexanedithiol,[4] 500 ml of air-free 1-butanol, and 14.6 g (0.365 mol) of sodium hydroxide in 20 ml of water, all at 60°, was added dropwise in 54 min 26.1 g (0.182 mol) of bis(2-chloroethyl)ether diluted with 70 ml of 1-butanol, and it was refluxed for 30 min. The mixture was cooled to 95°. Sodium hydroxide (14.6 g) in 20 ml of water was added, and then 26.1 g of bis(2-chloroethyl)ether diluted with 70 ml of 1-butanol was added dropwise in 57 min.

The mixture was filtered and evaporated (39.5 g of residue). This was dissolved in 200 ml of methylene chloride, washed with 200 ml of aqueous 5% sodium hydroxide (there was trouble due to emulsion), and evaporated. The residue, 31.5 g of brownish oil, was placed on a 1.75 × 6 in. column of alumina and eluted with benzene. The first 200 ml of eluate contained 18.9 g of the desired compound.

Preparation of 2,3,13,14-Dibenzo-1,4,7,9,12,15,18-heptaoxa-8-thiacycloeicosa-2,13-diene 8-Oxide (J).—1,17-Dihydroxy-4,5,13,-14-dibenzo-3,6,9,12,15-pentaoxaheptadeca-4,13-diene (1.89 g, 0.005 mol) dissolved in 200 ml of dry benzene was treated with 3.14 g (0.04 mol) of pyridine and 1.2 g (0.01 mol) of thionyl chloride, and warmed on a steambath for 1 hr. The mixture was filtered, and the filtrate was washed with 150 ml of water containing 5 ml of concentrated hydrochloric acid, dried, and evaporated. The residue was crystallized from a mixture of cyclohexane and benzene and yielded white crystals of the desired compound.

Preparation of Crystalline Silver Nitrate Complex of E.—A clear solution obtained by warming a mixture of 1.96 g (0.005 mol) of E, 50 ml of methanol, and 0.86 g (0.0051) mol of silver nitrate was cooled to room temperature and left in an open beaker protected from light. Large, off-white crystals were obtained melting at 197–203°. *Anal.* Calcd : C, 42.7; H, 4.3; S, 11.4; Ag, 19.2. Found: C, 42.8; H, 4.2; S, 11.5; Ag, 19.2.

On treating the above complex with sodium bromide in methanol, yellowish, fibrous crystals were recovered with a melting point above 210°. *Anal.* Calcd: Br, 13.8; Ag, 18.6. Found: Br, 12.7; Ag, 17.3.

Registry No.—A, 26736-17-4; B, 26736-18-5; C, 26736-19-6; D, 26850-07-7; E, 26736-20-9; F, 26736-21-0; G, 26778-70-1; H, 26736-22-1; J, 26736-23-2.

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(4) *trans*-1,2-Cyclohexanedithiol was prepared according to C. C. J. Culvenor, W. Davies, and K. H. Pausacker, *J. Chem. Soc.* (*London*), 1050 (1946).