

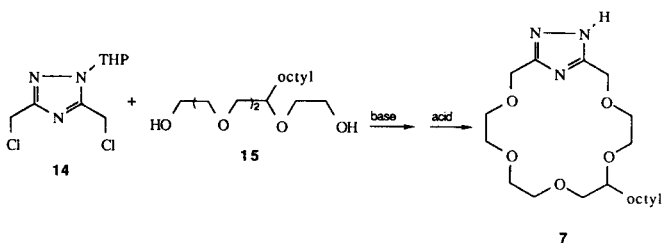
from the aqueous phase into an organic layer. Our new triazolo-crown compounds (**7** for example) are likewise important new cation transport agents. Preliminary work indicates that triazolo crown **7** is an even better carrier for potassium ions using our bulk liquid membrane system (see [12] for a description of the membrane system) than is 4-pyridino crown **4**. Compound **7** is also an effective transport agent for silver ions. A complete report on the transport of cations by these new triazole-containing crown compounds will be reported when the work is completed.

Results and Discussion.

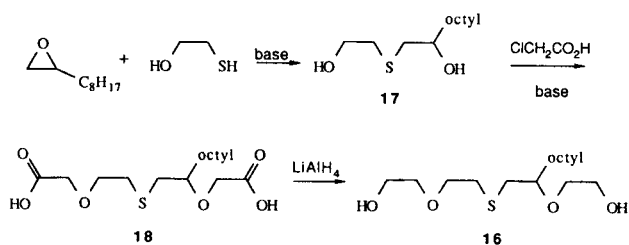
Compounds **6-13** were prepared from dichloride **14** [5] and the appropriate diol as shown in Scheme 1A. The diols have been reported previously except for sulfur-containing diol **16** (see Scheme 1B). Thus, the octyl containing triethylene and tetraethylene (**15**, Scheme 1A) glycols needed to prepare **6** and **7** were reported in references [13] and [4], respectively. The phenyl-substituted tetraethylene glycol needed for the preparation of **8** was also reported in reference [13]. The dioctyl-substituted tetraethylene glycol needed to prepare **9** was reported in reference [14]. 6-Thia-3,9-dioxo-1,11-undecanediol needed for the preparation of **10** has also been reported [15]. 4-Octyl thia glycol **16** was prepared as shown in Scheme 1B.

Scheme 1. Preparation of Compounds

A. Triazolo Crowns



B. Starting Thioglycol 16



The structures proposed for the new macrocyclic compounds are consistent with data obtained from their ir and nmr spectra, molecular weight determinations, combustion analyses and some crystal-structure determinations. Compounds **8**, **11**, **12**, and **13** were found to contain some water of hydration. The nmr spectra of all octyl-substituted crown compounds contained the same unsymmetrical peaks attributable to the hydrogens on carbons next to

the ether oxygen atoms as we have reported previously [13].

As mentioned earlier, ligands **1** and **2** formed complexes with benzyl amine. The structure of each of these compounds was shown to be one wherein the ionizable proton was removed by the amine to form an ammonium salt of the complex [2,3]. No complexes of any of these proton-ionizable crowns with metal cations wherein the anion is the deprotonated triazole or 4-pyridone group, have been reported. We have now found that triazolo-crown **5** [5] reacted with silver nitrate to form a crystalline complex composed of three silver cations and two nitrate ions and one crown **5** anion. The structure of the silver nitrate complex with **5** is shown in Figure 2. Atomic parameters are listed in Table I. The stoichiometry of the complex, $3\text{Ag} + 2\text{NO}_3 : 1$ ligand, clearly indicates that a hydrogen atom has been displaced from the ligand and that the ligand functions as an anion. It is not possible to state unambiguously which Ag^+ was the counter ion of the ligand as all three Ag^+ interact with the ligand. As indicated by the $\text{Ag}-\text{X}$ interatomic distances (see Table II) $\text{Ag}1$, which is approximately in the cavity, makes contacts with three ligand oxygen atoms, O7, O13 and O16 and one nitrate oxygen. $\text{Ag}2$ interacts with N1 of the ligand and N4 of a symmetry related ligand. $\text{Ag}2$ functions as a bridge binding two ligands together and it does not have any interactions with any nitrate oxygen and so could be the Ag^+ that causes the ionization of the ligand. However, this arrangement is complicated by the fact that $\text{Ag}3$ interacts with oxygens of two nitrate groups and N3 of the ligand.

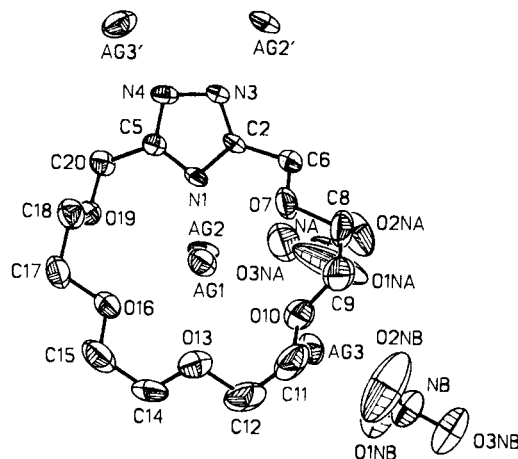


Figure 2. Computer drawing of the silver nitrate complex of **5** with hydrogen atoms omitted for clarity. The symmetry related $\text{Ag}2'$ and $\text{Ag}3'$ are included because of their role in the structure (see text). Thermal ellipsoids are drawn at the 50% probability level.

Table I

Positional ($\times 10^4$) and Thermal ($\text{\AA}^2 \times 10^3$) Parameters of the non-Hydrogen Atoms of 5-Silver Nitrate Complex with e.s.d. Values in Parenthesis

atom	x	y	z	U_{eq} [a]
AG1	2485(1)	1068(1)	3218(1)	49(1)
AG2	5492(1)	781(1)	2529(1)	46(1)
AG3	6648(2)	-298(1)	4203(1)	73(1)
N1	4458(11)	2317(5)	2303(4)	36(2)
C2	4531(12)	3273(6)	2638(5)	36(3)
N3	4154(9)	4100(5)	2272(4)	33(2)
N4	3749(11)	3691(6)	1659(4)	39(2)
C5	3956(11)	2625(7)	1705(4)	35(3)
C6	4990(15)	3353(8)	3350(5)	47(3)
O7	4004(12)	2659(7)	3687(4)	61(3)
C8	4562(22)	2583(11)	4375(6)	70(5)
C9	3527(27)	1888(11)	4716(6)	81(6)
O10	3545(12)	811(7)	4431(4)	61(3)
C11	2458(25)	101(14)	4742(5)	77(5)
C12	2321(23)	-918(13)	4375(7)	87(6)
O13	1615(13)	-655(7)	3768(4)	68(3)
C14	1562(21)	-1561(10)	3340(7)	67(5)
C15	624(19)	-1212(12)	2753(7)	74(5)
O16	1537(10)	-403(6)	2413(4)	50(2)
C17	703(16)	-98(10)	1822(6)	58(4)
C18	1334(14)	974(10)	1563(6)	54(4)
O19	2992(9)	860(6)	1366(3)	42(2)
C20	3612(14)	1851(8)	1156(5)	42(3)
NA	8887(12)	1474(7)	3517(6)	53(3)
O1NA	7721(24)	1375(11)	3849(11)	207(10)
O2NA	10142(14)	1911(11)	3649(8)	119(6)
O3NA	8711(19)	1228(11)	2938(7)	116(6)
NB	7446(15)	-655(11)	5566(5)	67(4)
O1NB	8319(25)	-1018(22)	5103(7)	189(11)
O2NB	6402(24)	-256(21)	5349(7)	193(11)
O3NB	7722(12)	-725(12)	6141(5)	98(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table II

Selected Silver Interatomic Distance (\AA) in the Silver Nitrate Complex of 5

AG1 - O7	2.509(9)
AG1 - O13	2.503(9)
AG1 - O16	2.563(8)
AG1 - O2NA	2.352(13)
AG2 - N1	2.122(7)
AG2 - N3	2.128(7)
AG3 - O1NA	2.352(16)
AG3 - O1NB	2.453(19)
AG3 - O2NB	2.344(14)
AG3 - N4	2.176(8)

Two other structures of triazolo-18-crown-6 type ligands are reported in this paper, namely the dibenzo derivative **12**, and the potassium thiocyanate complex of the dicyclohexano derivative **13**. The X-ray crystal structure of ligand **12** is shown in Figure 3. Atomic parameters for the atoms of **12** are listed in Table III. The conformation of the ether portion of the molecule is rather open. The steric requirements of the planar benzene rings and the triazole ring apparently cause the molecule to resemble other complexed 18-crown-6 derivatives, which have rather symmetrical shapes. The major difference found in **12** is the nearly planar five atom group, C12-C16. The largest deviation of any of the atoms from a least square plane containing them is 0.045 \AA . The plane makes an angle of 67° with the least-squares plane containing O4, O11, O17 and O24. The nearly circular cavity is indicated by the diagonal heteroatom interatomic distances which are N1-O14, 5.37 \AA , O4-O17, 5.64 \AA and O11-O24, 5.62 \AA . The shorter N1-O14 distance is a result of the C12-C16 plane.

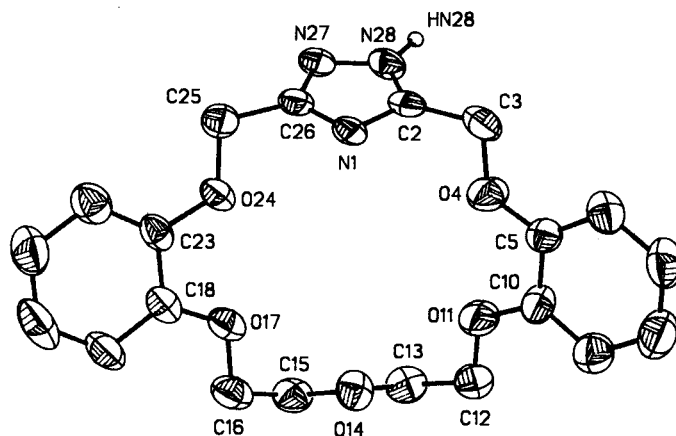


Figure 3. Computer drawing of **12** with all hydrogen atoms except HN28 omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

An unusual feature of the structure of **12** is the hydrogen bond linking N28 of one molecule to N1 of a neighboring molecule ($0.5 + x, 1.5 - y, -z$). The hydrogen bond data are N28 . . . N1, 2.811(6) \AA ; HN28 . . . N1, 1.92(6) \AA , and N28 - HN28 . . . N1, 158(5)°. This interaction makes N27 and N28 chemically non-equivalent and positions the hydrogen on N28. This causes a localization of the electrons in the triazole ring with the result that double bonds occur between N1 and C2 and C26 and N27. The triazolo bond lengths listed in Table IV, make the localization apparent in **12** and in the potassium thiocyanate complex of **13**.

Table III

Positional ($\times 10^4$) and Thermal ($\text{\AA}^2 \times 10^3$) Parameters of the non-Hydrogen Atoms, including HN28, of **12** with e.s.d. Values in Parenthesis.

atom	x	y	z	U_{eq} [a]
N1	1584(3)	7479(5)	1915(1)	42(1)
C2	2771(4)	7658(5)	2194(2)	41(2)
C3	2951(4)	8321(5)	2774(2)	54(2)
O4	2391(3)	7134(4)	3134(1)	62(1)
C5	2025(4)	7584(6)	3662(2)	45(2)
C6	2305(5)	9065(6)	3907(2)	56(2)
C7	1887(5)	9363(6)	4451(2)	66(2)
C8	1193(5)	8213(6)	4741(2)	77(3)
C9	911(5)	6726(6)	4489(2)	67(2)
C10	1323(5)	6403(6)	3949(2)	50(2)
C11	1087(3)	4973(4)	3660(1)	69(1)
C12	457(5)	3682(5)	3945(2)	59(2)
C13	146(5)	2371(6)	3519(2)	60(2)
O14	-879(3)	2901(4)	3120(1)	57(1)
C15	-1213(5)	1647(5)	2723(2)	59(2)
C16	-2159(4)	2244(6)	2253(2)	61(2)
O17	-1436(3)	3344(4)	1912(1)	60(1)
C18	-2032(4)	3773(5)	1398(2)	48(2)
C19	-3342(5)	3355(6)	1204(2)	63(2)
C20	-3824(5)	3840(6)	668(2)	81(3)
C21	-3035(6)	4704(8)	323(2)	80(3)
C22	-1719(5)	5171(6)	512(2)	59(2)
C23	-1233(4)	4694(5)	1046(2)	45(2)
O24	30(3)	5081(4)	1290(1)	49(1)
C25	858(4)	6200(6)	999(2)	50(2)
C26	1921(4)	6712(6)	1431(2)	43(2)
N27	3225(4)	6407(5)	1392(1)	48(2)
N28	3759(4)	7026(4)	1894(2)	46(2)
HN28	4705(43)	7040(52)	1991(17)	126 (18) [b]

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor. [b] Value is isotropic U .

Table IV

Interatomic Distances (\AA) in the Triazolo Portion of **12** and the Potassium Thiocyanate Complex of **13**

	12	KSCN Complex of 13
N1-C2	1.321(5)	1.314(13)
C26-N1	1.358(5)	1.352(13)
C26-N27	1.318(6)	1.336(11)
N27-N28	1.368(5)	1.378(13)
N28-C2	1.336(5)	1.368(10)

The structure of the potassium thiocyanate complex of **13** is shown in Figure 4. The configuration indicates that it is the *trans-syn-trans* or *meso* isomer. The positional parameters of the non-hydrogen atoms are listed in Table

V. It is unfortunate that it was not possible to locate a hydrogen atom on N27 or N28 as its position is of interest. The apparent localization of the electrons in the triazolo ring similar to that observed for **12** (Table IV) was apparent in both the room temperature and low temperature data. Based on these bond lengths, the hydrogen should be bonded to N28. This is supported by the short N28 - NT contact distance of 2.785 \AA which suggests a N28-H...NT hydrogen bond.

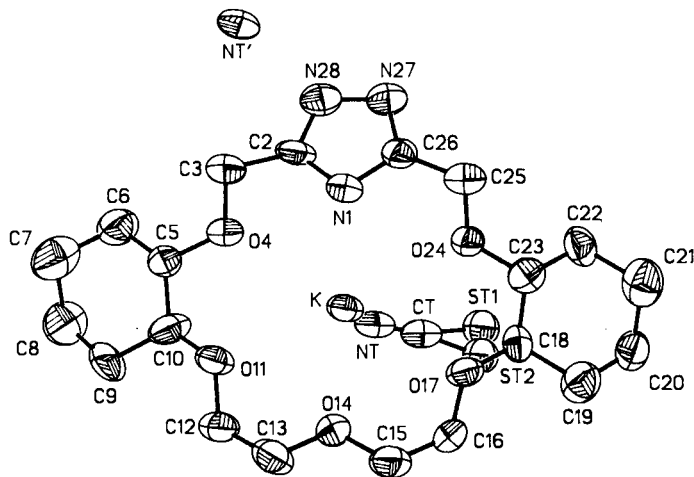


Figure 4. Computer drawing of the potassium thiocyanate complex of **13** with all hydrogen atoms omitted for clarity. NT', a symmetry related thiocyanated nitrogen, is included because of its proximity to N28 (see text). Thermal ellipsoids are drawn at the 50% probability level.

Table V

Positional ($\times 10^4$) and Thermal ($\text{\AA}^2 \times 10^3$) Parameters of the non-Hydrogen Atoms of 13-Potassium Thiocyanate Complex with e.s.d. Values in Parenthesis

atom	x	y	z	U_{eq} [a]
K	3884(1)	1333(1)	3281(1)	52(1)
NT	2916(5)	1293(6)	1273(5)	63(4)
CT	3282(6)	1250(7)	718(6)	56(4)
ST1	3745(6)	1535(17)	0(5)	75(4)
ST2	3780(4)	991(12)	-9(4)	71(3)
N1	4390(5)	3265(5)	4258(5)	55(4)
C2	3642(7)	3829(6)	4279(6)	55(4)
C3	2861(7)	3415(7)	4543(7)	74(6)
O4	2549(4)	2403(4)	4031(4)	68(3)
C5	1895(7)	1774(6)	4268(7)	57(5)
C6	924(7)	2350(8)	4074(8)	83(6)
C7	201(8)	1675(9)	4279(9)	105(7)
C8	37(7)	564(9)	3781(8)	101(7)
C9	1006(7)	-64(7)	4014(8)	80(6)
C10	1739(7)	636(7)	3835(7)	74(5)
O11	2672(4)	156(4)	4061(4)	59(3)
C12	2706(7)	-969(7)	3868(8)	81(6)
C13	3717(7)	-1361(7)	4099(7)	70(5)

O14	4174(5)	-802(5)	3625(5)	79(4)
C15	5103(7)	-1216(7)	3742(6)	67(5)
C16	5430(7)	-670(7)	3059(7)	70(5)
O17	5710(4)	421(4)	3310(4)	54(3)
C18	5983(6)	1039(7)	2658(6)	51(4)
C19	6789(7)	497(7)	2460(7)	76(5)
C20	7087(7)	1184(8)	1800(7)	77(5)
C21	7333(7)	2349(9)	2149(7)	87(6)
C22	6554(6)	2872(7)	2373(6)	65(5)
C23	6240(6)	2189(7)	3029(6)	55(4)
O24	5474(4)	2683(4)	3194(4)	52(3)
C25	5706(6)	3656(7)	3748(6)	60(4)
C26	4873(6)	3991(7)	3930(6)	52(4)
N27	4451(6)	4998(6)	3713(5)	60(4)
N28	3649(5)	4881(5)	3936(4)	60(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

The potassium ion of the potassium thiocyanate-**13** complex is located below the cavity of the macrocycle 0.496 Å from the least-squares plane of the oxygen atoms of the polyether. This arranges the heteroatoms of the 18-crown-6 portion of the molecule in a nearly circular arrangement though it is slightly elliptical with K - N1 and K - O14 being significantly shorter than the other K - O distances. The thiocyanate anion is coordinated to the K through the N, not through the sulfur. The C—C and C—O bond distances agree well with those reported for dicyclohexano-18-crown-6 complexes.

The transport of metal cations in the bulk membrane system by crown **7** has proved to be of interest. As expected, crown **7** is an excellent transport agent for potassium and silver cations. A complete description of the transport by these new lipophilic ligands will be reported when the work is completed.

EXPERIMENTAL

Infrared (ir) spectra were obtained on a Matson FTIR spectrometer. The proton nuclear magnetic resonance (nmr) spectra were obtained on a JEOL FX-90Q Spectrometer using deuteriochloroform unless otherwise indicated. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona. Molecular weights were determined by the electron impact method on a Finnegan 8430 High Resolution Mass Spectrometer. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Starting materials were purchased from commercial sources when available. Starting octyl- and phenyl-substituted glycols and the unsubstituted thia glycol were prepared as reported [4,13-15]. The octyl-substituted thia glycol was prepared as follows (Scheme 1B).

1-Octyl-3-thia-1,5-pentanediol (**17**).

2-Mercaptoethanol (10 g, 0.13 mole) and 30 g (0.19 mole) of 1,2-epoxydecane were added to 500 ml of isopropyl alcohol containing 3 g of potassium hydroxide and the mixture was stirred under nitrogen at 65° for 48 hours. The alcohol solvent was removed under vacuum and the residue was dissolved in 50 ml of ether. The ether mixture was washed with 25 ml of water and then dried over anhydrous magnesium sulfate. The ether

was removed under reduced pressure to give 3.5 g (80%) of crude product **17**; nmr: δ 0.88 (t, 3H), 1.28 (s, 12H), 1.42 (m, 2H), 2.44-2.78 (m, 5H, peaks at 2.44-2.50 disappeared in deuterium oxide), 3.28 (broad, 1H, disappeared in deuterium oxide), 3.78 (t, 2H), 3.92 (m, 1H). This material was used without further purification to prepare **18**.

4-Octyl-3,9-dioxa-6-thiaundecanedioic Acid (**18**).

Compound **17** (45 g, 0.19 mole) and 45 g (0.38 mole) of sodium chloroacetate were added to a mixture of 30 g of potassium *t*-butoxide and 150 ml of THF. The mixture was stirred under reflux for 24 hours. The cooled basic solution was added to 100 ml of aqueous sodium hydroxide. The organic layer was separated and washed with aqueous sodium hydroxide. The combined aqueous layers were acidified with hydrochloric acid and the acidified layer was washed twice with 100 ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate. The ether was evaporated under reduced pressure to give about 60 g (88%) of diacid **18** as a light yellow oil; nmr: δ 0.88 (t, 3H), 1.28 (s, 12H), 1.45 (m, 2H), 2.80 (t, 2H), 3.16 (m, 2H), 3.60-3.88 (m, 3H), 3.96-4.22 (m, 4H), 7.58 (s, 2H). This material was used without further purification to prepare **16**.

4-Octyl-3,9-dioxa-6-thia-1,11-undecanediol (**16**).

A mixture of 35 g (0.10 mole) of **18**, 10 g of lithium aluminum hydride and 500 ml of anhydrous ether was stirred at room temperature for 22 hours. Water (10 ml) was then added very slowly to the stirring mixture. Aqueous 3M sodium hydroxide (30 ml) was added to this mixture and the phases were separated. The organic phase was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The oily residue was distilled in a Kugel Rohr apparatus to give about 3.5 g of a light yellow oil, bp 100-130°/0.5 mm and 12.5 g (39%) of **16** as a yellow viscous oil, bp 145-160°/0.5 mm; nmr: δ 0.86 (t, 3H), 1.26 (s, 12H), 1.42 (m, 2H), 2.72 (m, 4H), 3.25-3.80 (m, 11H). The elemental analysis of **11**, a derivative of **16**, was satisfactory.

Synthesis of Crown Ethers **6-13** (Scheme 1A).

The starting *bis*-(chloromethyl)triazole **14** in dry tetrahydrofuran (THF) (about 0.1 mole of **14** per 500 ml of THF) and the oligoethylene glycol plus a 1.1 equivalent of potassium *t*-butoxide in a like amount of THF, were added simultaneously over a period of 2-4 hours to 300 ml of stirring and refluxing THF under an atmosphere of nitrogen. The mixture was stirred and refluxed for 24 hours and then cooled and filtered. Evaporation of the solvent yielded an oil. Some crowns were purified at this point by dissolving them in 300 ml of pyridine. A catalytic amount of 4-*N,N*-dimethylaminopyridine was added and all unreacted diols were acetylated with acetic anhydride. Ethanol was then added to react with the remaining anhydride. The solvent was then evaporated and the remaining oil was chromatographed on silica gel using a solution of 95% ethyl acetate, 4% ethanol and 1% triethylamine as eluant. The THP-protected product was reacted with methanolic hydrogen chloride for 1 hour at room temperature. The methanol was evaporated and the mixture was neutralized with aqueous sodium bicarbonate. The aqueous material was extracted with dichloromethane and dried over anhydrous magnesium sulfate to yield the product.

7-Octyl-3,6,9,12-tetraoxa-15,16,17-triazabicyclo[12.2.1]heptadecan-1(16),14-diene (**6**).

Compound **14** (3.77 g, 0.015 mole) was combined with 3.94 g (0.015 mole) of the octyl substituted triethylene glycol to give 12.13 g of crude THP-blocked product as an orange oil. After acetylation, chromatography, and deblocking, 1.27 g (24%) of a yellowish brown syrup was obtained; nmr: δ 0.87 (t, 3H), 1.25 (s, 14H), 3.54 (s, \approx 3H), 3.72 (s, 8H), 4.70 (two s, 4H), 12.90 (broad, 1H).

Anal. Calcd. for $C_{18}H_{33}N_3O_4$: C, 60.82; H, 9.35; M⁺, 355.47. Found: C, 60.64; H, 9.13; M⁺, 355.33.

7-Octyl-3,6,9,12,15-pentaoxa-18,19,20-triazabicyclo[15.2.1]eicosan-1(19)17-diene (**7**).

Compound **14** (11.86 g, 0.047 mole) and 14.53 g (0.047 mole) of the octyl-substituted diol **15** (Scheme 1A) were used to give 28.77 g of THP-blocked crude product as a red oil. The oil was extracted with heptane using a liquid-liquid extractor for 24 hours to give 12.97 g of a pale yellow oil. After acetylation, chromatography and deblocking, 6.74 g (36%) of a yellow oil was obtained. The oil partially solidified on standing; nmr: δ 0.88 (t, 3H), 1.27 (s, 14H), 3.54 (s, \approx 3H), 3.69 (m, 12H), 4.78 (two s, 4H), 12.80 (broad, 1H).

Anal. Calcd. for $C_{20}H_{33}N_3O_5$: C, 60.13; H, 9.33; N, 10.52; M^+ , 399.53. Found: C, 59.90; H, 9.50; N, 10.36; M^+ , 399.

7-Phenyl-3,6,9,12,15-pentaoxa-18,19,20-triazabicyclo[15.2.1]eicosa-1(19),17-diene (**8**).

Compound **14**, (4.44 g, 0.018 mole) and 4.8 g (0.018 mole) of the phenyl-substituted tetraethylene glycol were used to give 10.2 g of crude oil. After acetylation, chromatography, and deblocking, 3.12 g (48%) of a pale yellow oil was obtained; nmr: δ 3.5-3.75 (m, 14H), 4.64 (m, 1H), 4.84 (s, 4H), 7.36 (s, 5H), 12.10 (broad, 1H).

Anal. Calcd. for $C_{18}H_{25}N_3O_5 \cdot 1.75H_2O$: C, 54.75; H, 7.27; N, 10.64; M^+ , 363.41 (anhydrous). Found: C, 54.64; H, 6.94; N, 10.34; M^+ , 363.

4,14-Dioctyl-3,6,9,12,15-pentaoxa-18,19,20-triazabicyclo[15.2.1]eicosa-1(19),17-diene (**9**).

Compound **14** (10.0 g, 0.04 mole) and 16.75 g (0.04 mole) of the dioctyl substituted glycol were used to yield 20.23 g of THP-blocked crude pro-

duct as an orange oil. After acetylation, chromatography, and deblocking, 5.07 g (25%) of a yellowish-brown syrup was obtained; nmr: δ 0.87 (t, 6H), 1.25 (s, 28H), 3.53 (s, 6H), 3.69 (s, 8H), 4.73 (s, 4H), 12.60 (broad, 1H).

Anal. Calcd. for $C_{28}H_{43}N_3O_5$: C, 65.72; H, 10.44; M^+ , 511.74. Found: C, 65.81; H, 10.31; M^+ , 512.

3,6,12,15-Tetraoxa-9-thia-18,19,20-triazabicyclo[15.2.1]eicosa-1(19),17-diene (**10**).

Compound **14** (2.50 g, 0.01 mole) and 2.10 g (0.01 mole) of the thia glycol were used to give 6.1 g of an oil. The oil was extracted with heptane for 24 hours. After evaporation of the solvent, 1.77 g of a clear oil remained. After acetylation, chromatography, and deblocking, 0.59 g of a yellow oil was obtained. The oil solidified on standing. The solid was recrystallized from acetone and pentane to give 0.51 g (17%) of white crystals, mp 95.5-97.0°; nmr: δ 2.79 (t, 4H), 3.72 (m, 12H), 4.69 (s, 2H), 4.77 (s, 2H), 12.00 (broad, 1H).

Anal. Calcd. for $C_{12}H_{21}N_3O_4S$: C, 47.51; H, 6.98; N, 13.85; M^+ , 303.36. Found: C, 47.49; H, 7.08; N, 13.63; M^+ , 304.

7-Octyl-3,6,12,15-tetraoxa-9-thia-18,19,20-triazabicyclo[15.2.1]eicosa-1(19),17-diene (**11**).

Compound **14** (3.21 g, 0.013 mole), and 4.24 g (0.013 mole) of diol **16** were used to give 10.22 g of a dark orange oil. After acetylation, chromatography, and deblocking, 0.48 g (9%) of a yellow oil was isolated; nmr: δ 0.88 (t, 3H), 1.26 (s, 14H), 2.81 (m, 4H), 3.73 (m, 11H), 4.73 (two s,

Table VI

Crystal and Experimental Data

	12	AgNO ₃ with 5	KSCN with 13
Formula	$C_{20}H_{24}N_3O_5$	$Ag_3C_{12}H_{20}N_3O_5 \cdot 2NO_3$	$[C_{20}H_{33}N_3O_5] \cdot KSCN$
Formula weight	386.4	733.92	492.66
Crystal size, mm	0.40 × 0.17 × 0.05	.30 × .25 × .20	0.45 × 0.40 × 0.20
Temperature	22	22	about -150
μ , cm ⁻¹	0.91	28.10	3.29
Number of data used in lattice parameter determination	18	25	17
2 θ range of data used in lattice parameter determination	7-21	11-25	11-18
Space group	P2 ₁ /a	P2 ₁ 2 ₁	P2 ₁ /n
a, Å	9.853(3)	8.196(2)	14.870(8)
b, Å	8.249(3)	12.309(4)	12.003(7)
c, Å	23.535(8)	20.357(7)	15.135(11)
β , deg.	92.85(3)	90	115.34(5)
V, Å ³	1911(1)	2054(1)	2441(3)
Z	4	4	4
D _x , gcm ⁻³	1.33	2.37	1.34
Scan rate range, deg. min. ⁻¹	3-30	4-30	2-30
total unique reflection	2728	2699	3185
unobserved	1144	305	1243
observed	1584 F \geq 3 σ (F)	2394 F \geq 4 σ (F)	1942 F \geq 3 σ (F)
Sin θ/λ	0.54 [a]	0.65	0.54
R	0.076	0.053	0.096
Rw	0.036	0.058	0.075
max peaks	0.33, -.31	1.20, -1.15	0.37, -0.38
in Δ map eÅ ⁻³			

[a] The data include 239 reflections in the 2 θ range of 45 to 50°. However, because only 7% of the data were greater than 2 σ (I) and only 3 reflections were greater than 3 σ (I), data collection in this range was terminated.

4H), 9.70 (broad, 1H).

Anal. Calcd. for $C_{20}H_{37}N_3O_4S \cdot H_2O$: C, 55.40; H, 9.07; N, 9.69; M⁺, 415.59 (anhydrous). Found: C, 55.67; H, 9.18; N, 9.47; M⁺, 416.

4,5,13,14-Dibenzo-3,6,9,12,15-pentaoxa-18,19,20-triazabicyclo[15.2.1]eicosa-1(19),17-diene (**12**).

Compound **14** (2.50 g, 0.01 mole) and 2.90 g (0.01 mole) of dibenzotetraethylene glycol (Parish Chemical, recrystallized twice from methanol) were used to give 7.3 g of dark orange oil. The crude oil was chromatographed on silica gel. The combined fractions were evaporated and the product was deblocked to give 2.7 g (71%) of a white solid, mp 203.5-204.5°; nmr: δ 3.95 (s, 4H), 4.21 (s, 4H), 5.28 (s, 4H), 6.99 (s, 8H); the N-H peak was not observed.

Anal. Calcd. for $C_{20}H_{23}N_3O_5 \cdot 0.25H_2O$: C, 61.92; H, 5.59; N, 10.83; M⁺, 383.40 (anhydrous). Found: C, 61.63; H, 5.64; N, 10.69; M⁺, 384.

4,5,13,14-Dicyclohexano-3,6,9,12,15-pentaoxa-18,19,20-triazabicyclo[15.2.1]eicosa-1(19),17-diene (**13**).

Compound **14** (5.0 g, 0.02 mole) and 6.05 g (0.02 mole) of the dicyclohexano tetraethylene glycol [**14**] were used to give 13.04 g of the THP-blocked crude product as a yellow oil. The oil was extracted continuously with hexane for 3 hours to yield 6.52 g of a colorless oil. The oil was deblocked to give 3.13 g (40%) of **12** as a colorless oil; nmr: δ 1.18 (m, 8H), 1.6-2.0 (m, 8H), 3.50-3.80 (m, 12H), 4.82 (m, 4H), 12.0 (broad, 1H).

Anal. Calcd. for $C_{20}H_{23}N_3O_5 \cdot 0.5H_2O$: C, 59.38; H, 8.47; mol wt. 395.5. Found: C, 59.33; H, 8.34; mol. wt. 396.0.

X-ray Determinations.

Crystal and intensity data for the three crystals used in the X-ray structure studies reported in this paper were obtained using a Nicolet R3 automated diffractometer which used graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal and experimental data are summarized in Table VI. Lattice parameters were determined using a least-squares procedure involving angle settings for several carefully centered reflections for each compound. Intensity data for each crystal were measured using a variable scan speed θ - 2θ scan procedure. Structure refinement for each structure was performed using a cascading blocked least-squares procedure. Weights were based on counting statistics. An empirical extinction correction was applied to each set of data. However no absorption correction was applied to any data set. All computer programs used in the solution and display of the three structures are contained in the SHELXTL [16] program package. Atomic scattering factors were obtained from the International Tables for X-ray crystallography [17].

The structure of **12** was solved using direct methods. Positions for all the hydrogen atoms except that of the triazolo moiety were calculated based on geometrical conditions. It was possible to locate the hydrogen on the triazolo ring, HN28, in the difference fourier map. All non-hydrogen atoms were refined anisotropically while HN28 was refined isotropically. The rest of the hydrogen atoms were allowed to ride on their neighboring carbon atom with the isotropic thermal parameter set at a value 1.2 times the initial equivalent thermal parameter of that carbon.

Single crystals of the silver nitrate complex of **5**, suitable for X-ray determination were prepared by dissolving a 4.5:1 ratio of silver nitrate:crown in water and evaporating to dryness. A trial model for the structure was obtained using a combination of heavy atoms and direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated based on stereochemical considerations and were allowed to ride on their neighboring carbon atoms during the refinement process.

The crystals of **13** with potassium thiocyanate appeared to have rather large thermal motion as there were very few spots in the line up photograph that corresponded to a 2θ value of greater than 12° . Peak scans were significantly broader than usual. A room temperature solution of the structure did show large thermal motion particularly for the sulfur atom of the thiocyanate. The large thermal motion caused the number of

observed reflections to be unacceptably low. For these reasons single crystal and intensity data were collected at low temperature, approximately -150° . This temperature was achieved using a Nicolet LT-1 low temperature apparatus attached to the diffractometer which blows a stream of nitrogen vapor on the crystal. The intensity of the larger 2θ value reflections increased significantly at low temperature but reflections with 2θ values greater than 30 degrees were still rather weak.

In the final refinement there were a total of 291 parameters which resulted in a data/parameter ratio of 6.7. The positional parameters of the room temperature structure were used as the initial parameters for the structure refinement and these were initially refined isotropically and then anisotropically for all non-hydrogen atoms. The differences between the room temperature and low temperature results generally involved the temperature parameter values. In addition, it was possible to resolve a disorder of the sulfur atom. The large Ueq value for this atom at room temperature (about 0.17 \AA^2) suggested disorder but the disorder could not be resolved using that data set. Using the low temperature data, the difference map clearly showed two peaks for the sulfur atom. These atom fractions were refined isotropically. The population parameters were also refined, their sum being equal to 1.012 in the final refinement. All of the other non-hydrogen atoms were refined anisotropically. Positions for hydrogen atoms bonded to carbon atoms were calculated based on geometrical conditions and the hydrogen atoms were allowed to ride on neighboring carbon atoms during the final refinement. It was not possible to find a peak in the difference map for the hydrogen on the triazolo portion of the structure.

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