electron-exchange mechanism (as discussed above) must be involved.

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Molecular Complexes of Cyclic Polyethers. 6. Structure of and Binding Interactions in a Host–Guest Complex of a Macrocyclic Hexaether with *tert*-Butylammonium Perchlorate. Survey of Crystallographic Data

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Abstract: This paper reports the crystal and molecular structures of a macrocyclic polyether ligand, 2,3:4,5-bis[1,2-(3-methylnaphtho)]-1,6,9,12,15,18-hexaoxacycloeicosa-2,4-diene ($C_{32}H_{36}O_6$, I), and of its 1:1 complex with *tert*-butylammonium perchlorate (II), as determined by X-ray diffraction methods. The inclusion complex crystallizes with 1 mol of benzene in the triclinic space group $P\bar{1}$ with a = 8.902 (5) Å, b = 11.117 (5) Å, c = 20.885 (12) Å, α = 91.69 (4)°, β = 91.07 (5)°, γ = 96.30 (4)°, and Z = 2. Crystal data of the uncomplexed hexaether: a = 8.738 (3) Å, b = 12.037 (5) Å, c = 13.771 (4) Å, α = 104.11 (3)°, β = 84.57 (3)°, γ = 96.46°, Z = 2, space group $P\bar{1}$. The host molecules are conformationally disordered in the crystal when uncomplexed, but have an ordered structure in the complex they form with $(CH_3)_3CNH_3^+ClO_4^-$. The observed geometry of the intermolecular host-guest type association is correlated with that found in previous studies of related compounds. Structural data confirm that two types of interactions binding an ammonium guest to a macrocyclic polyether host are important: (a) $^+NH\cdots O$ hydrogen bonds and (b) direct $N^+\cdots O$ pole-dipole attractions where one of the lone-pair orbitals of a donor oxygen is directed at the electrophilic N. Inspection of the molecular structures reveals that the preferred overall conformation of this ligand is asymmetric, the mean plane of the macroring forming an angle of about 40° with the 1,1′-dinaphthyl bond and approaching one of the methyl substituents. As a result, the two faces of the macrocyclic cavity are equivalent with respect to the complexation of an ammonium guest only by virtue of rapidly established equilibria in solution between conformers.

The occurrence of intermolecular complexes of macrocyclic polyether hosts with organic guests, and in particular with alkylammonium ions, is well documented in the literature on host-guest chemistry.[1-4] In their extensive chemical studies in solution, Cram and his co-workers have shown that the affinity of polyether ligands for ammonium substrates is largely dependent on the topological features of the interacting species.[2,3] They have also described relationships between the relative size and shape of optically pure components and the degree of stereoselectivity obtained in the complex-formation process.[5] In the course of our investigations into the structural chemistry of crown ether complexes, we have recently characterized by low-temperature X-ray analyses the geometry of interaction between polyether hosts and alkylammonium guests in several model compounds. Previous reports dealt with the complexes of 2,6-dimethylylbenzoic acid 18-crown-5,[6a] bis(2,3-naphtho-18-crown-6),[6b] and a hexaether host containing two 2,2′-substituted 1,1′-dinaphthyl units[6c] (formulas V, VI, and VII in Figure 2), and it has been established that lipophilization of RNH_3^+ salts by crown ethers is principally due to complexation through a tripod arrangement of $^+NH\cdots O$ hydrogen bonds. The latter complex provided also an illustration of the kinds of steric forces that affect chiral recognition among optically pure species, involving the *R* isomer of a primary amine salt $C_6H_5CH(CO_2CH_3)NH_3^+PF_6^-$ and the *S,S* isomer of host VII.

The present study is concerned with the hexaether host I, which contains a 3,3′-dimethyl-1,1′-dinaphthyl unit bound to oxygen in the 2,2′ positions (systematic name: 2,3:4,5-

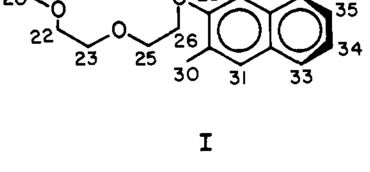

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Table I. Summary of Crystal Data and Experimental Parameters

	I		II	
formula	$C_{32}H_{36}O_6$		$C_{42}H_{54}ClNO_{10}$	
mol wt	516.6		768.4	
space group	$P\bar{1}$		$P\bar{1}$	
Z	2		2	
	300 K	193 K	300 K	113 K
a, Å	8.738(3)	8.637(5)	8.902(5)	8.848(3)
b, Å	12.037(5)	11.974(7)	11.117(5)	11.023(5)
c, Å	13.771(4)	13.740(7)	20.885(12)	20.750(10)
α, deg	104.11(3)	104.32(4)	91.69(4)	91.80(4)
β, deg	84.57(3)	85.20(4)	91.07(5)	91.41(4)
γ, deg	96.46(3)	97.36(5)	96.30(4)	95.63(3)
V, Å^3	1392.4	1363.5	2053.2	2012.3
d_c, g cm^{-3}	1.232	1.258	1.243	1.268
T (data collection)	193 ± 3 K		113 ± 5K	
λ(Mo Kα)	0.710 69 Å		0.710 69 Å	
crystal size	0.40 × 0.35 × 0.15 mm		0.25 × 0.20 × 0.10 mm	
2θ limits	0-46°		0-50°	
scan rate	4° min^{-1}		3° min^{-1}	
no. of unique data	3824		5364	
data with $I \geqslant 3\sigma_I$	2384		2862	
refined parameters	343		487	
$F(000)$	552 e		820 e	
$R = \Sigma(F_o - \lvert F_c \rvert)/\Sigma F_o$	0.099		0.043	
$[\Sigma w(\Delta F)^2/\Sigma w F_o{}^2]^{1/2}$	0.092		0.045	
"goodness of fit"	1.57 e		1.16 e	

bis[1,2-(3-methylnaphtho)]-1,6,9,12,15,18-hexaoxacycloeicosa-2,4-diene), and its 1:1 inclusion complex with *tert*-butylammonium perchlorate (II). Since it has been found that some macrocyclic polyethers shaped by one rigid 1,1′-dinaphthyl unit with attached substituents at its 3,3′ positions are effective in resolving amino acids or esters by cocrystallization,[3c,7] the potential significance of the results in furthering an understanding of the intermolecular interactions important in such systems is considerable. We report below the crystal and molecular structures of compounds I and II and examine the conformational details of the free and complexed ligand in the crystalline state, in order to describe the characteristic conformation of host I and how it is affected by the methyl substituents attached to the dinaphthyl unit. Of further interest are the structural details of the substrate-to-ligand binding site and their correlation with previously reported results for related complexes between (alkyl)ammonium guests and macrocyclic polyether hosts. This summary includes two additional structures of ammonium adducts with 18-crown-6[8a] and monopyrido-18-crown-6[8b] which have recently been published by others.

Experimental Section

Crystals of compounds I and II were kindly supplied by Professor Cram of the University of California, Los Angeles; the *tert*-butylammonium perchlorate complex crystallized with 1 mol of benzene. Preliminary Weissenberg and precession photographs revealed that both crystals had triclinic symmetry. Diffraction data were measured on a Syntex $P\bar{1}$ autodiffractometer equipped with a graphite monochromator, employing Mo Kα radiation. In order to obtain more precise structural parameters, the measurements were carried out at low temperatures: near −160 °C for the inclusion compound and near −80 °C for the free ligand. In the crystal structure of the latter there is an apparent phase transition at about −95 °C; however, our efforts to produce a single crystal of the new phase by a slow decrease of temperature below the transition point failed.

The experimental study was carried out in a manner similar to that described in ref 6c. After a careful inspection of relevant statistical distributions of the intensity data sets, space group $P\bar{1}$ was chosen for both structures and eventually confirmed by successful refinements. Crystal data and pertinent details of the experimental conditions are summarized in Table I. Intensity data were corrected for Lorentz and polarization effects but not for absorption or secondary extinction. After processing, only reflections with $F_o{}^2 \geqslant 3\sigma(F_o{}^2)$ were used in subsequent calculations.

Structure Determinations. The two structures were solved by a combination of direct methods (MULTAN 74)[9] and Fourier techniques, with some difficulties. A successful determination of phases for compound I emerged when the tangent-formula refinement was applied to 357 reflections with $|E| \geqslant 1.70$ and a complete list of the resulting 3171 Σ_2 relationships. Eight reflections were included in the starting set to fix the origin and provide a sufficient number of reference phases. Only 30 of the 38 nonhydrogen atoms of the structure were clearly located in subsequent E maps. Probable positions of the remaining atoms, which belong to the partly disordered aliphatic fragment of the molecule (see below), were found by difference Fourier calculations.

The crystal structure of the host-guest complex was determined from a preliminary set of room-temperature data.[10] A complete solution of this structure, with 54 nonhydrogen atoms of four different chemical species in the asymmetric unit, was obtained by a gradual procedure. At the initial stage, the phases of 224 reflections with $|E| \geqslant 1.92$ were developed by MULTAN from 8 reflections in the starting set and 872 triple-phase relationships. The E map corresponding to a solution with the highest combined figure of merit (but a rather large relative value of ψ_0) showed 24 distinct peaks which were assumed to compose two fragments of the host moiety. Recycled tangent-formula refinement, with phases calculated from the 24-atom set of coordinates, led to the location of the Cl atom and entire polyether molecule. Since an extension of the direct phase-determination procedure to 315 reflections with $|E| \geqslant 1.72$ and 2000 Σ_2 relationships did not seem to provide any further structural information, it was necessary to calculate several difference Fourier maps in order to find the approximate positions of the benzene of crystallization and *tert*-butylammonium perchlorate. An initial refinement of the trial model so derived indicated that the perchlorate anion and benzene molecule are disordered in the room-temperature structure. Subsequent calculations were based, therefore, on data collected near −160 °C.

Anisotropic refinement of the two structures proceeded by block-diagonal least-squares techniques. The 18 methyl and ammonium H atoms in complex II were located directly from electron density difference maps. All other hydrogens were introduced in calculated positions, assuming a trigonal or tetrahedral symmetry of the respective C atoms, a C–H bond distance of 1.04 Å, and similar configurations of the methyl groups attached to the ligand framework in both compounds. No attempt was made to refine the atomic positions or iso-

Table II. Atomic Fractional Coordinates of Host I[a]

	X	Y	Z		X	Y	Z
C(1)	.7396(8)	.8112(6)	.7988(5)	H(3)	1.0284	.8372	.7050
C(2)	.8031(8)	.8977(6)	.7466(5)	H(4)	1.1254	.9803	.6111
C(3)	.9577(9)	.8983(7)	.6994(6)	H(5)	.9622	1.1245	.5986
C(4)	1.0116(10)	.9813(7)	.6467(6)	H(6)	.7037	1.1367	.6823
C(5)	.9194(11)	1.0655(7)	.6396(6)	H(8)	.5004	1.0594	.7910
C(6)	.7737(11)	1.0699(7)	.6858(6)	H(10A)	.2895	.9860	.8926
C(7)	.7110(9)	.9871(6)	.7413(6)	H(10B)	.3515	.9185	.9749
C(8)	.5619(9)	.9901(6)	.7914(6)	H(10C)	.2663	.8390	.8694
C(9)	.5004(8)	.9885(6)	.8430(6)	H(13A)	.3324	.6458	.8342
C(10)	.3414(10)	.9140(8)	.8977(7)	H(13B)	.5001	.6189	.7638
C(11)	.5921(8)	.8192(7)	.8457(5)	H(14A)	.5785	.5182	.8826
O(12)	.5310(6)	.7372(4)	.8991(4)	H(14B)	.4144	.5480	.9560
C(13)	.4500(8)	.6353(7)	.8381(6)	H(16A)	.4958	.3153	.8550
C(14)	.4602(9)	.5332(7)	.8010(5)	H(16B)	.3217	.3336	.9199
O(15)	.3759(6)	.4369(4)	.8195(4)	H(17A)	.2678	.1613	.7974
C(16)	.3792(10)	.3310(7)	.8490(6)	H(17B)	.2022	.2625	.7490
C(17)	.3047(12)	.2352(8)	.7691(8)	H(19A)	.2325	.2360	.6034
O(18)	.4104(13)	.2062(9)	.6876(7)	H(19B)	.3980	.3274	.6306
C(19)	.3522(14)	.2407(15)	.6186(9)	H(20A)	.4486	.0928	.5230
C(20)	.4333(15)	.1755(13)	.5169(9)	H(20B)	.3634	.1685	.4544
O(21)	.5755(13)	.2307(10)	.5019(8)	H(22A)	.7838	.2159	.4401
C(22)	.6749(15)	.2288(14)	.4164(9)	H(22B)	.6486	.1607	.3533
C(23)	.6899(14)	.3442(13)	.3905(9)	H(23A)	.7527	.3363	.3213
O(24)	.7669(7)	.4267(7)	.4695(4)	H(23B)	.5772	.3605	.3824
C(25)	.7420(11)	.5413(10)	.4743(6)	H(25A)	.7843	.5664	.4080
C(26)	.8222(11)	.6173(9)	.5641(6)	H(25B)	.6205	.5499	.4822
O(27)	.7345(6)	.5965(4)	.6547(3)	H(26A)	.9372	.5962	.5637
C(28)	.8248(8)	.6127(6)	.7305(5)	H(26B)	.8296	.7051	.5643
C(29)	.8977(8)	.5172(6)	.7495(5)	H(30A)	.9262	.3384	.6977
C(30)	.8717(11)	.4002(7)	.6766(6)	H(30B)	.9155	.4060	.6039
C(31)	.9840(8)	.5323(6)	.8323(5)	H(30C)	.7514	.3721	.6720
C(32)	.9957(8)	.6384(6)	.9067(5)	H(31)	1.0405	.4640	.8399
C(33)	1.0829(9)	.6536(7)	.9937(6)	H(33)	1.1455	.5882	1.0085
C(34)	1.0908(9)	.7532(7)	1.0659(6)	H(34)	1.1534	.7617	1.1200
C(35)	1.0113(10)	.8453(7)	1.0565(6)	H(35)	1.0142	.9207	1.1125
C(36)	.9280(9)	.8351(6)	.9733(6)	H(36)	.8705	.9031	.9668
C(37)	.9177(8)	.7316(6)	.8959(5)				
C(38)	.8291(8)	.7169(6)	.8889(5)				

[a] Standard deviations are given in parentheses in units of the last decimal place.

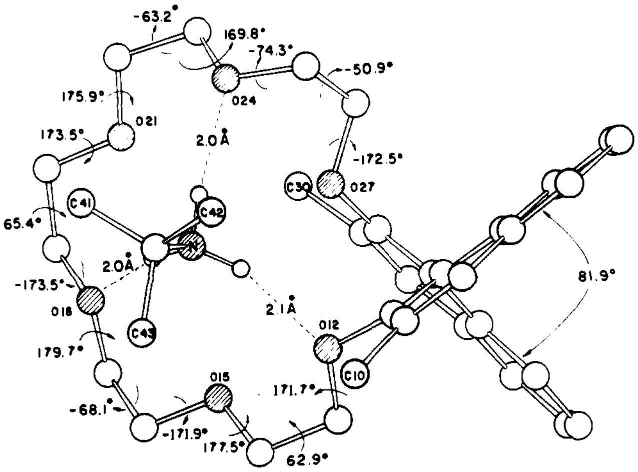

Figure 1. A perspective drawing of the host-guest complex. Torsion angles around the macroring as well as the H···O contacts which describe the hydrogen bonding association are shown.

tropic thermal parameters (U = 0.05 Å^2) of the H atoms. The least-squares function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where the relative weighting factor was $w = 1/\sigma^2(F_o)$. The atomic scattering factors for the nonhydrogen atoms were taken from ref 11a, and those for the H atoms from ref 11b. Anomalous dispersion terms were ignored.

The refinement of the free-ligand structure did not converge well even with the intensity data collected at −80 °C because of a significant conformational disorder within the aliphatic ring. The postulated disorder is most notably reflected in unreasonably large values of the refined thermal vibration parameters, particularly for atoms O(18) through C(25). Thus, in order to avoid unreliable distortion of the molecular geometry by the artificial effect of thermal motion, bond lengths C(19)-C(20) and C(22)-C(23) had to be constrained to 1.500 ± 0.003 Å (the usually observed value for a C-C bond in polyether rings) during the final calculations. With these assumptions the non-hydrogen-atom parameters were refined to R = 0.099 with 2384 observations above threshold. Some of the highest peaks (<1.2 e Å^{-3}) found on the final difference-Fourier maps could correspond to alternative positions of the most disordered C(19)-C(20) peripheral bond. Nevertheless, our attempts at defining a disordered structural model that would be statistically more consistent with the experimental data were unsuccessful. In spite of the fact that the description of this structure is clearly still incomplete, we believe that the overall geometric features of the uncomplexed ligand resulting from the present analysis are essentially correct and of considerable significance with respect to the discussion that follows.

On the other hand, the structure of complex II seems to be perfectly ordered at −160 °C. Its weighted least-squares refinement converged smoothly at R = 0.043 for 2862 reflections above threshold. The final difference-Fourier synthesis is mostly featureless (the highest peak and the deepest trough equal to 0.21 and 0.33 e Å^{-3}, respectively), with no indication of incorrectly placed or missing atoms.

Parameters of the refinement calculations are included in Table I. The final atomic positional parameters with estimated standard deviations in parentheses are listed in Tables II and III. It should be kept in mind that the refined positions of atoms in the disordered fragment of host I, particularly those of C(19) and C(20), represent only an average over a range of energetically preferred conformations (see paragraph at end of paper regarding supplementary material).

Discussion of Results

The conformational properties of macrocycle I and the geometry of its interaction with the *tert*-butylammonium ion are the main topics of the present discussion. The molecular structures and crystal packing arrangements of I and II are described in a later section of this report.

Intermolecular Binding Interactions. Figure 1 illustrates the observed host-to-guest association which, as anticipated, is mainly due to complexation through a tripod arrangement of $^+$NH···O hydrogen bonds on one face of the macrocyclic cavity.[6] The ammonium H atoms interact with three alternate ether oxygens (O(12), O(18) and O(24)), the C-NH_3^+ bond being nearly perpendicular to the mean plane of the complexation site. Geometrical parameters of the hydrogen bonds: O(12)···N(39) 3.00, O(12)···H(39*b*) 2.11 Å, N(39)-H(39*b*)···O(12) 154°; O(18)···N(39) 2.91, O(18)···H(39*a*) 1.96 Å, N(39)-H(39*a*)···O(18) 167°; O(24)···N(39) 2.95, O(24)···H(39*c*) 2.05 Å, N(39)-H(39*c*)···O(24) 161°. It appears that the spatial relationships between the *tert*-butyl group and the ligand molecule are free from severe steric constraints

Table III. Atomic Fractional Coordinates of Complex II

	X	Y	Z		X	Y	Z
C(1)	1.0589(4)	.7543(3)	.6520(2)	H(3)	.9557	.5502	.5802
C(2)	.9702(4)	.7448(3)	.5937(2)	H(4)	.8806	.5410	.4832
C(3)	.9226(4)	.6305(3)	.5615(2)	H(5)	.7129	.7257	.4395
C(4)	.8322(5)	.6248(4)	.5063(2)	H(6)	.7838	.9228	.4913
C(5)	.7829(5)	.7328(4)	.4809(2)	H(8)	.9393	1.0469	.5758
C(6)	.8271(5)	.8443(4)	.5104(2)	H(10A)	1.2362	1.1061	.6869
C(7)	.9219(4)	.8536(3)	.5667(2)	H(10B)	1.1193	1.1731	.6528
C(8)	.9723(5)	.9678(3)	.5965(2)	H(10C)	1.0717	1.1491	.7171
C(9)	1.0622(5)	.9779(3)	.6519(2)	H(13A)	1.3878	.9130	.7145
C(10)	1.1228(5)	1.1005(3)	.6817(2)	H(13B)	1.3399	.7690	.7378
C(11)	1.0976(4)	.8678(3)	.6886(2)	H(14A)	1.3611	.9871	.8243
O(12)	1.1654(3)	.8807(2)	.7421(1)	H(14B)	1.4951	.8877	.8195
C(13)	1.3249(4)	.8605(4)	.7470(2)	H(16A)	1.3132	.9319	.9380
C(14)	1.3795(4)	.8970(3)	.8144(2)	H(16B)	1.4662	.8467	.9267
O(15)	1.2977(3)	.8196(2)	.8581(1)	H(17A)	1.3232	.7617	1.0118
C(16)	1.3489(5)	.8463(4)	.9234(2)	H(17B)	1.2925	.6646	.9469
C(17)	1.2749(4)	.7506(4)	.9654(2)	H(19A)	1.0835	.6859	1.0553
O(18)	1.1158(3)	.7614(2)	.9680(1)	H(19B)	1.0722	.5844	.9920
C(19)	1.0445(5)	.6697(4)	1.0078(2)	H(20A)	.8463	.7590	1.0165
C(20)	.8748(5)	.6721(3)	1.0043(2)	H(20B)	.8245	.6107	1.0366
O(21)	.8223(3)	.6376(2)	.9399(1)	H(22A)	.6175	.7054	.9504
C(22)	.6595(5)	.6248(4)	.9348(2)	H(22B)	.6157	.5542	.9629
C(23)	.6140(5)	.5977(4)	.8658(2)	H(23A)	.4965	.5824	.8600
O(24)	.6686(3)	.7005(2)	.8273(1)	H(23B)	.6616	.5199	.8486
C(25)	.6534(5)	.6739(4)	.7594(2)	H(25A)	.6657	.7553	.7353
C(26)	.7681(4)	.5930(4)	.7350(2)	H(25B)	.5443	.6306	.7493
O(27)	.9158(3)	.6467(2)	.7585(1)	H(26A)	.7640	.5879	.6850
C(28)	1.0367(4)	.5906(3)	.7335(2)	H(26B)	.7456	.5058	.7524
C(29)	1.0866(4)	.4880(3)	.7655(2)	H(30A)	.9940	.5038	.8587
C(30)	1.0094(5)	.4413(4)	.8250(2)	H(30B)	.9130	.3879	.8196
C(31)	1.2098(5)	.4376(3)	.7412(2)	H(30C)	1.0840	.3879	.8430
C(32)	1.2869(4)	.4838(3)	.6868(2)	H(31)	1.2466	.3618	.7629
C(33)	1.4163(5)	.4316(4)	.6635(2)	H(33)	1.4505	.3540	.6849
C(34)	1.4956(5)	.4823(4)	.6131(2)	H(34)	1.5831	.4418	.5960
C(35)	1.4508(5)	.5895(4)	.5846(2)	H(35)	1.5139	.6298	.5474
C(36)	1.3255(4)	.6401(4)	.6059(2)	H(36)	1.2914	.7176	.5843
C(37)	1.2388(4)	.5895(3)	.6571(2)	H(39A)	.9998	.8213	.8960
C(38)	1.1083(4)	.6418(3)	.6819(2)	H(39B)	1.0161	.8307	.8169
N(39)	.9622(4)	.8459(3)	.8549(1)	H(39C)	.8735	.7872	.8515
C(40)	.9114(4)	.9735(3)	.8642(2)	H(41A)	.8612	.9538	.9631
C(41)	.8165(5)	.9739(4)	.9235(2)	H(41B)	.7702	1.0471	.9246
C(42)	.8217(5)	1.0006(3)	.8038(2)	H(41C)	.7246	.9103	.9208
C(43)	1.0541(5)	1.0626(3)	.8724(2)	H(42A)	.7801	1.0802	.8092
CL(44)	.5151(1)	.7511(1)	.1336(0)	H(42B)	.7429	.9393	.7977
O(45)	.5378(4)	.8469(3)	.0877(1)	H(42C)	.8735	.9971	.7631
O(46)	.5841(4)	.7931(3)	.1951(1)	H(43A)	1.1345	1.0614	.8480
O(47)	.5844(4)	.6462(3)	.1187(2)	H(43B)	1.0434	1.1471	.8785
O(48)	.3950(3)	.7190(3)	.1415(2)	H(43C)	1.1163	1.0400	.9092
C(49)	.1737(5)	.7142(4)	.3740(2)	H(49)	.0731	.6520	.3642
C(50)	.2161(5)	.7456(4)	.4373(2)	H(50)	.1542	.7099	.4754
C(51)	.3459(6)	.8292(4)	.4486(2)	H(51)	.3802	.8539	.4961
C(52)	.4280(5)	.8788(4)	.3983(2)	H(52)	.5231	.9405	.4073
C(53)	.3807(5)	.8451(4)	.3351(2)	H(53)	.4403	.8803	.2960
C(54)	.2526(5)	.7626(4)	.3244(2)	H(54)	.2172	.7373	.2774

and have, at most, a minor effect on the above scheme of hydrogen bonding (see below).

It has been suggested in several recent publications that, in addition to the hydrogen bonds, direct $N^+\cdots O$ contacts contribute as well to the binding energy of the formed complex.[2b,3a] These interactions most probably involve nonbonding electron pairs on the ether O atoms, and their strength is closely related to the distance between N^+ and O, the degree of basicity of the ligating atoms, and the mutual orientation of the groups containing donor oxygen and electrophilic nitrogen.[3c,6c] As shown in Figure 1 of the present structure, the oxygen atoms that are not hydrogen bonded also seem to be involved in stabilization of the complex through direct pole-dipole interactions with the positive charge of the guest ion. The O(15), O(21), and O(27) atoms are turned toward the center of the macroring, and are between 2.92 and 3.12 Å from the N^+. Moreover, simple geometrical considerations suggest that on both O(15) and O(21) the principal axis of one of the lone-pair orbitals points almost directly at N^+, while the $N\cdots O(27)$ line bisects the angle between the two lone-pair orbitals of O(27).

In order to get further insight into the geometry of interactions binding ammonium guests to penta- and hexadentate polyether hosts it is of interest to extend the present discussion to other closely related systems whose detailed structures are known (Figure 2 and Table IV). This includes the most recently investigated ammonium bromide complex of 18-crown-6 which is characterized by a pseudo-D_{3d} symmetrical conformation of the ligand, and an undistorted complementary arrangement of binding sites in the participating species.[8a] Table IV summarizes the relevant data for the $^+NH\cdots O$ and $N^+\cdots O$ interactions; the value of α in this table corresponds to an angle between the $N\cdots O(i)$ axis and its projection on a plane defined by the respective C-O(i)-C fragment of the ligand (in all cases examined the $N\cdots O$ vector lies very near the plane bisecting the C-O-C angle).

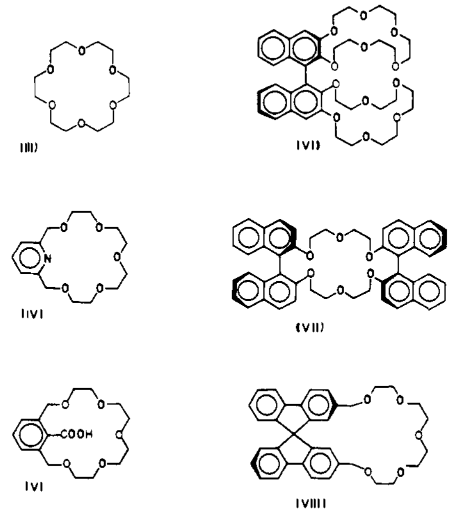

Figure 2. Structural formulas of other ligands included in the discussion.

Table IV. Geometry of Binding Interactions in Crystal Structures of Various Complexes[a]

	hydrogen bonds					$N^+\cdots O$ interactions	
contact	N···O, Å	H···O, Å	N-H···O, deg	α, deg	contact	N···O, Å	α,[b] deg
			Present Structure				
NH···O(12)	3.00	2.1	154	21	N···O(15)	3.01	54
NH···O(18)	2.91	2.0	167	29	N···O(21)	3.12	56
NH···O(24)	2.95	2.1	161	38	N···O(27)	2.92	3
			18-Crown-6 with NH_4Br (ref 8a)				
NH···O(2)	2.88	1.9	177	21	N···O(1)	3.00	60
NH···O(2′)	2.88	1.9	177	21	N···O(3)	3.13	66
NH···O(4)	2.86	1.9	179	17	N···O(3′)	3.13	66
			IV with $(CH_3)_3CNH_3^+ClO_4^-$ (ref 8b)				
NH···O(6)	2.94	2.1	173	23	N···O(3)	3.06	55
NH···O(12)	3.03	2.2	173	29	N···O(9)	3.07	54
NH···N(21)	3.00	2.1	174	17	N···O(15)	3.05	51
			V with $(CH_3)_3CNH_2$ (ref 6a)				
NH···O(4)	3.11	2.2	160	35	N···O(1)	3.11	47
NH···O(4′)	3.11	2.2	160	35	N···O(7)	3.48	57
NH···O(14)	2.68	1.7	170	—	N···O(7′)	3.48	57
			VI with $PF_6^{-+}NH_3(CH_2)_4NH_3^+PF_6^-$ (ref 6b)				
NH···O(6)	3.00	2.3	129	34	N···O(12)	3.10	43
NH···O(9)	2.97	2.0	170	37	N···O(15)	3.05	47
NH···O(18)	2.89	1.9	175	25	N···O(21)	3.14	50
			VII with $C_6H_5CH(CO_2CH_3)NH_3^+PF_6^-$ (ref 6c)				
NH···O(17)	2.90	2.1	160	13	N···O(11)	3.26	64
NH···O(41)	2.94	2.3	124	28	N···O(14)	3.10	43
NH···O(44)	2.90	2.2	136	29	N···O(38)	3.66	55
			VIII with NH_4NCS (ref 12)				
NH···O(27)	3.03	2.2	144	17	N···O(30)	3.08	80
NH···O(33)	2.92	1.9	168	11	N···O(36)	3.15	61
NH···O(39)	3.09	2.2	150	39			
av	2.95	2.1	161	26		3.15	53

[a] Atom numbering is the same as in the original publications referred to. Structural formulas of ligands IV–VIII are shown in Figure 2. [b] An angle between the N···O(i) vector and its projection on a plane defined by the respective C–O(i)–C fragment of the ligand.

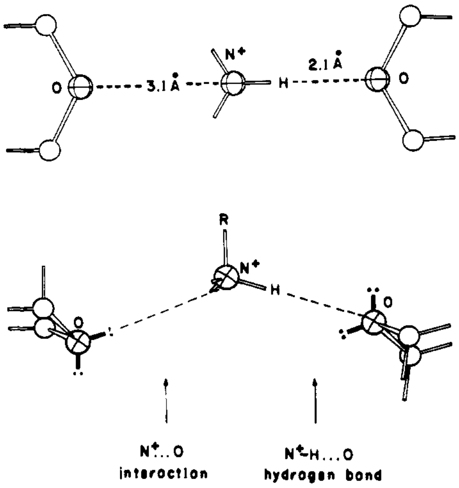

Figure 3. An illustration of the two types of interaction between an ammonium ion and ether O atoms; two transannular oxygens of 18-crown-6 are shown. The dark lines represent approximate orientations of oxygen lone-pair orbitals.

Evidently, all complexes between ammonium ions and macrocyclic polyethers that have been analyzed so far are stabilized by $^+NH\cdots O$ hydrogen bonds. Characteristic parameters of these interactions are N···O 2.95 ± 0.15 Å, H···O 2.0 ± 0.2 Å, and N–H···O 160 ± 20°. A typical arrangement has been observed in the structure of the NH_4Br adduct with unsubstituted 18-crown-6. The six nucleophilic oxygen atoms lie alternately about 0.25 Å below and above their mean plane and form a cavity 2.8 Å in diameter. The ammonium cation, being too large to fit into the cavity of this ligand, is displaced from the mean oxygen plane by 1.0 Å. Correspondingly, three O atoms situated on the complexed face of the "crown" are involved in N–H···O bonding, while the remaining oxygens located on the opposite side participate in $N^+\cdots O$ attractive interactions. Substitutions of bulky groups on the component moieties often prevent an unstrained organization of complexation sites and a linear geometry in the $^+NH\cdots O$ bonds. Inspection of the data given in Table IV for a series of ammonium complexes with polyether entities reveals an interesting geometric feature that is associated with the two types of interactions. If we assume that the symmetry of valent atomic orbitals on O is ideally tetrahedral, the angular value α will reflect the relative orientation of oxygen lone-pair orbitals with respect to N^+. The available data show a remarkable degree of consistency despite the fact that the organization of binding sites in each one of the structures is differently affected by steric constraints. Thus, within hydrogen-bonded parts of a complex the α values clearly tend to cluster between 20 and 40°. On the other hand, for oxygens located near the open side of the ligand and involved in direct $N^+\cdots O$ contacts, the α angles usually vary between 40 and 60° (with only a few exceptions); this suggests that one of the lone-pair orbitals of a donor O is directed at the electrophilic N^+. Largest deviations from these trends in complexes with hexadentate ligands involve aryl O atoms, probably owing to their relatively low nucleophilicity and proximity to rigid substituents. In a complex of VIII, the mutual arrangement of pentadentate spirobifluorene host and NH_4^+ guest is influenced by strong interaction between the ammonium cation and thiocyanate counterion.

Table V. Observed and Calculated Conformations of the Polyether Ring[a]

torsion angle	free ligand I obsd	free ligand I calcd	complex II obsd	complex II calcd
C(11)-O(12)-C(13)-C(14)	151.4(6)	147.9	171.7(3)	168.4
O(12)-C(13)-C(14)-O(15)	178.9(5)	175.5	62.9(4)	65.6
C(13)-C(14)-O(15)-C(16)	177.8(6)	180.0	177.5(3)	−175.8
C(14)-O(15)-C(16)-C(17)	−172.5(7)	−178.8	−171.9(3)	−174.9
O(15)-C(16)-C(17)-O(18)	79.3(10)	80.4	−68.1(4)	−74.0
C(16)-C(17)-O(18)-C(19)	−112.0(11)	−93.9	179.7(3)	−179.4
C(17)-O(18)-C(19)-C(20)	−161.8(10)	−175.1	−173.5(3)	−174.5
O(18)-C(19)-C(20)-O(21)	−85.6(15)	−82.6	65.4(4)	70.1
C(19)-C(20)-O(21)-C(22)	−164.0(16)	−156.9	173.5(3)	175.5
C(20)-O(21)-C(22)-C(23)	120.6(16)	98.8	175.9(3)	173.7
O(21)-C(22)-C(23)-O(24)	65.5(12)	63.2	−63.2(4)	−66.7
C(22)-C(23)-O(24)-C(25)	−159.1(8)	−159.4	169.8(3)	172.2
C(23)-O(24)-C(25)-C(26)	176.8(8)	173.6	−74.3(4)	−78.6
O(24)-C(25)-C(26)-O(27)	−70.9(9)	−71.3	−50.9(4)	−45.5
C(25)-C(26)-O(27)-C(28)	150.4(8)	150.1	−172.5(3)	−174.6

[a] The calculated conformations are based on force-field functions given in ref 15b.

The above-described geometric pattern of $^+NH\cdots O$ and $N^+\cdots O$ interactions, illustrated schematically in Figure 3, is due to two dominant factors; (a) an apparent tendency of the system to optimize simultaneously both types of binding interactions between the $-NH_3^+$ group penetrating into the polyether cavity and (b) the intrinsic "stability" of the ligand conformation. The second argument refers to the fact that the crown-type form of cyclic polyether species with a gauche arrangement within $-OCH_2CH_2O-$ groups, and the O atoms lying alternately above and below the mean plane of the cavity, corresponds to conformation of lowest torsional energy.[13] To the author's knowledge complexed structures containing two $R-NH_3^+$ groups bound to opposite sides of a single hexaether ring have not yet been found and characterized, in agreement with the present discussion. Ab initio molecular orbital calculations on simple model systems (e.g., NH_4^+ with $O(CH_3)_2$) have indicated that the energy of a hydrogen-bonding interaction is about three times that of the direct electrostatic interaction.[3a] This result correlates well with another observation made by Trueblood et al., in their analyses of thermal motion in complexes of IV and V,[8b] that the differences in the mean-square vibration amplitudes of the ammonium N^+ and ether O atoms along the lines between them are several times smaller for the hydrogen-bonded contacts than for the other $N\cdots O$ directions. In this respect, it would be interesting to relate the present structural correlations to experimental binding energies of the relevant compounds in a manner similar to that described in ref 3a.

Molecular Geometries. As is illustrated in Figure 4, the overall conformation of the complexed ligand is very similar to that of the uncomplexed molecule. In each structure the mean plane of the macroring forms a characteristic angle of about 40° with the C(1)-C(38) dinaphthyl bond, the $-CH_3(30)$ methyl substituent converging on and interacting with one face of the macrocyclic cavity. This is reflected in the intramolecular contacts $C(30)\cdots O(21)$ (3.68 Å) and $C(30)\cdots O(24)$ (3.16 Å) in compound I and $C(30)\cdots O(21)$ (3.70 Å) in compound II. Moreover, the dinaphthyl dihedral angles in I and II differ only by 12°. It is reasonable to assume, therefore, that the observed structure represents the most probable overall conformation of the present host in which the molecule is more stable (owing to more significant intramolecular van der Waals attractions) than in a conformation having the mean plane of the macrocycle perpendicular to the naphthalene rings. The above observation leads to a conclusion that in solution the two faces of macrocycle I are equivalent with respect to a complexation of potential guest species only by virtue of rapidly established equilibria between conformers.

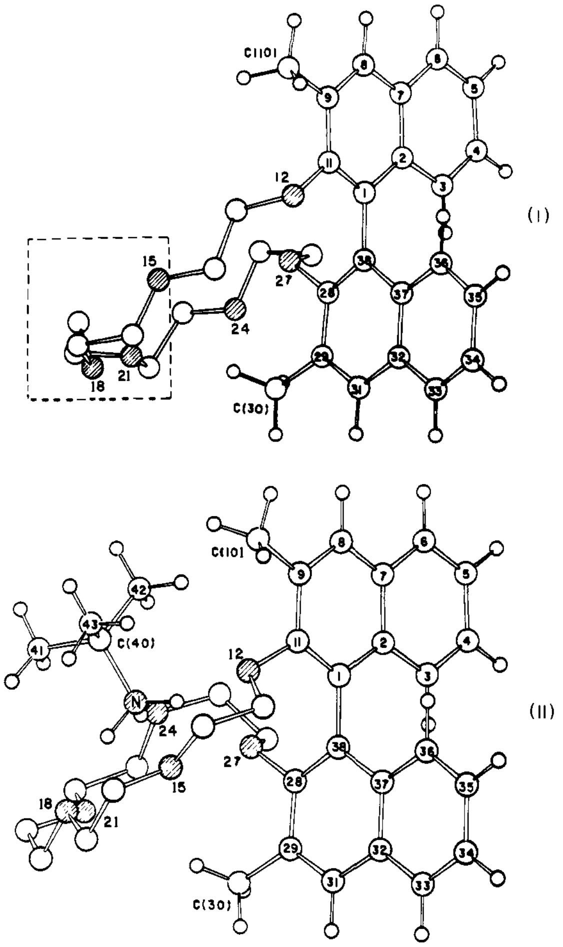

Figure 4. A view of the overall conformations of the complexed and uncomplexed ligand. Marked frame encloses the conformationally disordered part of host I in the crystal.

The detailed conformations of the polyether ring are described in terms of the torsion angles about the ring bonds (Table V). In the absence of an interacting guest, the conformation of one part of the uncomplexed macrocycle is severely disordered. The disordered fragment extends from O(18) through C(25), and is formally characterized (when we refer to the average structural model included in refinement) by an irregular pattern of torsion angles with magnitudes intermediate between gauche and anti geometries. The remaining part of the macroring is stabilized in an ordered conformation by

Table VI. Bond Distances (Å) and Bond Angles (deg) in Host I

C(1) - C(2)	1.430(11)	C(20) - O(21)	1.386(17)
C(2) - C(3)	1.435(10)	O(21) - C(22)	1.385(16)
C(2) - C(7)	1.432(11)	C(22) - C(23)	1.497
C(3) - C(4)	1.382(13)	C(23) - O(24)	1.420(13)
C(4) - C(5)	1.388(14)	O(24) - C(25)	1.401(15)
C(5) - C(6)	1.363(13)	C(25) - C(26)	1.502(12)
C(6) - C(7)	1.423(12)	C(26) - O(27)	1.460(10)
C(7) - C(8)	1.408(11)	O(27) - C(28)	1.404(9)
C(8) - C(9)	1.374(11)	C(28) - C(29)	1.419(11)
C(9) - C(10)	1.511(11)	C(28) - C(38)	1.375(9)
C(9) - C(11)	1.419(12)	C(29) - C(30)	1.510(9)
C(11) - C(1)	1.383(9)	C(29) - C(31)	1.374(11)
C(11) - O(12)	1.392(10)	C(31) - C(32)	1.418(9)
O(12) - C(13)	1.433(8)	C(32) - C(33)	1.427(11)
C(13) - C(14)	1.505(12)	C(32) - C(37)	1.419(11)
C(14) - O(15)	1.412(8)	C(33) - C(34)	1.349(10)
O(15) - C(16)	1.420(11)	C(34) - C(35)	1.408(13)
C(16) - C(17)	1.497(12)	C(35) - C(36)	1.373(12)
C(17) - O(18)	1.380(14)	C(36) - C(37)	1.418(9)
O(18) - C(19)	1.370(19)	C(37) - C(38)	1.435(10)
C(19) - C(20)	1.500	C(38) - C(1)	1.487(11)
C(2)-C(1)-C(11)	118.5(7)	C(19)-C(20)-O(21)	108.1(11)
C(2)-C(1)-C(38)	122.6(6)	C(20)-O(21)-C(22)	129.5(11)
C(38)-C(1)-C(11)	118.9(7)	O(21)-C(22)-C(23)	105.9(12)
C(1)-C(2)-C(3)	121.9(7)	C(22)-C(23)-O(24)	107.5(11)
C(1)-C(2)-C(7)	119.5(6)	C(23)-O(24)-C(25)	113.5(9)
C(3)-C(2)-C(7)	118.6(7)	O(24)-C(25)-C(26)	107.5(9)
C(2)-C(3)-C(4)	119.7(8)	C(25)-C(26)-O(27)	108.2(7)
C(3)-C(4)-C(5)	121.1(8)	C(26)-O(27)-C(28)	114.7(6)
C(4)-C(5)-C(6)	120.9(8)	O(27)-C(28)-C(29)	117.9(6)
C(5)-C(6)-C(7)	120.8(8)	O(27)-C(28)-C(38)	118.6(7)
C(6)-C(7)-C(8)	122.4(8)	C(29)-C(28)-C(38)	123.4(7)
C(6)-C(7)-C(2)	118.7(7)	C(28)-C(29)-C(30)	121.0(7)
C(2)-C(7)-C(8)	118.9(7)	C(28)-C(29)-C(31)	118.0(6)
C(7)-C(8)-C(9)	122.2(8)	C(30)-C(29)-C(31)	120.9(7)
C(8)-C(9)-C(10)	121.6(8)	C(29)-C(31)-C(32)	121.4(7)
C(8)-C(9)-C(11)	118.1(7)	C(31)-C(32)-C(33)	121.5(7)
C(10)-C(9)-C(11)	120.3(7)	C(31)-C(32)-C(37)	119.7(7)
C(9)-C(11)-O(12)	118.3(6)	C(33)-C(32)-C(37)	118.8(6)
C(9)-C(11)-C(1)	122.8(7)	C(32)-C(33)-C(34)	121.7(8)
C(1)-C(11)-O(12)	118.9(7)	C(33)-C(34)-C(35)	119.9(8)
C(11)-O(12)-C(13)	113.7(6)	C(34)-C(35)-C(36)	120.4(7)
O(12)-C(13)-C(14)	109.5(6)	C(35)-C(36)-C(37)	121.1(8)
C(13)-C(14)-O(15)	108.4(6)	C(36)-C(37)-C(38)	122.7(7)
C(14)-O(15)-C(16)	113.4(6)	C(36)-C(37)-C(32)	118.2(7)
O(15)-C(16)-C(17)	107.4(8)	C(32)-C(37)-C(38)	119.2(6)
C(16)-C(17)-O(18)	110.0(8)	C(37)-C(38)-C(28)	118.3(7)
C(17)-O(18)-C(19)	105.3(10)	C(37)-C(38)-C(1)	120.0(6)
O(18)-C(19)-C(20)	104.5(13)	C(28)-C(38)-C(1)	121.7(6)

intramolecular C(13)-H···O(27) attractions. Such an arrangement with relatively short nonbonding distances C(13)···O(27) (3.36 Å) and H(13*b*)···O(27) (2.4 Å) arises because the conformation about the C(13)-C(14) bond is antiplanar rather than gauche. This is similar to previous observations in other uncomplexed crystalline polyether hosts, where the cavities are filled with inward-turning methylene groups. The dihedral angle between the two naphthalene rings is 94°, the aryl O(12) and O(27) atoms being located at 3.76 Å from each other.

The complexed ligand exists in an ordered and unstrained conformation with characteristic synclinal and antiplanar torsion angles about the C-C and C-O bonds, respectively, and thus with all oxygens turning toward the center of the cavity. The only deviation from this pattern involves a gauche conformation about the O(24)-C(25) bond. In order to optimize the complementary arrangement of binding sites on the host and guest moieties the dinaphthyl dihedral angle and the O(12)···O(27) nonbonding distance are decreased to 82° and 3.26 Å, respectively. Although space-filling molecular models suggest that in an isolated 2,2′-O-substituted 1,1′-dinaphthyl group the dihedral angle can vary between extremes of about 60 and 120°, in the relevant structures analyzed so far the observed dihedral angles are near 80-90° in five cases and 108° in one case.[6,14] Apparently, in the observed conformation steric repulsions between the methyl substituents of the component species are not significant; the shortest relevant nonbonding distances are C(42)···C(10) (3.83 Å) and H(42*c*)···H(10*c*) (2.5 Å). This allows a nearly ideal arrangement of the complementary binding sites. However, replacement of the CH_3 arms attached at the 3,3′ positions of the 1,1′-dinaphthyl unit by bulkier R(10) and R(30) substituents may introduce a considerable steric hindrance within the ligand (via R(30)), and affect its complexing ability and selectivity toward potential chiral and achiral alkylammonium guest moieties (according to the size and functionality of R(10)).[3c,6c,7]

Bond lengths and angles found in both structures are listed in Tables VI and VII. The dimensions of the naphthalene substituents are consistent with the known picture of incomplete delocalization in this molecule, while those of the macroring, the *tert*-butylammonium cation, and the perchlorate anion are similar to intramolecular bond distances and angles usually reported for such species.[6,8] In an attempt to relate the observed structures to least energy conformations of host I we have made some intramolecular potential energy calculations, using an updated version of the CFF program of Niketic and Rasmussen.[15a] Energy minimizations were based on the PEF400 set of force-field functions (comprising harmonic terms for bond length, bond angle, and torsion angle deformations and Lennard-Jones and Coulomb terms for nonbonded interactions).[15b] The experimental geometries found in structures I and II served as starting models for two independent calculations. The resulting geometries of the macroring (Table V), which are characterized by the same general pattern of bond lengths and bond angles, correspond to two different local minima of the potential energy of conformation. Deviations between the observed and calculated torsion angles do not exceed 6° in compound II and in ordered parts of compound I; in the disordered fragment of the latter, where the energy minimization led to a folded conformation, they differ by as much as 22°. This is perhaps another indication that the present determination of the molecular structure of uncomplexed host I is incomplete.

Table VII. Bond Distances (Å) and Bond Angles (deg) in Complex II

C(1) - C(2)	1.423(5)	O(27) - C(28)	1.389(5)
C(2) - C(3)	1.427(5)	C(28) - C(29)	1.430(5)
C(2) - C(7)	1.437(5)	C(29) - C(30)	1.505(6)
C(3) - C(4)	1.377(5)	C(29) - C(31)	1.366(6)
C(4) - C(5)	1.413(6)	C(31) - C(32)	1.418(5)
C(5) - C(6)	1.381(6)	C(32) - C(33)	1.420(6)
C(6) - C(7)	1.416(5)	C(32) - C(37)	1.431(5)
C(7) - C(8)	1.412(5)	C(33) - C(34)	1.375(6)
C(8) - C(9)	1.377(5)	C(34) - C(35)	1.425(6)
C(9) - C(10)	1.512(5)	C(35) - C(36)	1.366(6)
C(9) - C(11)	1.427(5)	C(36) - C(37)	1.422(5)
C(11) - C(1)	1.376(5)	C(37) - C(38)	1.439(5)
C(11) - O(12)	1.393(4)	C(38) - C(28)	1.367(5)
O(12) - C(13)	1.452(5)	C(38) - C(1)	1.501(5)
C(13) - C(14)	1.490(5)	N(39) - C(40)	1.526(5)
C(14) - O(15)	1.426(5)	C(40) - C(41)	1.506(6)
O(15) - C(16)	1.430(4)	C(40) - C(42)	1.520(5)
C(16) - C(17)	1.501(6)	C(40) - C(43)	1.525(5)
C(17) - O(18)	1.426(5)	CL(44)- O(45)	1.448(3)
O(18) - C(19)	1.433(5)	CL(44)- O(46)	1.443(3)
C(19) - C(20)	1.504(6)	CL(44)- O(47)	1.435(3)
C(20) - O(21)	1.433(4)	CL(44)- O(48)	1.441(3)
O(21) - C(22)	1.435(5)	C(49) - C(50)	1.381(6)
C(22) - C(23)	1.507(6)	C(50) - C(51)	1.410(6)
C(23) - O(24)	1.440(5)	C(51) - C(52)	1.383(7)
O(24) - C(25)	1.432(5)	C(52) - C(53)	1.393(6)
C(25) - C(26)	1.501(6)	C(53) - C(54)	1.391(6)
C(26) - O(27)	1.447(4)	C(54) - C(49)	1.352(6)
C(2)-C(1)-C(11)	118.9(3)	O(27)-C(28)-C(38)	117.8(3)
C(2)-C(1)-C(38)	120.2(3)	C(29)-C(28)-C(38)	123.3(4)
C(11)-C(1)-C(38)	120.9(3)	C(28)-C(29)-C(30)	120.8(4)
C(1)-C(2)-C(7)	119.1(3)	C(28)-C(29)-C(31)	117.3(3)
C(3)-C(2)-C(7)	118.2(3)	C(30)-C(29)-C(31)	121.9(4)
C(2)-C(3)-C(4)	120.9(4)	C(29)-C(31)-C(32)	122.6(4)
C(3)-C(4)-C(5)	120.5(3)	C(31)-C(32)-C(37)	119.1(4)
C(4)-C(5)-C(6)	120.3(4)	C(37)-C(32)-C(33)	119.3(3)
C(5)-C(6)-C(7)	120.5(4)	C(32)-C(33)-C(34)	120.5(4)
C(6)-C(7)-C(2)	119.5(3)	C(33)-C(34)-C(35)	120.4(4)
C(8)-C(7)-C(2)	119.1(3)	C(34)-C(35)-C(36)	119.8(4)
C(7)-C(8)-C(9)	122.8(4)	C(35)-C(36)-C(37)	121.6(4)
C(8)-C(9)-C(10)	121.8(3)	C(36)-C(37)-C(32)	118.2(4)
C(8)-C(9)-C(11)	117.7(3)	C(38)-C(37)-C(32)	118.5(3)
C(10)-C(9)-C(11)	120.5(3)	C(37)-C(38)-C(28)	119.1(3)
C(1)-C(11)-C(9)	122.8(3)	C(37)-C(38)-C(1)	119.0(3)
C(1)-C(11)-O(12)	121.1(3)	C(28)-C(38)-C(1)	121.9(3)
C(9)-C(11)-O(12)	116.0(3)	N(39)-C(40)-C(41)	107.8(3)
C(11)-O(12)-C(13)	116.5(3)	N(39)-C(40)-C(42)	107.5(3)
O(12)-C(13)-C(14)	107.3(3)	N(39)-C(40)-C(43)	107.4(3)
C(13)-C(14)-O(15)	108.7(3)	C(41)-C(40)-C(42)	112.1(3)
C(14)-O(15)-C(16)	111.6(3)	C(41)-C(40)-C(43)	111.5(3)
O(15)-C(16)-C(17)	108.7(3)	C(42)-C(40)-C(43)	110.3(3)
C(16)-C(17)-O(18)	110.1(3)	O(45)-CL(44)-O(46)	109.5(2)
C(17)-O(18)-C(19)	110.3(3)	O(45)-CL(44)-O(47)	109.3(2)
O(18)-C(19)-C(20)	110.1(3)	O(45)-CL(44)-O(48)	103.9(2)
C(19)-C(20)-O(21)	108.4(3)	O(46)-CL(44)-O(47)	109.3(2)
C(20)-O(21)-C(22)	111.3(3)	O(46)-CL(44)-O(48)	109.1(2)
O(21)-C(22)-C(23)	108.8(3)	O(47)-CL(44)-O(48)	109.6(2)
C(22)-C(23)-O(24)	109.0(3)	C(50)-C(49)-C(54)	121.4(4)
C(23)-O(24)-C(25)	112.4(3)	C(49)-C(50)-C(51)	117.7(4)
O(24)-C(25)-C(26)	113.1(3)	C(50)-C(51)-C(52)	121.5(4)
C(25)-C(26)-O(27)	107.8(3)	C(51)-C(52)-C(53)	119.0(4)
C(26)-O(27)-C(28)	114.1(3)	C(52)-C(53)-C(54)	119.2(4)
O(27)-C(28)-C(29)	118.7(3)	C(53)-C(54)-C(49)	121.3(4)

Molecular Packing. The crystal structure of complex II can be described as composed of sheets of different molecular fragments perpendicular to the *c* axis. Sheets comprising the rigid aromatic groups (benzene and naphthalene) alternate with sheets containing the aliphatic moieties, as shown in Figure 5. Similar packing modes have been observed previously.[6c] The ClO_4^- ions and benzene molecules of crystallization are located in cavities between adjacent units of the complex. Correspondingly, the average squared amplitude of

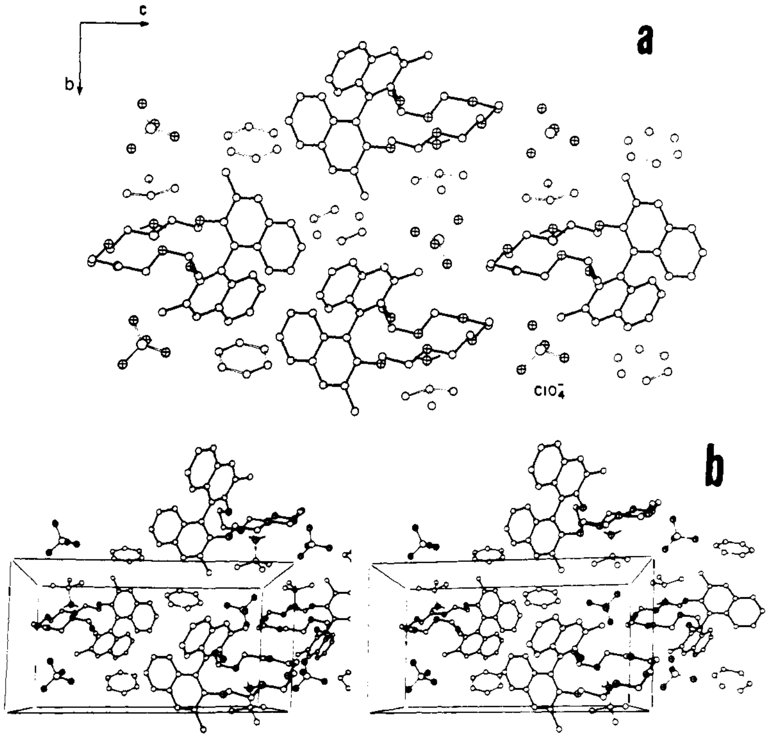

Figure 5. Crystal structure of complex II viewed down the *a** axis. The drawing includes more than one complete unit cell, in order to show all packing interactions: (a) parallel; (b) stereoscopic projections.

their thermal vibration (~0.055 Å^2) is about twice as large as that of the remaining individual atoms. The shortest distances involving the perchlorate oxygens and atoms that belong to the nearest alkylammonium cation and two polyether macrorings are O(45)···C(43) (3.72 Å), O(46)···C(43) (3.76 Å), O(48)···C(42) (3.75 Å), O(46)···C(14) (3.41 Å), and O(47)···C(23) (3.13 Å), respectively. The closest intercomplex contact between adjacent naphthalene groups located across the 0, 0, ½ center of inversion is C(6)···C(8) (3.48 Å); between the aliphatic rings related by inversion at 0, ½, 0 it is C(19)···C(19) (3.75 Å). Within the crystal structure of host I, all intermolecular distances are longer than or approximately equal to the sums of the corresponding van der Waals radii. The only exception is an apparent short approach between C(14) and disordered C(20) (3.32 Å) in the two neighboring molecules of the unit cell.[16]

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Supplementary Material Available: Structure factor tables for I and II plus a table of thermal parameters for II (19 pages). Ordering information is given on any current masthead page.

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(16) NOTE ADDED IN PROOF: Professor J. M. Lehn suggested an alternative description of the two types of interaction between an ammonium guest and ether O atoms: (a) NH^+···O hydrogen bonds and (b) direct N···O dipole-dipole attractions, implying that most of the positive charge of an ammonium ion is delocalized on the hydrogen atoms (private communication, 1980).