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Macrocyclic Receptor Molecules for Guanidinium Cations. 2.[1] Synthesis and X-ray Structures of 2,6-Pyrido Crown Ethers and Their Guanidinium Complexes

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A series of 2,6-pyrido crown ethers with ring sizes of 15–33 ring atoms has been synthesized. Their complexation with guanidinium salts has been studied by using two phase extraction experiments. The crystal and molecular structures of 2,6-pyrido-27-crown-9–guanidinium perchlorate (1:1), 2,6-pyrido-30-crown-10–guanidinium perchlorate (1:1), 2,6-pyrido-27-crown-9–guanidinium thiocyanate–ethanol (2:3:1), 2,6-pyrido-27-crown-9–picric acid (1:1), and the free 2,6-pyrido-24-crown-8 have been determined by X-ray crystallography. In the free and protonated crown ethers, the cavity is occupied by the aromatic ring of the crown ether. In the complexes with guanidinium salts the guest molecule is *encapsulated* within the cavity, using all its hydrogen atoms for H-bonding between host and guest. The best fit for the guanidinium ion is found for the 27-membered macrocycle with a complementary host–guest H-bonding scheme. Crown ethers with 18 ring atoms form *perching* complexes.

Introduction

The synthesis of a selective receptor molecule for urea would be of practical importance for the selective removal of urea from dialysis liquid. In relation to this objective we are presently interested in the complexation of both neutral and charged *polyfunctional* guest molecules. If guest molecules similar to urea form complexes with macrocyclic hosts, examination of the structures and properties of these complexes may assist in the design of host molecules for urea.

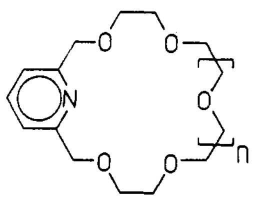
Previously we have shown that urea can form a complex with 18-crown-6.[2] In this 1:5 complex two urea molecules are H-bonded to the crown ether in a *perching*[3] position. The other urea molecules form layers in which they are mutually H-bonded.

We assume that such polyfunctional organic molecules are most strongly bound by crown ethers when they form *encapsulated*[3] complexes with the macrocycle because in such complexes all possible binding interactions between host and guest will be used. From Corey–Pauling–Koltun models, X-ray structure analysis and extraction experiments we have found that urea and urea analogues like uronium[4] and guanidinium[1] cations can only form encapsulated complexes with complementary H-bonding schemes if the crown ether has at least 27 ring atoms. With smaller rings, perching complexes are formed, as was shown by Truter and co-workers[5] for the complex of 18-crown-6 with guanidinium nitrate (1:2) and by our group for the complexes of 18-crown-6 with uronium[4] and *S*-*tert*-butyl thiouronium[6] salts.

From our measurements[7] of the association constants of complexes of CH_3NO_2, CH_3CN, and $CH_2(CN)_2$ with 18-crown-6, we know that complexes of crown ethers with neutral molecules are far less stable than complexes with charged species like metal or alkylammonium cations. As a consequence our concept for the design of a selective receptor molecule for urea is to protonate the urea molecule prior to or during complexation. We have proven that this works if an external strong acid is used to protonate urea, i.e., benzo-27-crown-9 transfers urea from an aqueous into an organic phase as a uronium perchlorate (1:1) complex,[4] in the presence of $HClO_4$. Our ultimate goal is to employ a crown ether with an acidic functionality, which is capable of protonating urea prior to or during its complexation.

We are using guanidine as a model for urea, because it is isoelectronic with urea, and it has the same size and shape, but it is a much stronger base, which facilitates proton transfer. We assume that if guanidine fits well in the cavity of a crown ether, then this cavity will be likely to have the right shape and size to form a stable complex with urea.[1,4]

In this paper[8] we report the results of a systematic study of the complexation of guanidinium cations by 2,6-pyrido crown ethers (1). In the protonated form these crown ethers possess an intraannular proton donating group. Previously crown ethers with acidic units incorporated in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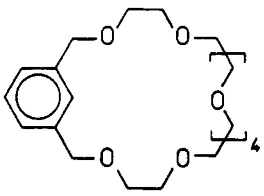
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Table I. 500-MHz ^{1}H NMR Spectral Data ($CDCl_3$) of 2,6-Pyrido Crown Ethers

crown ether 1, *n* =	Ar 4-H	Ar 3,5-H	$ArCH_2$	OCH_2	OCH_2	OCH_2	OCH_2	OCH_2
1	7.66 (t, 1 H)	7.25 (d, 2 H)	4.77 (s, 4 H)	3.76–3.74 (m, 4 H)	3.69–3.67 (m, 4 H)	3.63–3.58 (m, 4 H)	3.60–3.58 (m, 4 H)	
2	7.69 (t, 1 H)	7.32 (d, 2 H)	4.72 (s, 4 H)	3.77–3.75 (m, 4 H)	3.70–3.68 (m, 4 H)	3.60 (s, 8 H)	3.59 (s, 4 H)	
3	7.81 (t, 1 H)	7.48 (d, 2 H)	4.71 (s, 4 H)	3.75–3.73 (m, 4 H)	3.70–3.68 (m, 4 H)	3.64–3.62 (m, 12 H)	3.60–3.59 (m, 4 H)	
4	7.81 (t, 1 H)	7.49 (d, 2 H)	4.70 (s, 4 H)	3.75–3.73 (m, 4 H)	3.71–3.69 (m, 4 H)	3.67–3.64 (m, 12 H)	3.62–3.61 (m, 4 H)	3.60 (s, 4 H)
5	7.78 (t, 1 H)	7.45 (d, 2 H)	4.69 (s, 4 H)	3.77–3.73 (m, 4 H)	3.73–3.70 (m, 4 H)	3.68–3.65 (m, 12 H)	3.63–3.61 (m, 8 H)	3.60–3.57 (m, 4 H)
6	7.75 (t, 1 H)	7.43 (d, 2 H)	4.69 (s, 4 H)	3.75–3.73 (m, 4 H)	3.73–3.71 (m, 4 H)	3.68–3.65 (m, 12 H)	3.64–3.62 (m, 8 H)	3.61–3.60 (m, 8 H)

the cavity have been synthesized with aromatic hydroxyl[9-11] and carboxyl[12] groups. These macrocycles are not ideally designed for complexation of urea or guanidine because the incorporated subunits occupy part of the cavity, thus giving rise to steric repulsion of the guest to be complexed. In the case of pyridinium crowns, the entire cavity is available for complexation.

2,6-Pyrido-15-crown-5[13] (1, *n* = 0) and 2,6-pyrido-18-crown-6[14] (1, *n* = 1) have been synthesized previously from 2,6-bis(hydroxymethyl)pyridine and poly(ethylene glycol) ditosylates with KO-*t*-Bu or NaH as a base. The synthesis of 2,6-pyrido-21-crown-7 and 2,6-pyrido-24-crown-8 (1, *n* = 2, 3) has been reported in low overall yield from the corresponding thionodiesters by reductive desulfurization.[15] Other macrocycles containing pyridyl groups have been reported with macrocyclic rings which contain *o*-xylylene groups,[16] catechol units,[17] ketone functions,[18] lactone groups,[19] diester groups,[20] and macrocyclic rings connected to the pyridyl unit with an oxygen atom.[21] A number of macrobicyclic polyethers containing a pyridyl unit were reported.[22] In virtually all cases the macrocyclic polyether rings contain less than 24 ring atoms.

Previously we have reported encapsulated complexes of guanidinium salts of benzo-27-crown-9, dibenzo-27-crown-9, and dibenzo-30-crown-10.[1] In solution such a complex has been postulated for a 27-crown-9 hexacarboxylate.[23] A perching complex of guanidinium nitrate with 18-crown-6 has been described by Truter and coworkers.[5]

Results

Synthesis and Purification of the Crown Ethers. The 2,6-pyrido crown ethers (1, *n* = 0–6) were synthesized by reaction of 2,6-bis(bromomethyl)pyridine[24] and the appropriate poly(ethylene glycols) in THF, using NaH as base. Purification of the products was effected by acid/base extraction, followed by chromatography. In the case of the 18-membered ring, we have used the method described for the isolation and purification of 18-crown-6.[25] Nitromethane was added to the crude reaction mixture of 2,6-pyrido-18-crown-6 in diethyl ether. The 1:2 (host:guest) complex crystallized immediately and could be dissociated readily in vacuo to give the crown ether in an overall yield of 55%. The larger crown ethers (*n* = 2–6) could be isolated in yields of 37–72%. The yield of the 15-membered macrocycle was rather low (15%).

1,3-Xylylene-27-crown-8 (2) was prepared by the method used for the pyrido crown ethers, from 1,3-bis(bromomethyl)benzene and heptaethylene glycol.[26]

All pyrido crown ethers showed 80-MHz ^{1}H NMR spectra in agreement with their structures. In these spectra, only the CH_2 groups adjacent to the aromatic ring can be distinguished from the other OCH_2 groups, except for 2,6-pyrido-15-crown-5 (1, *n* = 0) where all signals can be assigned to separate OCH_2 groups. In the 500-MHz ^{1}H NMR spectra however, all pyrido crown ethers show separate absorptions for the three OCH_2 units that are closest to the aromatic ring. Details are given in Table I.

The ^{13}C NMR spectra of all pyrido crown ethers showed absorptions at ~158, 137, and 120 ppm for the heteroaromatic carbon atoms. The benzylic carbons exhibit an absorption at ~74 ppm and the other OCH_2 groups gave signals between ~72 and 68 ppm.

In the mass spectra of all pyrido crown ethers, the molecular ion peak was observed. All mass spectra show a pattern in which C_2H_4O fragments are lost successively. The base peak in the spectra is at m/e 122, which can be ascribed to the fragment C_7H_8NO.[13]

The crystalline crown ethers 1 (*n* = 1, 3) and 3 gave satisfactory elemental analyses (C, H, N). The crown ethers 1 (*n* = 4, 5) and 2 were analyzed as the corresponding guanidinium perchlorate complexes.

Synthesis of Protonated Crown Ethers. For a better understanding of complexation it is important to have structural information about both the free and complexed form of the macrocycles involved. Of the larger macrocycles only the 24-membered crown ether (1, *n* = 3) could

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Table II. Extraction Experiments

crown ether	ring size	mmol crown transferred to aqueous phase	mmol Li transferred to organic phase	mmol guanidinium transferred to organic phase	mmol water transferred to organic phase
1, $n = 0$	15	0.43	0.44	0.08	<0.02
1, $n = 1$	18	0.02	0.03	0.32	0.81
1, $n = 2$	21	0.25	0.16	0.29	0.60
1, $n = 3$	24	0.07	0.02	0.23	0.72
1, $n = 4$	27	0.01	<0.002	0.97	<0.02
1, $n = 5$	30	0.11	<0.002	0.84	<0.02
1, $n = 6$	33	0.07	<0.002	0.70	<0.02
2	27	0.14	<0.002	0.85	<0.02

be obtained in the crystalline form. The structure of this crown ether was determined by X-ray crystallography (vide infra).

Because the basis of our concept is the protonation of the guest by means of an intra-annular group, structures of the protonated crown ethers are of interest. We were able to prepare the picrate and tetraphenylborate salts of the 27-membered macrocycle (1, $n = 3$). The structure of the picrate salt was determined by single-crystal X-ray analysis (vide infra).

Liquid–Liquid Phase Transfer of Guanidinium Perchlorate. The complex formation of the 2,6-pyrido crown ethers and guanidinium perchlorate was studied by means of two phase liquid–liquid extraction experiments. An aqueous solution of guanidinium sulfate and lithium perchlorate was equilibrated with a solution of the crown ether in $CDCl_3$. The amount of guanidinium salt transferred was determined from the ratio of the absorptions of the guanidinium cation (6 H) and the benzylic crown ether absorptions (4 H) in the ^1H NMR spectra. The amount of lithium transferred was determined by atomic absorption spectrometry and the amount of water transferred was obtained from the absorption in the ^1H NMR spectrum. In a separate experiment the amount of crown ether transferred to the aqueous phase was determined from the ratio of the absorptions of the crown ether using 1,2,4,5-tetramethylbenzene as an internal NMR standard. Details of the extraction conditions are given in the experimental section.

The results of the extraction experiments, summarized in Table II, show a pronounced shape selectivity of the 2,6-pyrido macrocycles toward guanidinium salts.

Under standard conditions, the 15-, 18-, 21-, and 24-membered macrocycles (1, $n = 0$–3) extracted only small quantities of guanidinium perchlorate into the organic phase. This low extraction efficiency was generally accompanied by coextraction of a considerable amount of water, proportional to the amount of guanidinium ion extracted. In the ^1H NMR spectra the water could clearly be detected as a broad singlet in the 2.5–3.5 ppm region. Especially the 15- and 21-membered ligands extracted considerable amounts of $LiClO_4$ into the organic phase.

In the case of 2,6-pyrido-18-crown-6, a crystalline compound could be obtained from the dried $CDCl_3$ layer upon addition of a small amount of diethyl ether. This proved to be the complex of 2,6-pyrido-18-crown-6, guanidinium perchlorate, and $CDCl_3$ of approximate 1:1:0.9 stoichiometry as determined by ^1H NMR spectroscopy and elemental analysis. A broad singlet at 6.7 ppm (6 H) corresponds to the guanidinium cation.[1]

These results for the 18-membered pyrido crown ether are in line with our earlier extraction experiments with 18-crown-6 and with 1,3-xylylene-18-crown-5. For these crown ethers we have also found low extraction efficiency and in some cases crystallization at the interphase.[1]

2,6-Pyrido-27-crown-9 (1, $n = 4$) extracts guanidinium perchlorate quantitatively into the organic phase without loss of crown ether from the $CDCl_3$ layer. Neither lithium salt nor water were coextracted.

Upon evaporation of the solvent a crystalline product was obtained from the $CDCl_3$ layer. This material was recrystallized from ethanol/diethyl ether, to give colorless crystals, mp 112–113 °C. From ^1H NMR spectroscopy, a broad singlet at 7.0 ppm (6 H) and a characteristic change in the splitting pattern of the methylene protons of the crown ether, showed that a 1:1 complex with guanidinium perchlorate was formed and a satisfactory elemental analysis (C, H, N) and single-crystal X-ray analysis (vide infra) were obtained.

In order to study the effect of the pyrido moiety on the complexation of guanidinium salts, we studied the complexation behavior of the corresponding 1,3-xylylene-27-crown-8 with guanidinium perchlorate. In this compound the pyridyl unit is replaced by a 1,3-xylylene unit which cannot be involved in H-bonding with the guanidinium cation. Therefore a lower efficiency of extraction of guanidinium perchlorate is expected.

Surprisingly, 1,3-xylylene-27-crown-8 (**2**) extracted guanidinium perchlorate into the organic phase quantitatively, with transfer of 0.14 mmol of crown ether into the aqueous phase. No $LiClO_4$ was extracted into the $CDCl_3$ phase. We isolated a crystalline product from the $CDCl_3$ phase by evaporation of the solvent. The complex was recrystallized from ethanol/diethyl ether to give colorless crystals, mp 74–75 °C. In the ^1H NMR spectra a broad singlet at 6.2 ppm of the guanidinium protons and a broadening of the signals for the methylene protons was observed upon complexation. Elemental analysis proved this compound to be the 1,3-xylylene-27-crown-8–guanidinium perchlorate (1:1) complex, which was supported by X-ray analysis (vide infra).

The larger pyrido crown ethers (1, $n = 5$,6) showed a slightly lower extraction efficiency for guanidinium ions. Neither $LiClO_4$ nor H_2O were transferred to the organic phase. In the case of 2,6-pyrido-30-crown-10 (1, $n = 5$), a crystalline product was obtained from the organic phase after evaporation of the solvent (mp 64–67 °C). ^1H NMR and elemental analysis proved this to be the 2,6-pyrido-30-crown-10–guanidinium perchlorate (1:1) complex. An X-ray structural analysis was carried out for this compound (vide infra).

The 2,6-Pyrido-27-crown-9–Guanidinium Thiocyanate–Ethanol (2:3:1) Complex. To investigate the effect of the anion on the complex structure we have synthesized the complex of 2,6-pyrido-27-crown-9 and guanidinium thiocyanate by dissolving the crown ether and the salt in ethanol in a ratio of 1:1 or 1.5:1. Upon the addition of diethyl ether a complex crystallized which from ^1H NMR, elemental analysis, and X-ray analysis (vide infra) proved to contain crown ether, guanidinium thiocyanate, and ethanol in a ratio of 2:3:1. The product was recrystallized from ethanol/diethyl ether, mp 69–72 °C.

In a liquid–liquid extraction experiment, 2,6-pyrido-27-crown-9 extracted 1.00 equiv of guanidinium thio-

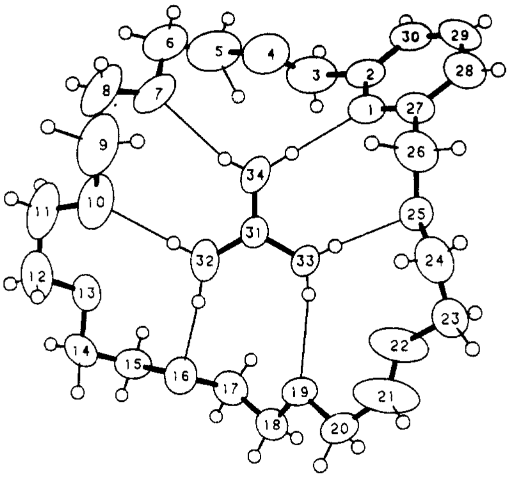

Figure 1. View of the 1:1 complex of guanidinium perchlorate with 2,6-pyrido-27-crown-9, showing atom numbering. The perchlorate ion (numbered Cl35, O36–O39) is omitted.

cyanate into the organic phase.

X-ray Structures. Structures of four complexes of guanidinium salts with 2,6-pyrido or 1,3-xylylene crown ethers, of the picrate salt of 2,6-pyrido-27-crown-9, and of the uncomplexed 2,6-pyrido-24-crown-8 have been determined by X-ray crystallography. Details of the structure determinations are given in the Experimental Section. Stereoscopic ORTEP[27] views of the complexes, including atom numbering, are given in Figures 1–6, using 70% probability ellipsoids for all non-hydrogen atoms. The radii of the hydrogen atoms have been chosen arbitrarily. Positional and equivalent isotropic thermal parameters[28] of the non-hydrogen atoms are collected in Table III. Torsion angles in the macrorings are given in Table IV. H-bond parameters are presented in Table V.

The macroring in the 1:1 complex of 2,6-pyrido-27-crown-9 with guanidinium perchlorate and one of the macrorings in the 2,6-pyrido-27-crown-9–guanidinium thiocyanate–ethanol (2:3:1) complex (numbered N31-C60) are slightly disordered, as may be seen from the probability ellipsoids of some atoms (Figures 1 and 4) and from the positional and thermal parameters of these atoms (Table III). Consequently, the torsion angles involving these atoms are unreliable (Table IV). In the former complex only one hydrogen atom at C21 could be located. No hydrogens of the ethanol molecule in the latter complex could be located.

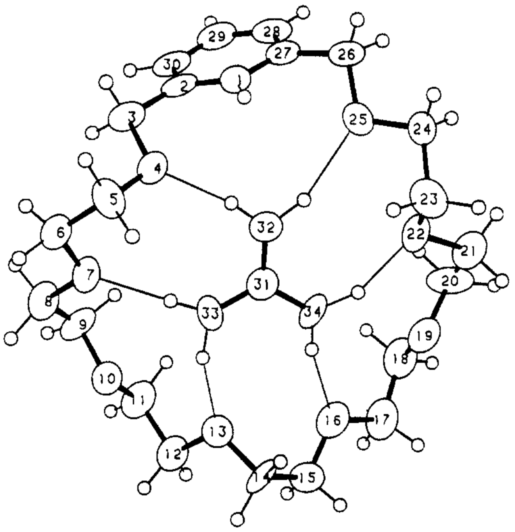

Figure 2. View of the 1:1 complex of guanidinium perchlorate with 1,3-xylylene-27-crown-8, showing atom numbering. The perchlorate ion (numbered Cl35, O36–O39) is omitted.

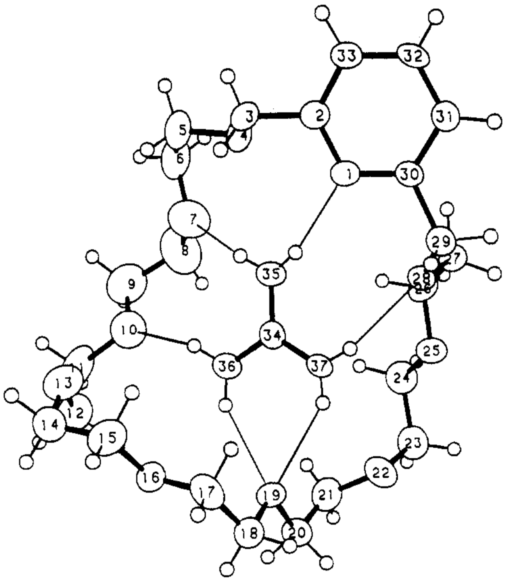

Figure 3. View of the 1:1 complex of guanidinium perchlorate with 2,6-pyrido-30-crown-10, showing atom numbering. The perchlorate ion (numbered Cl38, O39–O42) is omitted.

The polyether in the 1:1 complex of 2,6-pyrido-27-crown-9 (1, $n = 4$) with guanidinium perchlorate (Figure 1) encapsulates the cation, using the pyridyl nitrogen as a H-bond acceptor. The aromatic ring is almost coincident with the least-squares plane of the macrocycle. The perchlorate ion is not in close contact with the cation or crown ether. Every NH_2 group of the cation forms two short H-bonds with next-nearest hetero atoms of the macrocycle. The complexation scheme is therefore similar to the two complexes of guanidinium perchlorate with benzo-27-crown-9 and dibenzo-27-crown-9.[1] The lengths of the H-bonds are in the same range (N···X: 2.92–3.02 Å, X = N or O, see Table V). The macroring adopts an $ag^{+}a$ $ag^{-}a$ $ag^{+}a$ $ag^{-}a$ $ag^{+}a$ $ag^{-}a$ $g^{-}g^{-}a$ $ag^{-}a$ $ag^{+}a$ conformation, with some torsion angles deviating strongly from the ideal staggered angles, probably partly as the result of the disorder (Table IV). (Some torsion angles must necessarily deviate from the ideal values, corresponding with the torsion code, as the first 18 symbols of the code define the well-known D_{3d} conformation of an 18-membered ring, if perfect staggered torsion angles are assumed.)

The X-ray structure determination of the 1:1 complex of 1,3-xylylene-27-crown-8 (**2**) with guanidinium perchlorate (Figure 2) reveals a complexation between the guanidinium guest and the macrocycle analogous to the aforementioned complex, i.e., an encapsulated complex, in which each NH_2 group of the guest forms two H-bonds to next-nearest oxygen neighbor atoms of the host (range of N···O distances of the H-bonds: 2.87–3.12 Å, see Table V). The perchlorate ion is again not involved in short contacts with crown ether or cation.

The xylylene moiety is oriented almost perpendicular to the plane of the macrocycle, avoiding steric hindrance with the guanidinium cation. The macroring adopts the conformation with torsion code $ag^{+}a$ $ag^{+}g^{+}$ $ag^{-}a$ $ag^{+}a$ $ag^{+}g^{+}$ $ag^{-}a$ $ag^{+}a$ $ag^{+}g^{+}$ $ag^{-}a$. This conformation differs from the conformations encountered in the 1:1 complex of guani-

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dinium perchlorate with 2,6-pyrido-27-crown-9 and in the 1:1 complexes of the salt with 27-membered benzo crown ethers,[1] although it resembles the conformation of the macroring in the 1:1 complex of uronium perchlorate with benzo-27-crown-9.[4] If the xylylene ring is neglected, it has almost perfect 3-fold symmetry (C_3), which seems favorable for complexation with the guanidinium ion.

The crystalline 1:1 complex of 2,6-pyrido-30-crown-10 (1, n = 5) with guanidinium perchlorate (Figure 3) is shown to consist of crown ethers encapsulating guanidinium ions, and perchlorate ions, which are not involved in short contacts with macrocycles or cations. Like the complex of the guanidinium salt with 2,6-pyrido-27-crown-9 the pyridyl nitrogen is used as H-bond acceptor. However, contrary to the polyether in the latter complex, the 2,6-pyrido-30-crown-10 is evidently too large to encapsulate the guanidinium cation without a considerable folding of the macrocycle. Unlike the 1:1 complex of guanidinium perchlorate with dibenzo-30-crown-10,[1] all six guanidinium hydrogens are used in relatively strong H-bonds with the host (N···X: 2.88–3.10 Å, X = N or O, see Table V). Therefore, the 2,6-pyrido-30-crown-10 is likely more flexible than the dibenzo-30-crown-10. The macroring has a saddle-like shape with torsion code $ag^+g^+\ ag^-a\ ag^+g^+\ ag^+a\ ag^+a\ ag^-g^+\ ag^+a\ ag^-g^-\ ag^+a\ ag^-a$.

X-ray analysis revealed that the 2:3:1 complex of 2,6-pyrido-27-crown-9 (1, n = 4) with guanidinium thiocyanate and ethanol (Figure 4) consists of three separate entities, namely two crown ether–cation (1:1) complexes (Figures 4a and 4b) and a third "cluster", consisting of the third guanidinium cation surrounded by three thiocyanate anions and an extra molecule (Figure 4c). Although the nature of this latter molecule is not certain due to its large thermal parameters (Table III) and the resulting impossibility to locate its hydrogen atoms, it is assumed to be ethanol, which is in agreement with the observed bond lengths and bond angle and with the ^{1}H NMR and elemental analysis.

The two almost identical crown ether–cation moieties form encapsulated complexes with each six H-bonds between host and guest (including H-bonds to the pyridyl nitrogen atoms). The H-bond distances (N···X: 2.84–2.98 Å for the first and 2.87–3.04 Å for the second crown ether/cation moiety, X = N or O, see Table V) are in the same range as found for the other complexes of guanidinium with 27-membered macrocycles. Both macrocycles adopt the same conformation (torsion code $ag^+g^+\ ag^-a\ ag^+a\ ag^+g^+\ ag^-a\ ag^+a\ ag^+g^+\ ag^-a\ ag^+a$), the RMS and maximum deviations between the corresponding torsion angles of the macrocycles being 6.0 and 13.0°, respectively (omitting the deviations involving the disordered C45-C47 part of the second macroring). This happens to be the same conformation as encountered for the macrocycle in the 1:1 complex of guanidinium perchlorate with 1,3-xylylene-27-crown-8, except for the position of the aromatic ring (which may result from the different orientation of the aromatic ring relative to the macroring in both complexes, i.e., almost coincident in this complex and almost perpendicular in the complex with the xylylene crown ether).

The third guanidinium ion forms six H-bonds to the nitrogen atoms of the three thiocyanate anions (two of which act as acceptor atoms of two H-bonds) and to the ethanol oxygen atom (Table V).

The remarkable difference between the two complexes of 2,6-pyrido-27-crown-9 with guanidinium perchlorate and with guanidinium thiocyanate is assumed to stem from the greater ability of the thiocyanate ion to form H-bonds as compared to the perchlorate ion.

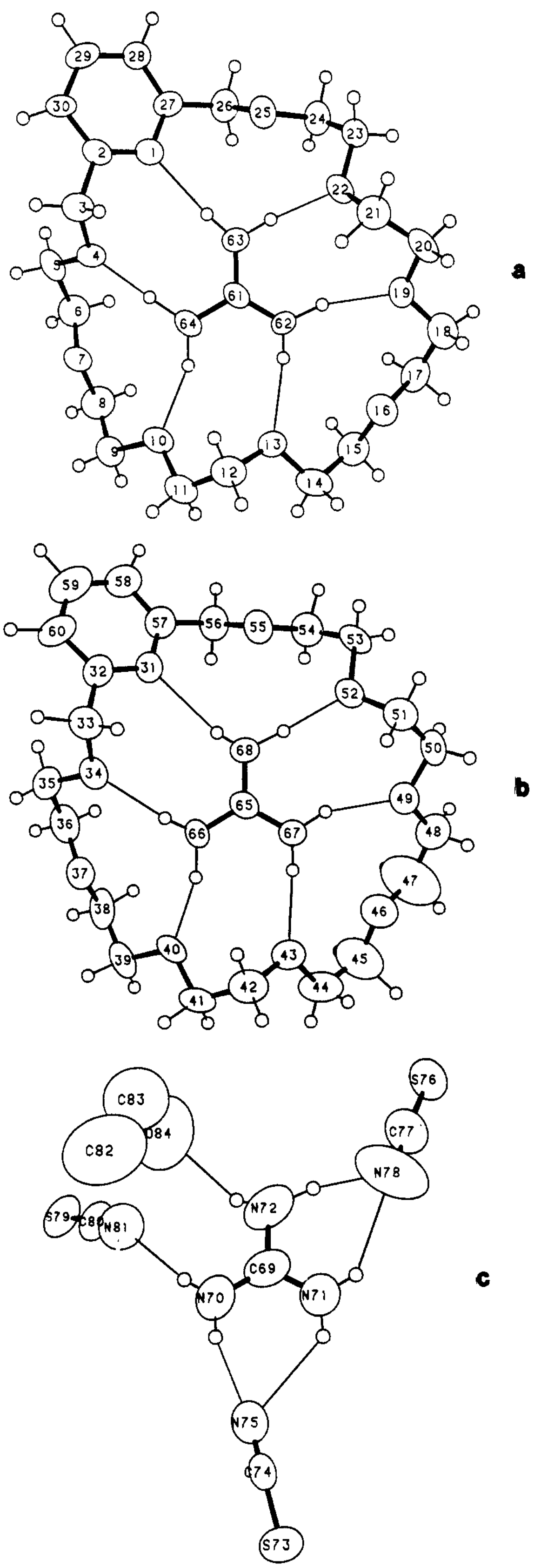

Figure 4. Views of the three entities in the 3:2:1 complex between guanidinium thiocyanate, 2,6-pyrido-27-crown-9, and ethanol, showing atom numbering.

The X-ray structure determination of uncomplexed 2,6-pyrido-24-crown-8 (1, n = 3) in the crystalline state (Figure 5) reveals a structure in which the pyrido ring is oriented such as to fill the cavity of the macrocycle. The macrocycle adopts an $aag^-\ ag^-g^-\ ag^-a\ ag^-a\ ag^+a\ ag^+a\ g^+g^+a\ g^+aa$ conformation with approximate mirror symmetry.

Table III. Fractional Coordinates[a] (*10⁴) and Equivalent Isotropic Thermal Parameters[a,b] (*10⁴) of the Non-Hydrogen Atoms in the Compounds[c]

atom	x	y	z	U_{eq}
		3		
N1	9265 (3)	7906 (3)	14024 (4)	373 (15)
C2	10224 (3)	7952 (4)	13629 (5)	414 (18)
C3	10577 (4)	7101 (6)	14150 (8)	657 (30)
O4	10507 (3)	7431 (3)	15775 (5)	710 (19)
C5	10856 (5)	6716 (7)	16419 (9)	937 (38)
C6	10563 (6)	6872 (6)	17991 (9)	960 (38)
O7	9522 (3)	6380 (3)	18216 (4)	677 (18)
C8	9164 (7)	6462 (7)	19771 (8)	987 (43)
C9	8049 (6)	6116 (6)	19913 (7)	923 (39)
O10	7556 (3)	4912 (3)	19143 (4)	661 (18)
C11	7663 (5)	4022 (5)	19755 (6)	645 (29)
C12	6841 (5)	2877 (6)	19245 (6)	557 (27)
O13	6925 (2)	2530 (3)	17655 (3)	412 (13)
C14	6226 (4)	1380 (4)	17081 (6)	506 (22)
C15	6323 (4)	1099 (4)	15406 (6)	450 (21)
O16	5884 (2)	1798 (3)	14840 (3)	421 (13)
C17	5965 (4)	1558 (5)	13219 (5)	445 (21)
C18	5164 (4)	1845 (4)	12652 (6)	460 (22)
O19	5348 (2)	3089 (3)	12979 (3)	442 (13)
C20	4535 (4)	3398 (5)	12563 (9)	564 (26)
C21	4810 (5)	4535 (5)	12296 (10)	1077 (43)
O22	5539 (4)	5312 (5)	12372 (10)	1971 (46)
C23	5647 (5)	6482 (6)	12174 (11)	963 (41)
C24	6210 (4)	7471 (6)	13339 (8)	671 (32)
O25	7219 (2)	7490 (3)	13292 (3)	408 (13)
C26	7850 (4)	8606 (4)	14128 (6)	502 (22)
C27	8926 (3)	8690 (4)	13665 (5)	370 (17)
C28	9516 (4)	9540 (4)	12882 (6)	503 (22)
C29	10487 (4)	9577 (5)	12503 (7)	554 (24)
C30	10854 (4)	8790 (5)	12875 (6)	470 (21)
C31	2496 (3)	4760 (4)	4697 (4)	301 (16)
N32	2816 (4)	5692 (4)	4085 (5)	490 (20)
N33	2866 (3)	4827 (4)	5979 (4)	389 (18)
N34	1808 (3)	3756 (4)	4078 (5)	452 (19)
Cl35	2856 (1)	521 (1)	9769 (1)	429 (5)
O36	3865 (3)	1040 (3)	9274 (4)	689 (17)
O37	2325 (4)	-307 (6)	8550 (8)	1695 (37)
O38	2857 (4)	16 (7)	10900 (9)	1947 (52)
O39	2389 (3)	1389 (4)	10262 (6)	1041 (26)
		4		
C1	1891 (1)	6885 (2)	787 (2)	281 (12)
C2	2183 (1)	5997 (2)	977 (2)	281 (12)
C3	2218 (1)	5063 (3)	472 (2)	366 (13)
O4	1704 (1)	4956 (1)	121 (1)	303 (7)
C5	1701 (2)	4235 (3)	-473 (2)	327 (13)
C6	1782 (1)	3108 (3)	-257 (2)	334 (13)
O7	1365 (1)	2835 (1)	247 (1)	321 (7)
C8	1452 (1)	1823 (3)	566 (2)	358 (13)
C9	1108 (1)	1726 (3)	1223 (2)	348 (13)
O10	552 (1)	1628 (1)	1031 (1)	299 (8)
C11	208 (1)	1561 (3)	1641 (2)	347 (13)
C12	-373 (1)	1581 (3)	1398 (2)	341 (13)
O13	-477 (1)	2601 (1)	1104 (1)	323 (8)
C14	-1040 (1)	2802 (3)	941 (2)	330 (13)
C15	-1347 (1)	3231 (3)	1563 (2)	382 (14)
O16	-1093 (1)	4199 (2)	1774 (1)	359 (8)
C17	-1399 (1)	4769 (3)	2294 (2)	422 (14)
C18	-1080 (2)	5714 (3)	2536 (2)	454 (15)
O19	-1013 (1)	6452 (2)	1971 (1)	361 (8)
C20	-773 (2)	7416 (4)	2217 (2)	591 (18)
C21	-628 (2)	8098 (3)	1597 (2)	513 (16)
O22	-196 (1)	7616 (2)	1206 (1)	349 (8)
C23	-13 (2)	8249 (3)	615 (2)	396 (13)
C24	493 (1)	8852 (3)	794 (2)	403 (14)
O25	919 (1)	8110 (1)	916 (1)	327 (7)
C26	1437 (1)	8607 (3)	1058 (2)	376 (13)
C27	1827 (1)	7740 (2)	1249 (2)	289 (12)
C28	2101 (1)	7715 (3)	1901 (2)	363 (13)
C29	2413 (1)	6849 (3)	2090 (2)	374 (13)
C30	2441 (1)	5991 (3)	1640 (2)	340 (13)
C31	312 (1)	5003 (3)	858 (1)	228 (12)
N32	686 (1)	5709 (3)	677 (1)	296 (11)
N33	408 (1)	3988 (2)	754 (1)	306 (11)
N34	-157 (1)	5320 (3)	1136 (1)	313 (11)
Cl35	6788 (0)	4892 (1)	6408 (0)	344 (3)
O36	7168 (1)	5750 (2)	6412 (1)	652 (10)
O37	7070 (1)	3908 (2)	6307 (1)	493 (8)
O38	6409 (1)	5025 (2)	5827 (1)	526 (8)
O39	6496 (1)	4866 (2)	7074 (1)	512 (8)
		5		
N1	8829 (3)	6252 (2)	5655 (1)	230 (13)
C2	9972 (4)	5743 (3)	5836 (2)	235 (15)
C3	11197 (4)	6324 (4)	6109 (2)	291 (19)
O4	11034 (3)	6682 (2)	6671 (1)	319 (12)
C5	12227 (5)	7141 (4)	6988 (2)	416 (21)
C6	11932 (5)	7643 (4)	7519 (2)	418 (21)
O7	10980 (3)	8382 (2)	7341 (1)	494 (14)
C8	10727 (7)	9020 (5)	7801 (3)	588 (27)
C9	11432 (6)	9980 (4)	7810 (2)	535 (24)
O10	10915 (3)	10490 (2)	7281 (1)	446 (13)
C11	11498 (5)	11462 (4)	7280 (3)	538 (24)
C12	11088 (5)	11915 (4)	6684 (3)	494 (23)
O13	11680 (3)	11393 (2)	6294 (2)	492 (14)
C14	11537 (5)	11835 (4)	5729 (3)	549 (24)
C15	10406 (5)	11422 (4)	5289 (3)	458 (22)
O16	9147 (3)	11725 (2)	5407 (1)	302 (12)
C17	8063 (5)	11345 (4)	4976 (2)	344 (20)
C18	6763 (5)	11688 (4)	5108 (2)	354 (19)
O19	6563 (3)	11221 (2)	5636 (1)	297 (11)
C20	5493 (5)	11681 (4)	5860 (3)	404 (22)
C21	5130 (6)	11082 (4)	6339 (3)	408 (22)
O22	4427 (3)	10235 (2)	6091 (1)	343 (12)
C23	3904 (5)	9677 (4)	6514 (2)	375 (20)
C24	4853 (5)	8859 (4)	6769 (2)	341 (19)
O25	4795 (3)	8112 (2)	6329 (1)	270 (11)
C26	5650 (5)	7324 (3)	6553 (2)	306 (19)
C27	5648 (5)	6592 (3)	6071 (2)	310 (18)
O28	6221 (3)	7042 (2)	5616 (1)	238 (11)
C29	6467 (5)	6352 (4)	5187 (2)	299 (19)
C30	7715 (4)	5749 (3)	5407 (2)	220 (15)
C31	7711 (4)	4743 (3)	5341 (2)	272 (17)
C32	8897 (4)	4236 (3)	5527 (2)	296 (18)
C33	10044 (4)	4741 (3)	5773 (2)	272 (17)
C34	8261 (4)	9080 (3)	6094 (2)	228 (15)
N35	8939 (4)	8273 (3)	6270 (2)	287 (17)
N36	8716 (5)	9939 (3)	6316 (2)	336 (17)
N37	7121 (4)	9043 (3)	5692 (2)	271 (16)
Cl38	4304 (1)	4228 (1)	6567 (1)	537 (5)
O39	4654 (4)	4999 (2)	6962 (2)	591 (15)
O40	3500 (3)	4499 (3)	6034 (2)	684 (16)
O41	4222 (6)	3307 (3)	6773 (2)	1285 (27)
O42	5642 (4)	4053 (4)	6341 (3)	1498 (32)
		6		
N1	9332 (2)	2045 (2)	9988 (2)	279 (17)
C2	10114 (2)	2008 (3)	9926 (3)	270 (21)
C3	10709 (3)	2981 (3)	10308 (3)	355 (25)
O4	10347 (2)	3567 (2)	11282 (2)	308 (14)
C5	10417 (3)	3343 (3)	12096 (3)	348 (27)
C6	9958 (3)	3972 (3)	13057 (3)	394 (27)
O7	10372 (2)	4966 (2)	13138 (2)	319 (14)
C8	9969 (4)	5617 (3)	14024 (3)	454 (30)
C9	10330 (4)	6633 (3)	13999 (3)	385 (28)
O10	10044 (2)	6745 (2)	13257 (2)	348 (15)
C11	10215 (3)	7726 (3)	13300 (3)	386 (28)
C12	10017 (3)	7747 (3)	12401 (3)	398 (27)
O13	9132 (2)	7350 (2)	12409 (2)	351 (15)
C14	8619 (3)	8060 (3)	12897 (4)	454 (28)
C15	7716 (3)	7543 (4)	12852 (3)	448 (27)
O16	7659 (2)	7142 (2)	11829 (2)	365 (15)
C17	6826 (3)	6570 (3)	11732 (3)	382 (26)
C18	6822 (3)	6117 (3)	10640 (3)	421 (28)
O19	7336 (2)	5420 (2)	10176 (2)	338 (15)
C20	7380 (3)	4939 (4)	9125 (3)	423 (29)
C21	8045 (3)	4364 (3)	8705 (4)	392 (28)
O22	7814 (2)	3607 (2)	9145 (2)	375 (15)
C23	7363 (3)	2691 (3)	8600 (4)	386 (27)

Table III (Continued)

atom	x	y	z	U_{eq}
C24	7191 (3)	1996 (3)	9148 (4)	413 (28)
O25	8006 (2)	1837 (2)	9055 (2)	344 (15)
C26	7920 (3)	1273 (4)	9681 (3)	355 (27)
C27	8793 (2)	1205 (3)	9607 (3)	274 (21)
C28	9029 (3)	334 (3)	9156 (3)	354 (25)
C29	9842 (3)	306 (3)	9110 (3)	491 (27)
C30	10398 (3)	1162 (3)	9517 (3)	397 (26)
N31	6896 (2)	960 (2)	2014 (2)	310 (18)
C32	7615 (2)	806 (3)	2030 (3)	377 (23)
C33	8301 (3)	1685 (3)	2344 (3)	391 (26)
O34	8015 (2)	2296 (2)	3337 (2)	369 (15)
C35	8034 (4)	1946 (4)	4092 (3)	411 (30)
C36	7543 (3)	2484 (3)	5065 (3)	478 (30)
O37	7913 (2)	3486 (2)	5296 (2)	394 (16)
C38	7411 (3)	4038 (3)	6168 (3)	509 (30)
C39	7791 (3)	5102 (3)	6355 (3)	519 (30)
O40	7684 (2)	5381 (2)	5581 (2)	408 (15)
C41	7940 (3)	6412 (3)	5805 (4)	501 (28)
C42	7899 (3)	6654 (4)	4930 (4)	482 (29)
O43	7046 (2)	6365 (2)	4789 (2)	438 (16)
C44	6520 (3)	7008 (4)	5449 (4)	695 (35)
C45	5720 (3)	6778 (4)	5273 (4)	859 (35)
O46	5547 (2)	6215 (2)	4383 (2)	591 (18)
C47	4807 (4)	5883 (5)	4165 (4)	1241 (44)
C48	4612 (4)	5323 (4)	3244 (4)	567 (32)
O49	5179 (2)	4712 (2)	2562 (2)	395 (16)
C50	4954 (3)	4200 (4)	1607 (3)	456 (29)
C51	5614 (3)	3631 (3)	926 (4)	409 (29)
O52	5535 (2)	2821 (2)	1234 (2)	369 (15)
C53	5006 (3)	1932 (3)	746 (3)	355 (26)
C54	4830 (3)	1218 (3)	1282 (4)	416 (29)
O55	5605 (1)	992 (2)	1185 (2)	367 (15)
C56	5454 (3)	389 (4)	1774 (4)	406 (28)
C57	6277 (2)	180 (3)	1703 (3)	397 (23)
C58	6361 (3)	−751 (3)	1408 (3)	516 (27)
C59	7108 (3)	−899 (3)	1443 (3)	651 (30)
C60	7746 (3)	−102 (3)	1764 (3)	531 (27)
C61	8889 (2)	4750 (2)	11153 (3)	300 (21)
N62	8487 (3)	5383 (3)	11239 (3)	368 (24)
N63	8743 (2)	3851 (3)	10525 (3)	390 (22)
N64	9455 (2)	5004 (3)	11715 (3)	399 (21)
C65	6766 (2)	3763 (3)	3188 (3)	310 (22)
N66	7265 (2)	3873 (3)	3756 (3)	378 (22)
N67	6479 (3)	4525 (3)	3309 (3)	393 (24)
N68	6543 (3)	2930 (3)	2503 (3)	398 (23)
C69	2279 (3)	108 (3)	3799 (3)	521 (25)
N70	3009 (3)	239 (3)	3155 (4)	616 (28)
N71	1627 (3)	389 (3)	3823 (4)	530 (26)
N72	2167 (4)	−289 (4)	4523 (5)	854 (38)
S73	2655 (1)	2536 (1)	1206 (1)	495 (8)
C74	2724 (2)	1802 (3)	1707 (3)	348 (22)
N75	2775 (2)	1291 (2)	2067 (3)	529 (22)
S76	409 (1)	1587 (1)	3217 (1)	497 (7)
C77	−113 (3)	855 (3)	3839 (3)	532 (25)
N78	−469 (3)	319 (3)	4304 (3)	1075 (29)
S79	4636 (1)	7148 (1)	11979 (1)	664 (9)
C80	4287 (3)	8147 (3)	12606 (3)	555 (27)
N81	4040 (3)	8861 (3)	13023 (3)	774 (26)
C82	4664 (4)	11344 (5)	5278 (5)	1739 (57)
C83	4120 (4)	10552 (4)	5788 (4)	1216 (39)
O84	3634 (3)	9836 (3)	5125 (3)	1573 (35)
		7		
N1	7931 (1)	−4942 (1)	4709 (1)	224 (3)
C2	8341 (1)	−4176 (1)	3825 (1)	215 (3)
C3	9110 (1)	−4911 (1)	2763 (1)	257 (4)
O4	9553 (1)	−4127 (1)	1814 (1)	250 (3)
C5	8689 (1)	−4051 (1)	517 (1)	278 (4)
C6	9194 (1)	−3012 (1)	−232 (1)	299 (4)
O7	9289 (1)	−1683 (1)	665 (1)	277 (3)
C8	8221 (1)	−1004 (1)	444 (1)	307 (4)
C9	8452 (1)	380 (1)	1428 (1)	325 (4)
O10	8428 (1)	298 (1)	2958 (1)	253 (3)
C11	8895 (1)	1521 (1)	3990 (1)	266 (4)
C12	8863 (1)	1383 (1)	5582 (1)	283 (4)
O13	7647 (1)	1299 (1)	5844 (1)	250 (2)
C14	7620 (1)	1417 (1)	7414 (1)	295 (4)
C15	6347 (1)	1276 (1)	7671 (2)	318 (4)
O16	5921 (1)	−103 (1)	7305 (1)	305 (3)
C17	4700 (1)	−297 (1)	7507 (2)	354 (5)
C18	4371 (1)	−1772 (1)	7299 (1)	344 (4)
O19	4997 (1)	−2255 (1)	8544 (1)	305 (3)
C20	4606 (1)	−3607 (1)	8564 (2)	357 (5)
C21	5088 (1)	−4654 (1)	7446 (1)	317 (4)
O22	6351 (1)	−4670 (1)	7929 (1)	281 (3)
C23	6959 (1)	−5291 (1)	6762 (1)	277 (4)
C24	7318 (1)	−4357 (1)	5779 (1)	218 (3)
C25	7075 (1)	−3009 (1)	5985 (1)	229 (4)
C26	7470 (1)	−2245 (1)	5029 (1)	237 (4)
C27	8116 (1)	−2825 (1)	3932 (1)	226 (3)
		8		
N1	1107 (1)	4404 (3)	7054 (1)	269 (9)
C2	1443 (1)	3407 (3)	7074 (1)	289 (11)
C3	1462 (1)	2456 (4)	6543 (1)	363 (13)
O4	1776 (1)	1279 (2)	6636 (1)	373 (8)
C5	2152 (1)	1478 (5)	6344 (1)	421 (14)
C6	2470 (1)	2654 (5)	6619 (1)	449 (15)
O7	2649 (1)	2119 (2)	7174 (1)	350 (8)
C8	2928 (1)	3198 (4)	7483 (1)	369 (14)
C9	3050 (1)	2611 (4)	8082 (1)	348 (13)
O10	2661 (1)	2642 (2)	8364 (1)	352 (8)
C11	2745 (1)	2127 (4)	8943 (1)	338 (13)
C12	2329 (1)	2253 (4)	9205 (2)	364 (13)
O13	2249 (1)	3819 (2)	9332 (1)	343 (8)
C14	1847 (1)	4007 (4)	9568 (1)	394 (14)
C15	1820 (1)	5582 (5)	9796 (1)	436 (15)
O16	1696 (1)	6650 (3)	9344 (1)	444 (9)
C17	1674 (1)	8169 (4)	9559 (2)	491 (16)
C18	1451 (1)	9198 (5)	9109 (2)	561 (17)
O19	1014 (1)	8760 (3)	8973 (1)	524 (10)
C20	719 (1)	10014 (4)	8843 (2)	596 (17)
C21	747 (2)	10714 (4)	8251 (2)	619 (18)
O22	587 (1)	9607 (3)	7830 (1)	533 (10)
C23	636 (2)	10055 (4)	7256 (2)	607 (18)
C24	490 (1)	8749 (4)	6862 (2)	505 (16)
O25	782 (1)	7469 (2)	6951 (1)	413 (9)
C26	674 (1)	6453 (4)	7385 (1)	316 (12)
C27	1047 (1)	5360 (3)	7488 (1)	277 (11)
C28	1345 (1)	5321 (4)	7983 (1)	315 (12)
C29	1694 (1)	4322 (4)	8013 (1)	324 (12)
C30	1741 (1)	3341 (4)	7563 (1)	308 (12)
C31	10279 (1)	4590 (3)	892 (1)	235 (11)
C32	10494 (1)	3506 (3)	567 (1)	235 (10)
C33	10270 (1)	2515 (3)	170 (1)	294 (12)
C34	9818 (1)	2538 (3)	82 (1)	278 (11)
C35	9583 (1)	3484 (3)	402 (1)	294 (12)
C36	9808 (1)	4420 (3)	797 (1)	242 (10)
O37	10456 (1)	5622 (2)	1215 (1)	299 (8)
N38	10967 (1)	3425 (3)	616 (1)	325 (10)
O39	11188 (1)	4463 (3)	863 (1)	466 (9)
O40	11138 (1)	2329 (3)	404 (1)	584 (10)
N41	9590 (1)	1533 (3)	−346 (1)	388 (10)
O42	9810 (1)	776 (3)	−646 (1)	501 (10)
O43	9190 (1)	1493 (3)	−393 (1)	528 (9)
N44	9552 (1)	5383 (3)	1140 (1)	326 (10)
O45	9228 (1)	6043 (3)	885 (1)	459 (9)
O46	9663 (1)	5473 (3)	1659 (1)	428 (9)

[a] Estimated standard deviations given in parentheses in units of the least significant digit. [b] Defined according to Willis and Pryor.[28] [c] 3: 2,6-pyrido-27-crown-9–guanidinium perchlorate (1:1). 4: 1,3-xylylene-27-crown-8–guanidinium perchlorate (1:1). 5: 2,6-pyrido-30-crown-10–guanidinium perchlorate (1:1). 6: 2,6-pyrido-27-crown-9–guanidinium thiocyanate–ethanol (2:3:1). 7: 2,6-pyrido-24-crown-8. 8: 2,6-pyrido-27-crown-9–picric acid (1:1).

Although the aromatic hydrogens point into the macrocyclic cavity and are directed more or less to oxygen atoms of the polyether, the distances involved are too long to denote these contacts as H-bonds. CPK-models indicate

Table IV. Torsion Angles[a] (deg) in the Macrocycles of the Compounds[b]

3	
N1–C2–C3–O4	–62.1 (4)
C2–C3–O4–C5	–177.9 (4)
C3–O4–C5–C6	–166.6 (5)
O4–C5–C6–O7	68.4 (5)
C5–C6–O7–C8	178.0 (7)
C6–O7–C8–C9	170.2 (5)
O7–C8–C9–O10	61.0 (6)
C8–C9–O10–C11	68.4 (6)
C9–O10–C11–C12	159.2 (5)
O10–C11–C12–O13	60.9 (4)
C11–C12–O13–C14	174.3 (5)
C12–O13–C14–C15	177.4 (4)
O13–C14–C15–O16	–74.4 (3)
C14–C15–O16–C17	179.7 (4)
C15–O16–C17–C18	155.4 (3)
O16–C17–C18–O19	71.3 (4)
C17–C18–O19–C20	–174.8 (4)
C18–O19–C20–C21	–155.8 (5)
O19–C20–C21–O22	–3 (1)
C20–C21–O22–C23	–173.9 (8)
C21–O22–C23–C24	132.6 (9)
O22–C23–C24–O25	64.8 (5)
C23–C24–O25–C26	164.6 (6)
C24–O25–C26–C27	–163.9 (4)
O25–C26–C27–N1	–66.6 (4)
C26–C27–N1–C2	180.0 (3)
C27–N1–C2–C3	176.2 (4)
4	
C1–C2–C3–O4	–36.8 (3)
C2–C3–O4–C5	168.7 (2)
C3–O4–C5–C6	67.7 (3)
O4–C5–C6–O7	57.1 (2)
C5–C6–O7–C8	–171.4 (2)
C6–O7–C8–C9	163.5 (2)
O7–C8–C9–O10	71.2 (2)
C8–C9–O10–C11	–178.5 (3)
C9–O10–C11–C12	173.8 (2)
O10–C11–C12–O13	–67.0 (2)
C11–C12–O13–C14	–171.3 (2)
C12–O13–C14–C15	87.4 (3)
O13–C14–C15–O16	59.5 (2)
C14–C15–O16–C17	170.9 (3)
C15–O16–C17–C18	174.6 (2)
O16–C17–C18–O19	66.3 (2)
C17–C18–O19–C20	172.3 (3)
C18–O19–C20–C21	170.9 (2)
O19–C20–C21–O22	–67.8 (3)
C20–C21–O22–C23	–177.3 (3)
C21–O22–C23–C24	99.5 (3)
O22–C23–C24–O25	64.8 (2)
C23–C24–O25–C26	177.0 (3)
C24–O25–C26–C27	174.3 (2)
O25–C26–C27–C1	53.5 (3)
C26–C27–C1–C2	–170.7 (3)
C27–C1–C2–C3	176.8 (2)
5	
N1–C2–C3–O4	69.9 (3)
C2–C3–O4–C5	172.9 (4)
C3–O4–C5–C6	170.5 (3)
O4–C5–C6–O7	–62.8 (4)
C5–C6–O7–C8	–171.8 (4)
C6–O7–C8–C9	101.1 (4)
O7–C8–C9–O10	64.6 (4)
C8–C9–O10–C11	176.1 (4)
C9–O10–C11–C12	171.5 (4)
O10–C11–C12–O13	–67.3 (4)
C11–C12–O13–C14	–171.0 (4)
C12–O13–C14–C15	–97.3 (4)
O13–C14–C15–O16	72.2 (4)
C14–C15–O16–C17	178.7 (4)
C15–O16–C17–C18	–179.2 (3)
O16–C17–C18–O19	–69.5 (3)
C17–C18–O19–C20	166.9 (4)
C18–O19–C20–C21	169.6 (3)
O19–C20–C21–O22	–72.8 (3)
C20–C21–O22–C23	–173.1 (4)
C21–O22–C23–C24	–95.2 (4)
O22–C23–C24–O25	–73.3 (3)
C23–C24–O25–C26	–178.9 (4)
C24–O25–C26–C27	–175.8 (3)
O25–C26–C27–O28	64.4 (3)
C26–C27–O28–C29	170.1 (4)
C27–O28–C29–C30	–77.5 (3)
O28–C29–C30–N1	–48.7 (4)
C29–C30–N1–C2	–177.6 (3)
C30–N1–C2–C3	179.8 (3)
6	
N1–C2–C3–O4	49.5 (3)
C2–C3–O4–C5	83.5 (4)
C3–O4–C5–C6	–176.3 (3)
O4–C5–C6–O7	–61.5 (3)
C5–C6–O7–C8	179.2 (4)
C6–O7–C8–C9	–171.1 (3)
O7–C8–C9–O10	71.4 (3)
C8–C9–O10–C11	168.7 (4)
C9–O10–C11–C12	171.2 (3)
O10–C11–C12–O13	63.1 (3)
C11–C12–O13–C14	91.6 (4)
C12–O13–C14–C15	–179.7 (3)
O13–C14–C15–O16	–64.6 (3)
C14–C15–O16–C17	175.1 (4)
C15–O16–C17–C18	–176.3 (4)
O16–C17–C18–O19	67.3 (3)
C17–C18–O19–C20	–179.9 (3)
C18–O19–C20–C21	170.6 (3)
O19–C20–C21–O22	64.1 (3)
C20–C21–O22–C23	92.5 (4)
C21–O22–C23–C24	178.9 (3)
O22–C23–C24–O25	–67.8 (3)
C23–C24–O25–C26	172.2 (4)
C24–O25–C26–C27	–175.7 (3)
O25–C26–C27–N1	65.5 (3)
C26–C27–N1–C2	–179.5 (3)
C27–N1–C2–C3	176.4 (3)
N31–C32–C33–O34	59.7 (3)
C32–C33–O34–C35	80.0 (4)
C33–O34–C35–C36	–166.9 (3)
O34–C35–C36–O37	–60.1 (4)
C35–C36–O37–C38	173.7 (4)
C36–O37–C38–C39	–175.3 (3)
O37–C38–C39–O40	70.6 (3)
C38–C39–O40–C41	172.3 (4)
C39–O40–C41–C42	174.2 (3)
O40–C41–C42–O43	62.8 (3)
C41–C42–O43–C44	79.7 (5)
C42–O43–C44–C45	175.3 (4)
O43–C44–C45–O46	–21.7 (6)
C44–C45–O46–C47	173.0 (7)
C45–O46–C47–C48	177.8 (6)
O46–C47–C48–O49	27.9 (8)
C47–C48–O49–C50	–176.8 (5)
C48–O49–C50–C51	176.5 (4)
O49–C50–C51–O52	71.3 (3)
C50–C51–O52–C53	92.3 (4)
C51–O52–C53–C54	–168.1 (3)
O52–C53–C54–O55	–63.9 (3)
C53–C54–O55–C56	174.3 (4)
C54–O55–C56–C57	–177.9 (3)
O55–C56–C57–N31	59.5 (3)
C56–C57–N31–C32	175.4 (3)
C57–N31–C32–C33	177.9 (3)
7	
N1–C2–C3–O4	179.83 (7)
C2–C3–O4–C5	–80.82 (9)
C3–O4–C5–C6	170.43 (8)
O4–C5–C6–O7	–66.91 (8)
C5–C6–O7–C8	–87.3 (1)
C6–O7–C8–C9	–179.00 (8)
O7–C8–C9–O10	–75.56 (8)
C8–C9–O10–C11	167.21 (9)
C9–O10–C11–C12	–179.47 (8)

Table IV (Continued)

O10-C11-C12-O13	-69.48 (8)
C11-C12-O13-C14	-169.33 (8)
C12-O13-C14-C15	-177.86 (7)
O13-C14-C15-O16	78.50 (8)
C14-C15-O16-C17	-179.09 (9)
C15-O16-C17-C18	-172.56 (9)
O16-C17-C18-O19	70.05 (8)
C17-C18-O19-C20	171.12 (9)
C18-O19-C20-C21	77.22 (9)
O19-C20-C21-O22	69.31 (9)
C20-C21-O22-C23	-161.52 (9)
C21-O22-C23-C24	84.85 (8)
O22-C23-C24-N1	177.83 (7)
C23-C24-N1-C2	-176.80 (8)
C24-N1-C2-C3	174.76 (8)
8	
N1-C2-C3-O4	-170.0 (2)
C2-C3-O4-C5	-110.3 (3)
C3-O4-C5-C6	75.8 (3)
O4-C5-C6-O7	65.3 (2)
C5-C6-O7-C8	-175.6 (3)
C6-O7-C8-C9	172.7 (2)
O7-C8-C9-O10	-68.4 (2)
C8-C9-O10-C11	-179.0 (3)
C9-O10-C11-C12	178.0 (2)
O10-C11-C12-O13	-75.6 (2)
C11-C12-O13-C14	178.2 (2)
C12-O13-C14-C15	169.1 (2)
O13-C14-C15-O16	78.7 (2)
C14-C15-O16-C17	-179.2 (3)
C15-O16-C17-C18	-167.4 (3)
O16-C17-C18-O19	65.4 (3)
C17-C18-O19-C20	144.4 (3)
C18-O19-C20-C21	74.3 (3)
O19-C20-C21-O22	67.5 (3)
C20-C21-O22-C23	-174.1 (3)
C21-O22-C23-C24	175.5 (3)
O22-C23-C24-O25	-68.4 (3)
C23-C24-O25-C26	87.9 (3)
C24-O25-C26-C27	-170.7 (2)
O25-C26-C27-N1	-66.4 (2)
C26-C27-N1-C2	176.6 (2)
C27-N1-C2-C3	-178.7 (2)

[a] See footnote a of Table III. [b] See footnote c of Table III.

Table V. Hydrogen-Bond Parameters[a] for the Compounds[b]

compd	donor atom, D	acceptor atom, A	distance D···A, Å	distance H···A, Å	angle D-H···A, deg
3	N32	O10	2.950 (6)	2.13 (5)	168 (6)
	N32	O16	2.962 (6)	1.99 (6)	169 (6)
	N33	O19	2.965 (6)	2.22 (5)	168 (6)
	N33	O25	3.020 (7)	2.21 (6)	172 (7)
	N34	N1	2.922 (6)	1.97 (5)	177 (6)
	N34	O7	2.955 (6)	2.21 (4)	163 (5)
4	N32	O4	2.868 (3)	2.00 (3)	175 (3)
	N32	O25	3.117 (4)	2.33 (3)	156 (3)
	N33	O7	2.921 (4)	2.07 (4)	166 (4)
	N33	O13	2.867 (4)	2.01 (4)	171 (4)
	N34	O16	2.948 (3)	2.11 (3)	161 (3)
	N34	O22	2.905 (4)	2.05 (4)	165 (3)
5	N35	N1	3.097 (5)	2.34 (4)	163 (5)
	N35	O7	2.880 (5)	2.07 (4)	158 (4)
	N36	O10	2.906 (5)	2.20 (5)	139 (4)
	N36	O19	2.982 (5)	2.21 (4)	150 (4)
	N37	O19	3.029 (5)	2.33 (4)	146 (4)
	N37	O28	2.878 (5)	2.15 (4)	165 (5)
6	N62	O13	2.878 (5)	2.05 (4)	173 (7)
	N62	O19	2.931 (5)	1.93 (5)	164 (5)
	N63	N1	2.984 (6)	2.07 (5)	173 (6)
	N63	O22	2.836 (5)	1.84 (4)	174 (6)
	N64	O4	2.840 (5)	1.72 (5)	176 (6)
	N64	O10	2.885 (5)	1.95 (4)	153 (4)
	N66	O34	2.868 (6)	2.00 (4)	166 (5)
	N66	O40	2.908 (5)	1.92 (5)	157 (5)
	N67	O43	2.908 (5)	2.02 (4)	172 (6)
	N67	O49	2.931 (5)	2.02 (5)	157 (5)
	N68	N31	3.036 (6)	2.26 (4)	168 (5)
	N68	O52	2.877 (5)	1.84 (4)	176 (6)
	N70	N75	2.880 (7)	2.06 (6)	158 (5)
	N70	N81	3.088 (7)	2.27 (5)	164 (5)
	N71	N75	3.194 (6)	2.48 (5)	135 (4)
	N71	N78	3.391 (7)	2.44 (4)	139 (4)
	N72	N78	2.844 (8)	1.78 (6)	166 (6)
	N72	O84	2.860 (8)	2.27 (6)	135 (5)
8	N1	O37	2.622 (3)	1.72 (3)	169 (4)

[a] See footnote *a* of Table III. [b] See footnote *c* of Table III.

that this type of conformation would be impossible for the smaller 2,6-pyrido-18-crown-6. Instead X-ray structure analysis reveals a structure,[29] in which the pyrido nitrogen atom is in the macrocyclic cavity. The macrocycle adopts an elliptical shape, with some hydrogen atoms pointing into

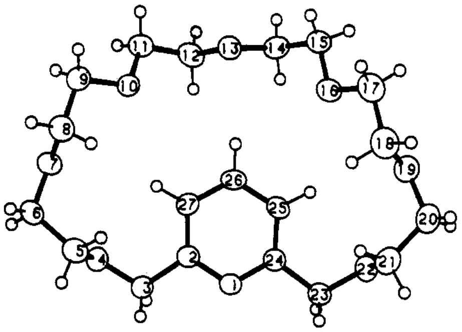

Figure 5. View of 2,6-pyrido-24-crown-8, showing atom numbering.

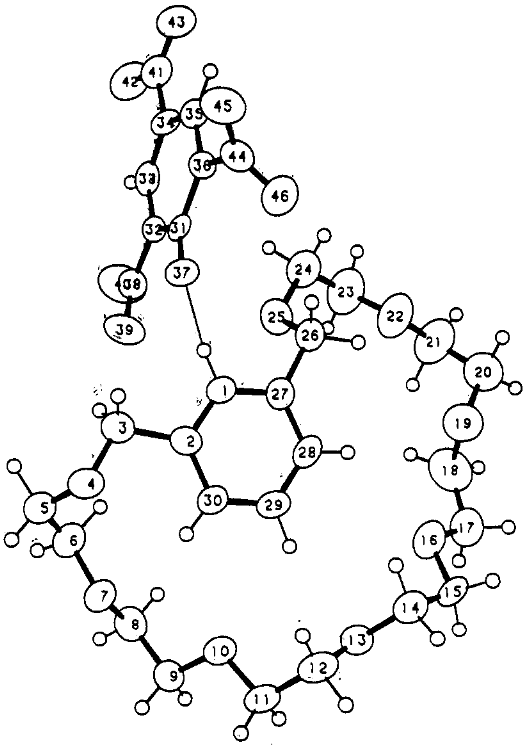

Figure 6. View of 2,6-pyrido-27-crown-9–picric acid (1:1), showing atom numbering.

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(29) Grootenhuis, P. D. J.; van Staveren, C. J.; den Hertog, H. J., Jr.; Reinhoudt, D. N.; Bos, M.; Uiterwijk, J. W. H. M.; Kruise, L.; Harkema, S. *J. Chem. Soc., Chem. Commun.* **1984**, 1412–1413.

the cavity. In either case, there is no "hole" as such within the macroring, in agreement with the well-known phenomenon that macrocycles tend to adopt "dense" conformations in the absence of guests.

X-ray analysis of 2,6-pyrido-27-crown-9 (**1**, $n = 4$)–picric acid (1:1) (Figure 6) showed that the polyether is protonated at the pyrido nitrogen atom, analogous to the salt formed from 2,6-pyrido-18-crown-6 and perchloric acid.[29] However, contrary to the latter complex where the protonated pyridyl nitrogen points into the cavity and forms a H-bond with an encapsulated guest (water), the N–H group in this complex is directed outwards, forming a strong H-bond (N···O 2.62 Å) with the phenolic oxygen atom of the picrate anion.

The macroring adopts a conformation with torsion code $ag^+a\ g^-g^+a\ ag^-g^-\ ag^-a\ ag^-a\ ag^+a\ ag^+a\ ag^-g^-\ g^+aa$, the pyrido ring thereby filling the macrocyclic cavity, although no appreciable H-bonding with the oxygen atoms of the polyether is observed. The conformation of the macrocycle is therefore of the same type as the conformation of uncomplexed 2,6-pyrido-24-crown-8 in the crystalline state.

The picrate anion is oriented almost perpendicular to the pyrido ring, thereby minimizing the steric repulsion between the polyether ring and the two $-NO_2$ groups adjacent to the H-bonded oxygen atom.

Discussion

Ring Size. The selectivity of the crown ethers studied towards guanidinium cations changes markedly with ring size. The 15-membered ring **1** ($n = 0$) extracts little guanidinium into the organic phase. The 18-, 21- and 24-membered macrocycles **1** ($n = 1$–3) only extract a slightly larger amount of guanidinium. Molecular (Corey–Pauling–Koltun) models show that these crown ethers can only form perching complexes. The noncomplexed part of the cation is highly hydrated, as can be seen from the ^{1}H NMR spectra. The smaller crown ethers **1** ($n = 0$–3) extract some lithium ions, with an optimum extraction of lithium for the 21-membered macrocycle.

Crown ethers with a ring size of 27 ring atoms or larger can form encapsulated complexes with guanidinium ions, as is shown by their X-ray structural analyses. This is in line with our previous findings[1] with benzo crown ethers. An optimal fit of the guanidinium ion in the cavity is found for the 27-membered rings (**1**, $n = 4$ and **2**). These macrocycles are highly selective for guanidinium ions, as they have a structure which offers H-bond acceptors complementary to the guanidinium ion. All hydrogens of the guest are therefore engaged in H-bonds between host and guest.

The larger 2,6-pyrido-30-crown-10 extracts guanidinium ions quite readily. From the X-ray analysis it is obvious that the crown ether is too large for the guanidinium cation. The macrocycle is folded over the guest in a saddle-like fashion to compensate for the difference in size between host and guest and for the lack of symmetry of the host. In contrast with the dibenzo-30-crown-10–guanidinium perchlorate[1] complex in which only 4 short H-bonds are formed, all six hydrogens of the guest are engaged in relatively strong H-bonds between host and guest.

The largest pyrido crown ether studied shows a lowering of efficiency of extraction, probably due to greater conformational flexibility of the macrocycle and lack of symmetry of the H-bond acceptor sites relative to the guanidinium cation.

1,3-Xylylene Unit Compared with 2,6-Pyrido Unit. In 1,3-xylylene-27-crown-8–guanidinium perchlorate (1:1), only one orientation of the guanidinium ion is possible if the guest uses all six hydrogens in H-bonds between host and guest. This is the orientation that is found in the X-ray analysis of the complex. The xylylene unit is almost perpendicular to the plane of the macrocycle thus avoiding steric interaction and giving stabilization of the complex by means of contact of the π electrons with the N^+ of the guanidinium cation.[30]

In the complexes of 2,6-pyrido-27-crown-9 with guanidinium salts there are two possible orientations for the guanidinium cation. Only the one in which a H-bond is formed preferentially with the pyridyl nitrogen is found in the crystal structures. Also in the 30-membered pyrido macrocycle the nitrogen atom is preferred as a H-bonding site over the ether oxygens. This indicates that the pyridyl nitrogen is a better hydrogen bond acceptor than the ether oxygens for the guanidinium cation. In both complexes the pyridyl ring is almost in the same plane as the macrocyclic ring.

These results are in agreement with the results of Cram and co-workers,[24,31] who have shown that in complexes of 18-membered rings with t-$BuNH_3$ cations the nitrogen atom is a better H-binding site than the ether oxygen.

The proton is not transferred to the pyridyl nitrogen. This is due to the larger basicity of guanidine (2,6-pyrido crown ethers **1**, $n = 0$–6, pK_a (H_2O, 25 °C) = 3.36–4.95;[29] guanidine, pK_a (H_2O, 25 °C) = 13.6).

Free and Protonated Crown Ethers vs. Crown Ether Complexes. To study the effect of complexation on the conformation of the crown ether the structures of a free crown ether should be compared with the same crown ether in the complex. As the 27-membered macrocycle could not be obtained in the crystalline form, we have studied the conformations of the free 24-membered cycle (**1**, $n = 3$), of the protonated crown ether in 2,6-pyrido-27-crown-9–picric acid (1:1) and of the macrocycle in the complex 2,6-pyrido-27-crown-9–guanidinium perchlorate (1:1). The X-ray structures show that in the crystalline state the free and protonated macrocycles have a conformation in which the aromatic ring fills the cavity. It is likely that this conformation is also adopted in solution if no complexation occurs. This means that the cavity is only formed upon complexation of a guest molecule.[32]

Newkome et al.[33] have reported a similar effect in a spherical cryptand which was synthesized from triethanolamine and 2,6-bis(chloromethyl)pyridine. In the crystal structure, one of the pyridyl rings is located inside the cavity of the cryptand. From the crystal structures of a free cylindrical cryptand, which consists of two diaza-18-crown-6 units, joined by naphthalene groups, and its pentamethylene diammonium complex an analogous effect can be seen.[34] The free cryptand resembles a skew cylinder. Upon complexation with a pentamethylene diammonium dication, the diaza-18-crown-6 units become parallel and a cavity is formed.

Influence of the Anion. From the structures of 2,6-pyrido-27-crown-9–guanidinium perchlorate (1:1) and

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2,6-pyrido-27-crown-9–guanidinium thiocyanate–ethanol (2:3:1), it is obvious that the negative ion has a profound influence on complexation. The perchlorate anion is not in close contact with either the guanidinium cation or the crown ether. The thiocyanate cation, however, has a large affinity for the guanidinium cation. Therefore one of the units of the complex is formed by a guanidinium ion, bound to three thiocyanate ions and one ethanol. The other two guanidinium cations are encapsulated by two crown ethers in much the same way as in 2,6-pyrido-27-crown-9–guanidinium perchlorate (1:1).

Also the conformation of the 2,6-pyrido-27-crown-9 in the complexes is dependent on the choice of the anion (perchlorate vs. thiocyanate), even though the anion is not bonded to the crown ether moiety! Therefore the conformation adopted may be determined to a large extent by crystal packing forces.

Conclusions

The selectivity for guanidinium cations over lithium ions of 2,6-pyrido crown ethers with 15–33 ring atoms changes markedly with ring size. An optimum extraction efficiency for guanidinium ions is found for the 27-membered macrocycle.

Because of similarities in size, shape, and H-bonding of urea and guanidine, effective complexation of uronium salts is expected in the case of the 27-membered pyrido crown ether.

In the complexes with guanidinium salts, the pyridyl nitrogen is used in a H-bond between host and guest. 1,3-Xylylene-27-crown-8 also forms a stable complex with guanidinium perchlorate.

In the crystalline state, the cavity of the free and protonated 2,6-pyrido crown ethers of 24 and 27 ring atoms is filled by the aromatic ring of the macrocycle itself. The cavity is only formed upon complexation with a guest.

The structures of the crystalline guanidinium complexes of 2,6-pyrido-27-crown-9 depend on the anion present.

Experimental Section

Melting points were determined with a Reichert melting point apparatus and are uncorrected. The ^{1}H NMR spectra were recorded with Bruker WP-80 and/or WM-500 spectrometers in $CDCl_3$ or Me_2SO-d_6, and the ^{13}C NMR spectra were recorded with a N.M.C. 1280 spectrometer, with Me_4Si as an internal standard. Mass spectra (MS) were obtained with a Varian Mat 311A. Elemental analyses were carried out by the department of analytical chemistry.

Materials. THF was freshly distilled from sodium/benzophenone prior to use. 2,6-Bis(bromomethyl)pyridine[24] and polyethylene glycols[9] were prepared according to the literature. All other chemicals were reagent grade and used without further purification.

General Procedure for the Synthesis of Pyrido Crown Ethers (1, *n* = 0–6). To a refluxing, stirred mixture of 0.04 mol of NaH (80% in oil) and 200 mL of dry THF were added over a period of 3 h separate solutions of 0.01 mol of 2,6-bis(bromomethyl)pyridine in 100 mL of dry THF and 0.01 mol of the appropriate polyethylene glycol in 100 mL of dry THF. The mixture was allowed to cool to 25 °C and 25 mL of water was added carefully to decompose residual NaH. The solvent was evaporated and the residue was mixed with 100 mL of $CHCl_3$ and extracted with 3 × 100 mL of 1 N aqueous HCl. After addition of aqueous 10% NaOH to pH = 10, the water layers were extracted with 3 × 100 mL of $CHCl_3$. The $CHCl_3$ layers were dried over $MgSO_4$, and the solvent was evaporated in vacuo. The crown ethers were then purified by chromatography or via complexation/decomplexation as the CH_3NO_2 complex. 500-MHz ^{1}H NMR data of **1** (*n* = 0–6) are tabulated in Table I.

2,6-Pyrido-15-crown-5 (1, *n* = 0). 2,6-Pyrido-15-crown-5 was prepared using triethylene glycol, according to the general procedure. Purification of the product was accomplished by column chromatography (silica, $CHCl_3$/EtOH 98/2 (v/v)). The product was obtained (15%) as an oil: ^{13}C NMR δ 157.9 (Ar C-2, Ar C-6), 136.6 (Ar C-4), 121.7 (Ar C-3, Ar C-5), 73.8 ($ArCH_2$), 70.7–70.0 (CH_2O); MS, *m/e* 253.132 (M^+; calcd 253.131).

2,6-Pyrido-18-crown-6 (1, *n* = 1). 2,6-Pyrido-18-crown-6 was prepared using tetraethylene glycol, according to the general procedure. Purification of the product was accomplished by precipitating the 2,6-pyrido-18-crown-6–nitromethane (1:2) complex by addition of CH_3NO_2 to a solution of the crown ether in diethyl ether. Dissociation of the complex in vacuo (0.2 Pa, 2–5 h) yielded (55%) the crown ether, as a white powder: mp 37–39 °C; ^{13}C NMR δ 158.0 (Ar C-2, Ar C-6), 136.7 (Ar C-4), 120.5 (Ar C-3, Ar C-5), 73.2 ($ArCH_2$), 68.4–72.1 (CH_2O); MS, *m/e* 297.157 (M^+; calcd 297.158). Anal. Calcd for $C_{15}H_{23}NO_5$: C, 60.59; H, 7.80; N, 4.71. Found: C, 60.81; H, 8.00; N, 4.48.

2,6-Pyrido-21-crown-7 (1, *n* = 2). 2,6-Pyrido-21-crown-7 was prepared using pentaethylene glycol, according to the general procedure. Purification of the product was accomplished by chromatography (neutral Al_2O_3, activity II–III, EtOAc), to give (59%) an oil: ^{13}C NMR δ 157.7 (Ar C-2, Ar C-6), 136.9 (Ar C-4), 120.8 (Ar C-3, Ar C-5), 74.0 ($ArCH_2$), 71.0–69.7 (CH_2O); MS, *m/e* 341.182 (M^+; calcd 341.184).

2,6-Pyrido-24-crown-8 (1, *n* = 3). 2,6-Pyrido-24-crown-8 was prepared using hexaethylene glycol, according to the general procedure. Purification of the product was accomplished by chromatography (neutral Al_2O_3, activity II–III, EtOAc). The product was obtained as an oil, but crystallized upon mixing with ether and cooling to −78 °C. The product was recrystallized (37%) from diethyl ether: mp 48–50 °C; ^{13}C NMR δ 157.9 (Ar C-2, Ar C-6), 137.5 (Ar C-4), 120.3 (Ar C-3, Ar C-5), 73.8 ($ArCH_2$), 70.8–70.6 (CH_2O); MS, *m/e* 385.211 (M^+; calcd 385.211). Anal. Calcd for $C_{19}H_{31}NO_7$: C, 59.20; H, 8.11; N, 3.63. Found: C, 59.13; H, 8.28; N, 3.66.

2,6-Pyrido-27-crown-9 (1, *n* = 4). 2,6-Pyrido-27-crown-9 was prepared by using heptaethylene glycol, according to the general procedure. Purification of the product was accomplished by column chromatography (silica gel, chloroform/ethanol 96/4 (v/v)), to give (72%) an oil: ^{13}C NMR δ 157.9 (Ar C-2, Ar C-6), 137.4 (Ar C-4), 119.9 (Ar C-3, Ar C-5), 73.8 ($ArCH_2$), 70.8–69.9 (CH_2O); MS, *m/e* 429.244 (M^+; calcd 429.236).

2,6-Pyrido-30-crown-10 (1, *n* = 5). 2,6-Pyrido-30-crown-10 was prepared using octaethylene glycol, according to the general procedure. Purification of the product was accomplished by column chromatography (silica gel, chloroform/ethanol 96/4 (v/v)) to give (60%) an oil. ^{13}C NMR δ 157.8 (Ar C-2, Ar C-6), 137.4 (Ar C-4), 120.0 (Ar C-3, Ar C-5), 73.8 ($ArCH_2$), 71.0–70.0 (CH_2O); MS, *m/e* 473.263 (M^+; calcd 473.261).

2,6-Pyrido-33-crown-11 (1, *n* = 6). 2,6-Pyrido-33-crown-11 was prepared using nonaethylene glycol, according to the general procedure. Purification of the product was accomplished by column chromatography (silica gel, chloroform/ethanol 92/8 (v/v), to give (55%) an oil. ^{13}C NMR δ 157.8 (Ar C-2, Ar C-6), 137.1 (Ar C-4), 119.7 (Ar C-3, Ar C-5), 73.7 ($ArCH_2$), 70.4–70.0 (CH_2O); MS, *m/e* 517.294 (M^+; calcd 517.289).

1,3-Xylylene-27-crown-8 (2). To a refluxing, stirred mixture of 0.04 mol of NaH (80% in oil) and 200 mL of dry THF were added over a period of 3 h separate solutions of 0.01 mol of 1,3-bis(bromomethyl)benzene in 100 mL of dry THF and 0.01 mol of heptaethylene glycol in 100 mL of dry THF. The mixture was allowed to cool to 25 °C, and 25 mL of water was added carefully to decompose residual NaH. The solvent was evaporated and the residue was mixed with 100 mL of CH_2Cl_2 and 100 mL of water. The water layer was extracted with 3 × 100 mL of $CHCl_3$. After being dried over $MgSO_4$, the solvent was evaporated in vacuo. The product was purified by chromatography (neutral Al_2O_3, activity II–III, EtOAc) to yield (65%) an oil: ^{13}C NMR δ 138.5 (Ar C-1, Ar C-3), 129.1–126.0 (Ar C-2, Ar C-4, Ar C-5, Ar C-6), 73.1 ($ArCH_2$), 71.8–68.3 (CH_2O); MS, *m/e* 428.238 (M^+; calcd 428.241).

Extraction Experiments. $CDCl_3$ (2 mL) containing 1 mmol of crown ether, and 2 mL of an aqueous solution containing 2 mmol of guanidinium sulfate and 2 mmol of lithium perchlorate were agitated for 18 h. The $CDCl_3$ layer was separated and filtered. The ratios of crown ether:guanidinium perchlorate and crown ether:water were determined from intensities in the ^{1}H

Table VI. Data-Collection Parameters of the X-ray Structure Determinations for the Compounds[a]

parameter	3	4	5	6	7	8
formula	$C_{22}H_{41}O_{12}N_4Cl$	$C_{23}H_{42}O_{12}N_3Cl$	$C_{24}H_{45}O_{13}N_4Cl$	$C_{50}H_{94}O_{17}N_{14}S_3$	$C_{19}H_{31}O_7N$	$C_{27}H_{38}O_{15}N_4$
lattice type	triclinic	orthorhombic	monoclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$Pbcn$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
T, K	193	144	145	169	145	145
cell dimensions						
a, Å	14.186 (6)	24.549 (7)	10.165 (2)	17.119 (9)	11.274 (1)	30.760 (23)
b, Å	12.134 (6)	12.630 (5)	13.670 (5)	15.350 (4)	10.141 (1)	8.725 (3)
c, Å	9.229 (3)	18.608 (6)	23.035 (9)	14.838 (8)	9.137 (1)	23.450 (12)
α, deg	105.26 (5)	90.0	90.0	113.24 (3)	101.41 (2)	90.0
β, deg	82.36 (3)	90.0	101.96 (2)	70.54 (5)	98.90 (2)	97.43 (4)
γ, deg	109.69 (3)	90.0	90.0	109.32 (3)	92.75 (2)	90.0
V, Å^3	1441 (2)	5769 (6)	3131 (3)	3287 (5)	1008.3 (5)	6240 (11)
Z	2	8	4	2	2	8
$D_{calcd} \times 10^{-3}$, kg·m^{-3}	1.357	1.354	1.343	1.272	1.270	1.402
radiation (graphite monochromated)	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
$\mu_{calcd} \times 10^{-3}$, m^{-1}	0.19	0.19	0.18	0.18	0.09	0.11
S range ($S = \sin\theta/\lambda$), Å^{-1}	0.10–0.59	0.10–0.48	0.07–0.54	0.07–0.48	0.07–0.59	0.10–0.54
no. of unique reflections measured	5057	2666	4081	6108	3337	4187
no. of reflections with $F_o > \sigma(F_o)$	4218	2386	3453	4622	3038	3410
final no. of variables	513[b]	521	560	1110[c]	369	568
final R, %	9.8	3.4	7.8	7.6	3.1	5.6
final R_w, %	10.6	3.5	8.1	6.6	3.3	5.3

[a] See footnote *c* of Table III. [b] One crown hydrogen could not be determined and was not used in refinement. [c] Six ethanol hydrogens could not be determined and were not used in refinement.

NMR spectra. The amount of lithium perchlorate transferred to the organic layer was determined by atomic absorption spectroscopy.

The amount of crown ether transferred to the aqueous phase was determined in a separate experiment. The same solutions and conditions were used, but the $CDCl_3$ layer contained about 0.04 mmol of 1,2,4,5-tetramethylbenzene. The amount of crown ether transferred was determined by ^1H NMR spectroscopy.

2,6-Pyrido-27-crown-9–guanidinium perchlorate (1:1) was isolated from the organic layer, by evaporation of the solvent: mp 112–115 °C (EtOH); ^1H NMR ($CDCl_3$) δ 7.9–7.2 (m, 3 H, ArH), 7.0 (s, 6 H, NH_2), 4.64 (s, 4 H, $ArCH_2$), 3.9–3.6 (m, 28 H, CH_2O); ^{13}C NMR δ 157.5 (CNH_2), 156.2 (Ar C-2, C-6), 138.5 (Ar C-4), 123.3 (Ar C-3, C-5), 73.7 ($ArCH_2$) 70.3 (CH_2O). Anal. Calcd for $C_{22}H_{41}N_4O_{12}Cl$: C, 44.86; H, 7.02; N, 9.51. Found: C, 44.75; H, 7.41; N, 9.41.

2,6-Pyrido-30-crown-10–guanidinium perchlorate (1:1) was isolated from the organic layer, by evaporation of the solvent and purified by trituration in $CHCl_3$: mp 64–67 °C; ^1H NMR ($CDCl_3$) δ 7.9–7.2 (m, 3 H, ArH), 6.8 (s, 6 H, NH_2), 4.65 (s, 4 H, $ArCH_2$), 3.7–3.6 (m, 32 H, CH_2O); ^{13}C NMR 157.9 (CNH_2), 156.7 (Ar C-2, C-6), 138.1 (Ar C-4), 122.8 (Ar C-3, C-5), 73.5 ($ArCH_2$), 70.3–69.6 (CH_2O). Anal. Calcd for $C_{24}H_{45}N_4O_{13}Cl$: C, 45.53; H, 7.16; N, 8.85. Found: C, 45.46; H, 7.20; N, 8.76.

1,3-Xylylene-27-crown-8–guanidinium perchlorate (1:1) was obtained from the organic layer after evaporation of the solvent: mp 74–75 °C (EtOH); ^1H NMR ($CDCl_3$) δ 7.5–7.2 (m, 4 H, ArH), 6.2 (s, 6 H, NH_2), 4.53 (s, 4 H, $ArCH_2$), 3.8–3.6 (m, 28 H, CH_2O); ^{13}C NMR δ 156.8 (CNH_2), 137.7 (Ar C-1, C-3), 129.0, 128.9, 128.6 (Ar C-2, C-4, C-5, C-6) 73.6 ($ArCH_2$), 70.1 (CH_2O). Anal. Calcd for $C_{23}H_{42}N_3O_{12}Cl$: C, 46.98; H, 7.20; N, 7.15. Found: C, 46.85, H, 7.26, N, 7.19.

2,6-Pyrido-27-crown-9–Guanidinium Thiocyanate–Ethanol (2:3:1). In a minimal amount of hot EtOH were dissolved 429 mg (1 mmol) of 2,6-pyrido-27-crown-9 and 128 mg (1 mmol) of guanidinium thiocyanate. The solution was allowed to cool to 25 °C, and the solvent was slowly evaporated until crystals were formed. The product was filtered: mp 69–72 °C (EtOH); ^1H NMR δ ($CDCl_3$) 7.8–7.2 (m, 6 H, ArH), 6.9 (s, 18 H, NH_2), 4.64 (s, 8 H, $ArCH_2$), 3.9–3.6 (m, 58 H, CH_2O, CH_2), 1.23 (t, J = 7 Hz, 3 H, CH_3), 1.95 (s, 1 H, OH); ^{13}C NMR δ 157.9 (CNH_2), 156.1 (Ar C-2, C-6), 138.4 (Ar C-4), 132.2 (SCN), 123.4 (Ar C-3, C-5), 73.8 ($ArCH_2$), 71.3–69.5 (CH_2O), 58.0 (CH_2), 18.4 (CH_3). Anal. Calcd for $C_{50}H_{94}N_{14}O_{17}S_3$: C, 47.68; H, 7.52; N, 15.57. Found: C, 47.26; H, 7.26; N, 15.47.

2,6-Pyrido-27-crown-9–Picric Acid (1:1). Picric acid (229 mg, 1 mmol) and 2,6-pyrido-27-crown-9 (429 mg, 1 mmol) were dissolved in a minimal amount of refluxing EtOH. The product crystallized upon cooling to 25 °C and slow evaporation of the solvent, and was filtered: mp 69–70 °C (EtOH); ^1H NMR ($CDCl_3$) δ 8.91 (s, 2 H, Ar′H), 8.8–8.1 (m, 3 H, ArH), 4.93 (s, 4 H, $ArCH_2$), 3.7–3.6 (m, 28 H, CH_2O); ^{13}C NMR δ 161.3 (Ar′ C-1), 154.1 (Ar C-2, C-6), 147.4 (Ar C-4), 141.7 (Ar′ C-2, C-6), 128.7 (Ar′ C-4), 126.1, 124.2 (Ar, Ar′ C-3, C-5), 71.2–70.0 (CH_2O), 68.3 ($ArCH_2$). Anal. Calcd for $C_{27}H_{38}N_4O_{15}$: C, 49.24; H, 5.82; N, 8.51. Found: C, 49.40; H, 5.91; N, 8.48.

2,6-Pyrido-27-crown-9–Hydrogen Tetraphenylborate (1:1). A solution of 429 mg (1 mmol) of 2,6-pyrido-27-crown-9 in 5 mL of $CHCl_3$ was stirred under nitrogen with a suspension of 343 mg (1 mmol) of sodium tetraphenyl borate and 123 mg (1 mmol) of uronium nitrate in H_2O (5 mL) for 18 h. The organic layer was dried and the solvent was evaporated. The product was crystallized from EtOH/Et_2O: mp 89–91 °C; ^1H NMR ($CDCl_3$) δ 7.5–6.7 (m, 23 H, Ar′H, ArH), 4.50 (s, 4 H, $ArCH_2$), 3.6–3.4 (m, 28 H, CH_2O); ^{13}C NMR δ 165.5, 164.6, 163.6, 162.6 (Ar′ C-1), 152.9 (Ar C-2, C-6), 145.7 (Ar C-4), 136.2 (Ar′ C-2, C-6), 125.6 (Ar′ C-3, C-5), 121.8 (Ar C-3, C-5) 70.8–69.9 (CH_2O), 68.0 ($ArCH_2$). Anal. Calcd for $C_{45}H_{56}BNO_8$: C, 72.09; H, 7.53; N, 1.87. Found: C, 71.90; H, 7.57; N, 1.94.

2,6-Pyrido-18-crown-6–guanidinium perchlorate–$CDCl_3$ (1:1:0.9) was isolated from the organic layer. Upon addition of 0.5 mL of diethyl ether the complex crystallized and was filtered: mp 80–83 °C; ^1H NMR (Me_2SO-d_6) δ 7.8–7.2 (m, 3 H, ArH), 6.7 (bs, 6 H, NH_2), 4.73 (s, 4 H, $ArCH_2$), 3.8–3.6 (m, 16 H, OCH_2); ^{13}C NMR δ 158.3 (CNH_2), 157.3 (Ar C-2, C-5), 136.9 (Ar C-4), 120.9 (Ar C-3, C-5), 78.6, 78.2, 78.0 ($CDCl_3$), 73.2 ($ArCH_2$), 69.3–70.2 (CH_2O). Anal. Calcd for $C_{16.9}H_{29}N_4O_9Cl_{3.7}D_{0.9}$: C, 35.91; H, 5.49; N, 9.91. Found: C, 36.14; H, 5.55; N, 9.74.

X-ray Diffraction. X-ray measurements were performed on a single-crystal diffractometer (Philips PW1100) using the ω–2θ scanning mode. The most important data-collection parameters are presented in Table VI. Measured intensities were corrected for the decrease in intensity during data collection, using the intensities of three standard reflections measured every hour.

The structures were solved by direct methods[35] and refined by full-matrix least-squares analysis,[36] using reflections having an intensity greater than the estimated standard deviation from counting statistics. In the 2,6-pyrido-27-crown-9–guanidinium perchlorate (1:1) complex part of the macroring is disordered. Consequently, one hydrogen at C21 could not be located. In the 2,6-pyrido-27-crown-9–guanidinium thiocyanate–ethanol (2:3:1) complex the ethanol shows very large thermal parameters, suggesting some degree of disorder or partial occupancy. No hy-

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drogens of the ethanol could be located. All other hydrogen atoms in the complexes could unambiguously be located from difference-Fourier maps.

Parameters refined were the overall scale factors, isotropic secondary extinction parameters, positional parameters of all atoms, anisotropic thermal parameters for non-hydrogen atoms, and isotropic thermal parameters for hydrogens. The weight for each reflection was taken to be $w = \{\sigma(F_o) + 0.01\,|F_o|\}^{-2}$, where $\sigma(F_o)$ is the estimated standard deviation of the observed structure factor (F_o) derived from counting statistics. Scattering factors for non-hydrogen atoms were taken from ref 37; for H the scattering factors of Stewart, Davidson, and Simpson[38] were used. No absorption corrections were applied.

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Registry No. 1 (n = 0), 77877-86-2; 1 (n = 1), 53914-89-9; 1 (n = 1)·quanidium perchlorate, 100840-33-3; 1 (n = 2), 86309-73-1; 1 (n = 3), 86309-74-2; 1 (n = 4), 95216-11-8; 1 (n = 4)·hydrogen tetraphenylborate, 100858-00-2; 1 (n = 5), 95216-12-9; 1 (n = 6), 95216-13-0; **2**, 57659-55-9; **3**, 95216-14-1; **4**, 100840-32-2; **5**, 95216-15-2; **6**, 100857-99-6; **8**, 95216-17-4; 2,6-bis(bromomethyl)pyridine, 7703-74-4; triethylene glycol, 112-27-6; tetraethylene glycol, 112-60-7; pentaethylene glycol, 4792-15-8; hexaethylene glycol, 2615-15-8; heptaethylene glycol, 5617-32-3; octaethylene glycol, 5117-19-1; nonaethylene glycol, 3386-18-3; 1,3-bis(bromomethyl)benzene, 626-15-3; guanidinium sulfate, 594-14-9; guanidinium thiocyanate, 593-84-0.

Supplementary Material Available: Lists of anisotropic thermal parameters for heavy atoms, positional and isotropic thermal parameters for hydrogens, and complete lists of bond lengths and bond angles (47 pages). Ordering information is given on any current masthead page.

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Electrophilic Aromatic Substitution. 9.[1] A Kinetic Study of the Friedel-Crafts Isopropylation Reaction in Nitromethane

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The kinetics of the aluminum chloride catalyzed reaction between isopropyl chloride and benzene or toluene were determined in solvent nitromethane by using vacuum-line techniques. The reaction at 25 °C was first order in isopropyl chloride and in aromatic hydrocarbon and first order in initial catalyst concentration. Noncompetitive results are $k_T/k_B = 2.0 \pm 0.7$ with the following toluene product isomer distribution: % ortho, 45.3 ± 1.5; % meta, 22.7 ± 1.1; % para, 32.0 ± 1.0. For competitive runs k_T/k_B was 2.3 ± 0.1 with the same isomer distribution. Rate constants at 25, 15, 0, −15, and −27 °C yielded $E_a = 78 \pm 4$ kJ/mol, $\Delta H^\ddagger = 76 \pm 4$ kJ/mol, $\Delta S^\ddagger = -13 \pm 14$ J/mol deg. The results are consistent with a σ complex-like transition state and a predominantly ionic mechanism.

Friedel-Crafts isopropylation has become another focal point in the controversy regarding the mechanisms of electrophilic aromatic substitution reactions. Despite the number of kinetic studies carried out, the order with respect to aromatic has yet to be established, and, furthermore, individual interpretations of various results have led to incompatible conclusions. For example, Brown[3] found the kinetic results of his study in excess aromatic to agree well with his linear free energy relationship (the Brown selectivity relationship) which is based upon a σ-complex mechanism, whereas Olah[4,5] and Nakane[6] found a correlation between their results and a mechanism involving a π-complex-like highest energy transition state. Thus, as a part of our ongoing attempts to assist in the resolution of the controversy, we undertook a kinetic study of the isopropylation reaction using vacuum-line techniques that yielded reproducible results differing substantially from those previously reported for the related ethylation[7] and benzylation[8] reactions. We now report noncompetitive kinetic results for the $AlCl_3$-catalyzed reaction of isopropyl chloride with benzene and toluene as a function of reagent concentrations and temperature, along with competitive kinetic results at 25 °C.

Experimental Section

Materials. The analysis, purification, drying (where necessary), and storage of the reagents benzene, toluene, catalyst aluminum chloride, and solvent nitromethane are described elsewhere.[8,9] Reagent isopropyl chloride contained approximately 2% n-propyl chloride (GC analysis). Since isopropyl halides undergo Frie-

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