after concentration, was subjected to preparative HPLC separation (25 in. × 10 mm Lichrosorb Si-60, 5- or 10-μm column with 2–10% ether in hexane as the solvent). Chloroform-*d* was used as the solvent for irradiation when benzanthrone was used as a sensitizer.

7-*cis*- and 7-*cis*,9-*cis*-β-Ionylidenefluoroacetaldehyde (1c,d). Rose Bengal sensitized irradiation gave a mixture of all four isomers in the following relative amounts (by ^{19}F nmr): 11%, 9%, 19%, and 61% all-trans, 9-cis, 7-cis, 7-cis, and 9-cis. They were separated by preparative HPLC (solvent 10% ether in hexane).

1c: ^{1}H NMR ($CDCl_3$) δ 1.04, 1.49, 2.11 (CH_3-1,5,9), 6.34 (H_7), 6.56 (H_8), 9.79 (H_{11}) ($J_{7,8}$ = 11.8 Hz, $J_{10,11}$ = 16.9 Hz, $J_{CHO,10}$ = 3.4 Hz); ^{19}F NMR ($CDCl_3$, $CFCl_3$) −129.4 ppm (F_{10}, $J_{H,F}$ = 16.9 Hz).

1d: ^{1}H NMR ($CDCl_3$) δ 1.04, 1.48, 1.94 (CH_3-1,5,9), 6.35 (H_7), 6.72 (H_8), 9.82 (H_{11}) ($J_{7,8}$ = 12.5 Hz, $J_{10,11}$ = 17.3 Hz, $J_{CH_3\text{-}9,10}$ = 4.3 Hz); ^{19}F NMR −131.0 ppm (F_{10}, $J_{H,F}$ = 17.3 Hz).

7-*cis*- and 7-*cis*,9-*cis*-*N*-Methyl-*N*-phenyl-β-ionylideneacetamide (1e,f). Rose Bengal sensitization resulted in a mixture containing a 2.5:1 ratio of the 7-cis,9-cis and 7-cis isomers with trace amounts of the two 7-trans isomers (in the order of HPLC elution time). They were separated by preparative HPLC (solvent 15% ether in hexane). Both cis isomers were viscous oils.

1e: ^{1}H NMR ($CDCl_3$) δ 0.89, 1.36, 2.13, 3.29 (CH_3-1,5,9 and NCH_3), 5.86–5.80 (H_7 and H_8), 5.65 (H_{10}).

1f: ^{1}H NMR ($CDCl_3$) δ 1.02, 1.46, 1.67, 3.30 (CH_3-1,5,9, N-CH_3), 5.42 (H_{10}), 6.10 (d, H_7), 7.09 (d, H_8) ($J_{7,8}$ = 12.6 Hz); ^{13}C NMR ($CDCl_3$) 28.7, 21.7, 21.5, 36.8 (CH_3-1,5,9, NCH_3), 39.1, 19.0 32.2 (CH_3-2,3,4) 34.2 (C-1), 130.1, 136.6, 129.8, 129.2, 148.3, 126.9, and 166.7 ppm (C-5,6,7,8,9,10,11, respectively).

7-*cis*-β-Ionylidenemalononitrile (1g). Rose Bengal sensitization of 7 only resulted in partial conversion (15%) to the 7-cis isomer. It was isolated by preparative HPLC (solvent 5% ether in hexane): ^{1}H nmr (CD_3COCD_3) δ 1.09, 1.55, 2.36, (CH_3-1,5,9), 6.71 (d, H_8), 6.86 (d, H_7) ($J_{7,8}$ = 12.2 Hz); UV (hexane) 267 nm.

7-*cis*-1,2-Bis(2,6,6-trimethylcyclohex-1-enyl)ethylene (6). Benzanthrone sensitization of 10 (in C_6D_6) resulted in quantitative conversion to the cis isomer. Passage through a short silica gel column gave the cis triene as a viscous oil: ^{1}H NMR (C_6D_6) δ 1.13, 1.84 (CH_3-1 and -5), 5.97 (vinyl H's).

***cis*-β-Ionyl Phenyl Sulfone (10). Preparative Irradiation.** A benzene (30 mL) solution of 1.15 g of 9 and catalytic amounts of β-acetonaphthone was distributed into four 13-mm test tubes. After being purged with N_2, the solution was irradiated with a 200-W Hanovia medium-pressure Hg lamp for 72 h. After evaporation of solvent, the mixture was chromatographed on a silica gel column with solvents starting with chloroform and going to 20% of ethyl acetate in chloroform. A total of 320 mg of a viscous oil was obtained. Its ^{1}H NMR spectrum ($J_{7,8}$ = 12 Hz) was consistent with the cis isomer. No residual trans isomer could be detected by NMR.

***cis*-9-Benzyl-β-ionyl Phenyl Sulfone (5).** To a mixture of 300 mg of 10 in 4 mL of DMA at −5 to −8 °C was added 400 mg of finely ground NaOH. The mixture was stirred for 10 min, and then a solution of 0.12 mL of benzyl chloride in 1 mL of DMA was added. The mixture was then allowed to warm to room temperature and stirred overnight. It was then extracted with petroleum ether. Attempts to crystallize the solid resulted in recovery of the purified white solid (165 mg, 40% yield: mp 150 °C dec). For the ^{1}H NMR see the text.

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Registry No. **1a**, 56013-12-8; **1b**, 56013-13-9; **1c**, 87782-35-2; **1d**, 87782-36-3; **1e**, 87782-37-4; **1f**, 87801-34-1; **1h**, 53402-96-3; **1i**, 53402-97-4; **2**, 24315-14-8; **3**, 67737-35-3; **4**, 74464-49-6; **5**, 87782-38-5; **6**, 67895-24-3; **7**, 56013-18-4; **8**, 3917-36-0; **9**, 87782-39-6; **10**, 61201-36-3.

Supplementary Material Available: Figures 3–6 showing representative experimental and calculated spectra of several 7-cis isomers (**1i**, **1d** and **5**) (5 pages). Ordering information is given on any current masthead page.

Macrocyclic Receptor Molecules for Guanidinium Cations. Preparation, X-ray Structures, and Kinetic Stabilities of 1:1 Complexes of Guanidinium Perchlorate with Benzo-27-crown-9, Dibenzo-27-crown-9, and Dibenzo-30-crown-10

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The complexation of guanidinium perchlorate with crown ethers of different ring size (18–33 ring atoms) and with different subunits, e.g., catechol and 1,3-xylyl moieties, has been studied by using two-phase extraction experiments. The results demonstrate that the 18-crown ethers are able to form *perching* complexes, whereas crown ethers with ⩾27 ring atoms have a suitable ring size to form *encapsulated* complexes with guanidinium perchlorate. Aromatic, catechol, and especially 1,3-xylyl moieties have a destabilizing effect on the complex formation. The crystal and the molecular structures of the 1:1 complexes of guanidinium perchlorate with benzo-27-crown-9 (7), dibenzo-27-crown-9 (8), and dibenzo-30-crown-10 (11) have been determined by X-ray crystallography. In these encapsulated complexes all hydrogen atoms of the guanidinium cation are used in hydrogen bonds to the macrocyclic host. The 27-crown ethers show an optimal fit between cation and the macrocyclic host with a complementary binding scheme. Dynamic 500-MHz ^{1}H NMR spectroscopy gave the kinetic stabilities of these complexes with $\Delta G_d^{\ddagger}$ values of 11.5, 11.2, and 12.0 kcal mol^{-1} for the complexes with benzo-27-crown-9, dibenzo-27-crown-9, and dibenzo-30-crown-10, respectively.

Introduction

With the ultimate objective of our work to find the optimal synthetic receptor molecule for urea we are currently interested in the complexation of crown ethers with both charged and neutral organic molecules. Previously we have shown[1] that 18-crown-6 does form an adduct with

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† Laboratory of Organic Chemistry.

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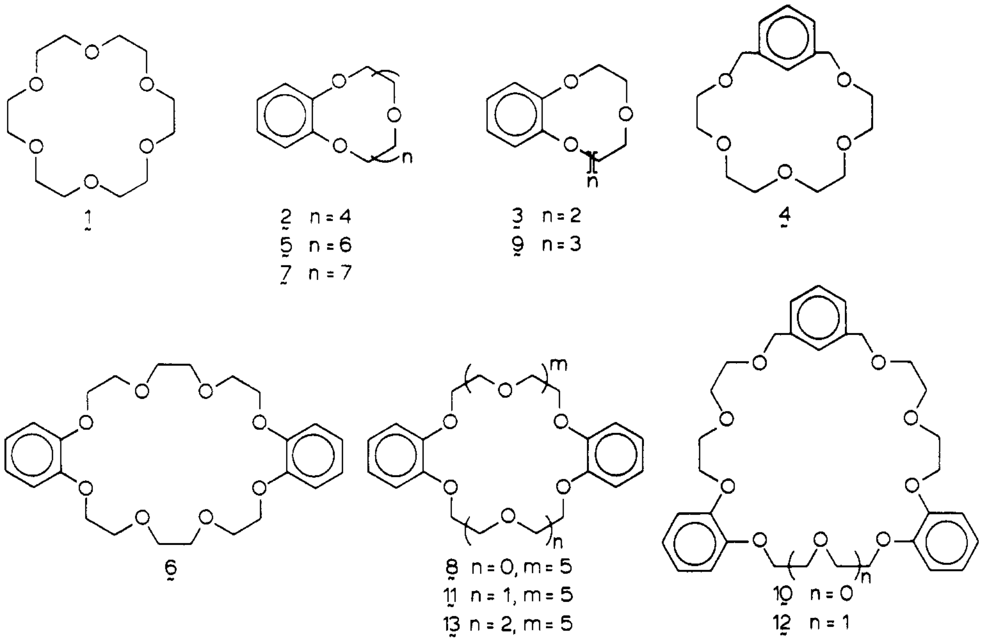
(1) Harkema, S.; van Hummel, G. J.; Daasvatn, K.; Reinhoudt, D. N. *J. Chem. Soc., Chem. Commun.* 1981, 368.

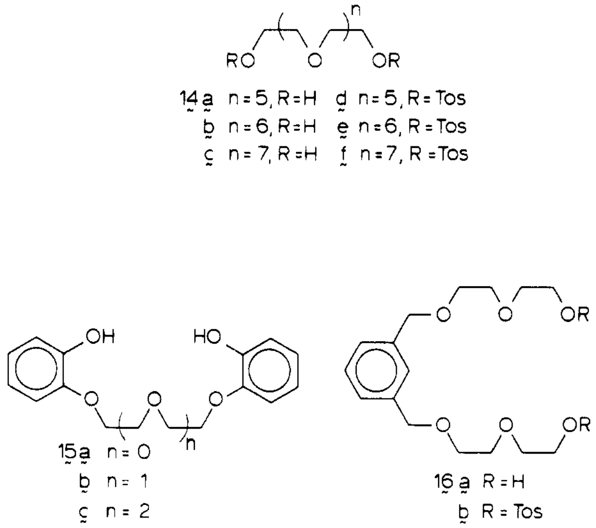
Chart I



urea in the solid state having a 1:5 (crown ether:urea) stoichiometry. In this adduct actually only two urea molecules are hydrogen bonded to both sides of an 18-crown-6 molecule in a perching[2] position, the remaining urea molecules forming hydrogen bonded layers. From our complexation studies[3] of 18-crown-6 with nitromethane, acetonitrile, and malonitrile we know that complexes of crown ethers with neutral molecules are rather weak compared with complexes with charged molecules.[4] These findings made us shift our attention to the complexation of charged analogues of urea, viz., uronium and guanidinium salts (guanidine is isoelectronic with urea but more basic, which facilitates its protonation). As far as the shape of the receptor molecule is concerned, we assumed that an optimal complexation will be found when all hydrogen atoms of such a guest molecule are involved in hydrogen bonds with the host molecule.[5]

18-Crown-6 does not satisfy this requirement as was shown by Truter and co-workers[6] for the 18-crown-6–guanidinium nitrate (1:2) complex. In this complex the two guanidinium cations are hydrogen bonded to both faces of 18-crown-6 each with just one hydrogen bond. The stability of complexes of guanidinium salts with larger macrocycles, benzo-27-crown-9[7] and 27-crown-9-hexacarboxylate[8] have led Cram and co-workers[7] and Lehn and co-workers[8] to postulate that the guanidinium cation fits in a 27-crown-9 molecule in an encapsulated position. In this paper we present the results of a more general study of the complexation in apolar solvents of guanidinium salts with a number of crown ethers, which varied in ring size and substituents, in order to find the optimal geometry of the receptor molecule and to establish the nature of the binding.

Chart II



Results[9]

Synthesis of the Crown Ethers. The crown ethers used for this study are collected in Chart I. Crown ethers 18-crown-6 (1),[10] benzo-18-crown-6 (2),[11] dibenzo-18-crown-6 (3),[12] 1,3-xylyl-18-crown-5 (4),[13] benzo-24-crown-8 (5),[14] benzo-27-crown-9 (7),[7] and tribenzo-27-crown-9 (9)[7]

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(5) (a) Recently we have shown[5b] that uronium perchlorate can form an encapsulated complex with benzo-27-crown-9. In this complex indeed all the hydrogen atoms of the guest are hydrogen bonded to the host. (b) Uiterwijk, J. W. H. M.; Harkema, S.; Reinhoudt, D. N.; Daasvatn, K.; den Hertog, H. J., Jr.; Geevers, J. *Angew. Chem.* **1982**, *94*, 462.

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were prepared according to known methods. Dibenzo-27-crown-9 (**8**) was synthesized by a reaction of 2,2′-(ethylenedioxy)bisphenol (**15a**)[15] and hexakis(ethylene glycol) ditosylate (**14d**)[7,16] (Chart II) in refluxing acetonitrile under nitrogen with CsF[14,16] as a base, thus making use of the template effect of the cesium cation, in a yield of 28%. Using similar procedures, we have synthesized a series of crown ethers having macrorings of 27–33 atoms including 8, 9, 10, or 11 oxygen atoms. The 1,3-xylyldibenzo-27-crown-8 (**10**), dibenzo-30-crown-10 (**11**), and the 1,3-xylyldibenzo-30-crown-9 (**12**) were obtained from the corresponding diols (**15**)[15,7] and ditosylates (**14d** or **16b**)[7,16] as outlined in Chart II, in yields of 41–68%. Dibenzo-33-crown-11 (**13**) was synthesized from **15c** and hexakis(ethylene glycol) ditosylate (**14d**) in refluxing THF, with KO-*t*-Bu as the base in a yield of 40%. This result shows that even for the preparation of large rings the potassium cation still acts as a template. The compounds were purified by chromatography on silica gel or alumina.

The 80-MHz ^{1}H NMR spectra of all the crown ethers showed absorptions in agreement with their structures. In these spectra only the ArOCH_2 ($\delta \sim$ 4.40–4.15), ArOCH$_2$CH_2- (δ 3.90–3.80), and the ArCH_2- ($\delta \sim$ 4.50) groups can be distinguished from the other OCH$_2$ groups ($\delta \sim$ 3.80–3.60). However when the 500-MHz ^{1}H NMR spectra of these compounds were recorded the resolution of the OCH$_2$ groups increases drastically. For example dibenzo-30-crown-10 (**11**) shows separate absorptions at δ 4.17 (t, 4 H, ArOCH$_2$), 4.12 (t, 4 H, ArOCH$_2$), 3.94 (t, 4 H, OCH$_2$), 3.84 (t, 4 H, OCH$_2$), 3.69 (m, 4 H, OCH$_2$), 3.62 (m, 4 H, OCH$_2$), and 3.58 (s, 8 H, OCH$_2$) for the OCH$_2$ groups. The ^{13}C NMR spectra of the crown ethers **5** and **7** show absorptions at ~149, ~121, and ~115 ppm for the aromatic carbon atoms of the catechol moiety, whereas the macrocycles **8**, **10**, **11**, and **12** exhibit double absorptions at ~149, ~121, and ~115 ppm. This can be attributed to the nonsymmetrical structure of the macroring in these compounds with respect to the catechol rings. The crown ether **13** shows four absorptions in this region. The ethylenic carbon atoms of all the macrocycles absorb at ~71–68 ppm. The crown ethers **10** and **12** also show absorptions at ~138 (one) and ~128.0–126.5 (three) ppm corresponding to the aromatic carbon atoms of the 1,3-xylyl moiety. The mass spectra of the compounds gave the *m*/*e* of the molecular ion and parent peaks at *m*/*e* 45. The macrocycles **5**, **7**, **8**, **11**, and **13** exhibit fragmentation patterns with successive loss of C_2H_4O fragments.[17] The crown ethers with a xylyl moiety gave mass spectra with most abundant peaks at *m*/*e* 104 and 105 in agreement with the literature.[18] The crystalline crown ethers **10**, **12**, and **13** gave satisfactory elemental analyses; crown ethers **8** and **11** were analyzed as the corresponding guanidinium perchlorate complexes (vide infra).

Extraction Experiments. The complex formation between crown ethers and salts, e.g., alkylammonium salts, has frequently been studied by equilibrating aqueous solutions of the salt and solutions of crown ethers in an apolar organic solvent.[19] The amount of salt that is transferred to the organic phase can be determined by using either a spectroscopic property of the anion, e.g., the picrate absorption in the UV spectrum,[20] or of the cation, e.g., the absorption of the *tert*-butyl group of the *t*-BuNH$_3^+$ in the ^{1}H NMR spectrum.[19] Although we have shown that this model cannot always be used to obtain (relative) association constants and thermodynamic constants of the complexation equilibrium, in particular when large rings are involved,[21] we have used this simple technique in order to obtain qualitative information on the relative complexing abilities of the crown ethers with guanidinium perchlorate (GuClO$_4$).[22] For details of the extraction conditions, see the experimental section.

18-Crown Ethers. Of the four crown ethers with an 18-membered macroring only 1,3-xylyl-18-crown-5 (**4**) failed completely to extract GuClO$_4$ from the aqueous into the organic layer. Under standard conditions (A) 18-crown-6 (**1**) extracted GuClO$_4$ to a ratio of salt to crown ether in the organic phase of 0.17 as measured by ^{1}H NMR spectroscopy. From the aqueous layer a 1:2 complex of 18-crown-6 and GuClO$_4$ crystallized.[23] When larger salt concentrations were used (condition B) the 1:2 complex precipitated at the interface. Benzo-18-crown-6 (**2**) gave a precipitate at the interface during the extraction (condition A), which was shown to be a benzo-18-crown-6·GuClO$_4$ complex with a 1:1 stoichiometry. This complex could be recrystallized from ethanol, giving white needles, mp 153–154 °C. Dibenzo-18-crown-6 (**3**) also gave a precipitate at the interface during extraction. This was found to be a dibenzo-18-crown-6·GuClO$_4$ adduct with a 3:2 stoichiometry (crown ether:GuClO$_4$).[24,25]

24-Crown Ethers. Benzo-24-crown-8 (**5**) and dibenzo-24-crown-8 (**6**) failed to transfer GuClO$_4$ to the organic layer under standard conditions (A). When larger salt concentrations were used (condition B) benzo-24-crown-8 extracted about 0.1 equiv of GuClO$_4$, whereas with dibenzo-24-crown-8 a precipitation occurred, which turned out to be an adduct of dibenzo-24-crown-8 with GuClO$_4$ in a 1:1.8 ratio as was determined by ^{1}H NMR spectroscopy.[24]

27-Crown Ethers. Benzo-27-crown-9 (**7**) extracted 1 equiv of GuClO$_4$ to the organic layer under standard conditions (A). From the organic phase, we isolated a solid which was recrystallized from ethanol to give colorless needles mp 113–114 °C. Elemental analysis and ^{1}H NMR spectroscopy proved that this compound was the benzo-27-crown-9·GuClO$_4$ (1:1) complex. Under similar conditions dibenzo-27-crown-9 (**8**) extracted 0.55 equiv of GuClO$_4$. The amount of extracted GuClO$_4$ could be increased to 0.90 equiv when larger salt concentrations (condition B) were applied. Evaporation of the solvent gave a solid which after recrystallization from ethanol gave white crystals, mp 140–141 °C. According to elemental analysis and ^{1}H NMR spectroscopy this was proven to be the dibenzo-27-crown-9·GuClO$_4$ (1:1) complex. Tribenzo-27-crown-9 (**9**) extracted about 0.3 equiv of GuClO$_4$ under standard conditions (A). When larger salt concentrations were used (condition B) a precipitate was formed, that according to ^{1}H NMR spectroscopy proved to be a tri-

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[21] de Jong, F.; Reinhoudt, D. N.; Smit, C. J. *Tetrahedron Lett.*, **1976**, 1371.

[22] For simplicity we use the abbreviation GuClO$_4$ for guanidinium perchlorate.

[23] This means that during extraction 18-crown-6 is distributed over the chloroform and aqueous layer as is also reported by Cram and coworkers.[19]

[24] An attempt to recrystallize the complex from ethanol failed. Only the crown ether crystallized from the solution as was proved by its ^{1}H NMR spectrum.

[25] Kyba et al.[7] reported a 2:3 stoichiometry (crown ether:salt) for the dibenzo-18-crown-6 guanidinium hexafluorophosphate complex.

Table I. Bond Distances[a] between Heavy Atoms in the 1:1 Complexes of Guanidinium Perchlorate with (a) Benzo-27-crown-9, (b) Dibenzo-27-crown-9, and (c) Dibenzo-30-crown-10

(a)		(b)		(c)	
C1 - O2	1.374(5)	C1 - O2	1.388(5)	C1 - O2	1.374(5)
C1 - C27	1.432(5)	C1 - C27	1.411(6)	C1 - C30	1.403(5)
C1 - C31	1.382(6)	C1 - C31	1.376(7)	C1 - C34	1.365(6)
O2 - C3	1.452(5)	O2 - C3	1.427(6)	O2 - C3	1.427(5)
C3 - C4	1.494(7)	C3 - C4	1.497(7)	C3 - C4	1.490(7)
C4 - O5	1.426(5)	C4 - O5	1.442(5)	C4 - O5	1.424(6)
O5 - C6	1.433(6)	O5 - C6	1.380(5)	O5 - C6	1.423(5)
C6 - C7	1.486(6)	C6 - C7	1.422(6)	C6 - C7	1.510(6)
C7 - O8	1.429(5)	C6 - C32	1.375(7)	C7 - O8	1.411(5)
O8 - C9	1.430(5)	C7 - O8	1.369(5)	O8 - C9	1.365(4)
C9 - C10	1.494(7)	C7 - C35	1.378(7)	C9 - C10	1.402(5)
C10 - O11	1.433(5)	O8 - C9	1.439(5)	C9 - C35	1.373(5)
O11 - C12	1.426(5)	C9 - C10	1.496(8)	C10 - O11	1.358(4)
C12 - C13	1.505(6)	C10 - O11	1.439(6)	C10 - C38	1.381(5)
C13 - O14	1.430(5)	O11 - C12	1.407(7)	O11 - C12	1.427(5)
O14 - C15	1.432(5)	C12 - C13	1.495(9)	C12 - C13	1.502(6)
C15 - C16	1.510(6)	C13 - O14	1.437(7)	C13 - O14	1.406(5)
C16 - O17	1.414(5)	O14 - C15	1.418(7)	O14 - C15	1.429(6)
O17 - C18	1.440(5)	C15 - C16	1.465(9)	C15 - C16	1.487(6)
C18 - C19	1.497(6)	C16 - O17	1.396(7)	C16 - O17	1.427(6)
C19 - O20	1.427(5)	O17 - C18	1.365(8)	O17 - C18	1.405(5)
O20 - C21	1.436(5)	C18 - C19	1.33(1)	C18 - C19	1.487(7)
C21 - C22	1.512(6)	C19 - O20	1.43(1)	C19 - O20	1.409(5)
C22 - O23	1.444(5)	O20 - C21	1.37(1)	O20 - C21	1.427(5)
O23 - C24	1.417(5)	C21 - C22	1.40(1)	C21 - C22	1.490(7)
C24 - C25	1.498(7)	C22 - O23	1.30(1)	C22 - O23	1.408(5)
C25 - O26	1.453(5)	O23 - C24	1.402(7)	O23 - C24	1.411(6)
O26 - C27	1.383(5)	C24 - C25	1.497(8)	C24 - C25	1.492(7)
C27 - C28	1.371(6)	C25 - O26	1.434(6)	C25 - O26	1.431(5)
C28 - C29	1.389(6)	O26 - C27	1.375(6)	O26 - C27	1.421(5)
C29 - C30	1.390(6)	C27 - C28	1.384(7)	C27 - C28	1.494(7)
C30 - C31	1.382(7)	C28 - C29	1.395(8)	C28 - O29	1.421(5)
C32 - N33	1.316(5)	C29 - C30	1.376(8)	O29 - C30	1.364(5)
C32 - N34	1.330(5)	C30 - C31	1.394(8)	C30 - C31	1.387(6)
C32 - N35	1.331(5)	C32 - C33	1.401(7)	C31 - C32	1.385(7)
CL36 - O37	1.434(3)	C33 - C34	1.386(7)	C32 - C33	1.365(7)
CL36 - O38	1.436(3)	C34 - C35	1.401(7)	C33 - C34	1.396(7)
CL36 - O39	1.433(3)	C36 - N37	1.324(6)	C35 - C36	1.388(6)
CL36 - O40	1.433(4)	C36 - N38	1.331(6)	C36 - C37	1.350(7)
		C36 - N39	1.324(7)	C37 - C38	1.385(6)
		CL40 - O41	1.427(4)	C39 - N40	1.320(6)
		CL40 - O42	1.420(4)	C39 - N41	1.312(5)
		CL40 - O43	1.433(4)	C39 - N42	1.320(6)
		CL40 - O44	1.429(4)	CL43 - O44	1.391(4)
				CL43 - O45	1.413(5)
				CL43 - O46	1.381(6)
				CL43 - O47	1.26(1)

[a] Estimated standard deviations given in parentheses in units of the least significant digit. The atomic numbering is according to Figures 1, 2, and 3, respectively.

benzo-27-crown-9·$GuClO_4$ (1:1) complex.[24,26] Under standard conditions (A) 1,3-xylyldibenzo-27-crown-8 (**10**) did not extract any $GuClO_4$. When larger salt concentrations were applied (condition B) only 0.1 equiv was extracted.

30- and 33-Crown Ethers. Under standard conditions (A) dibenzo-30-crown-10 (**11**) extracted 0.83 equiv of $GuClO_4$. After evaporation of the deuteriochloroform a solid remained, which could be recrystallized from EtOH–$CHCl_3$ (1%) to give white crystals, mp 122.5–123.5 °C. Elemental analysis and ^1H NMR spectroscopy proved that this solid was the dibenzo-30-crown-10·$GuClO_4$ (1:1) complex. With 1,3-xylyldibenzo-30-crown-9 (**12**) 0.48 equiv of $GuClO_4$ was extracted. This amount did not increase when larger salt concentrations (condition B) were used. Only at very large salt concentrations (condition C) was 0.95 equiv of $GuClO_4$ transferred to the organic layer. After evaporation of the deuteriochloroform we obtained an oil, which resisted all attempts to crystallize. Dibenzo-33-crown-11 (**13**) extracted 0.83 equiv of $GuClO_4$. After evaporation of the deuteriochloroform we obtained an oil which failed to crystallize. With larger salt concentrations (condition B) 0.95 equiv could be extracted. Also from this extraction experiment no crystals could be obtained.

X-ray Analysis of the 1:1 Complexes of Guanidinium Perchlorate with Benzo-27-crown-9 (7), Dibenzo-27-crown-9 (8), and Dibenzo-30-crown-10 (11). The structures of the 1:1 complexes of guanidinium perchlorate with **7**,[9] **8**, and **11** have been determined with X-ray diffraction. Details of the structure determination are given in the experimental section. Atom numbering is shown in Figures 1, 2, and 3. Perchlorate ions are omitted in all three complexes, as they are hydrogen bonded neither to the cation nor to the host molecule.

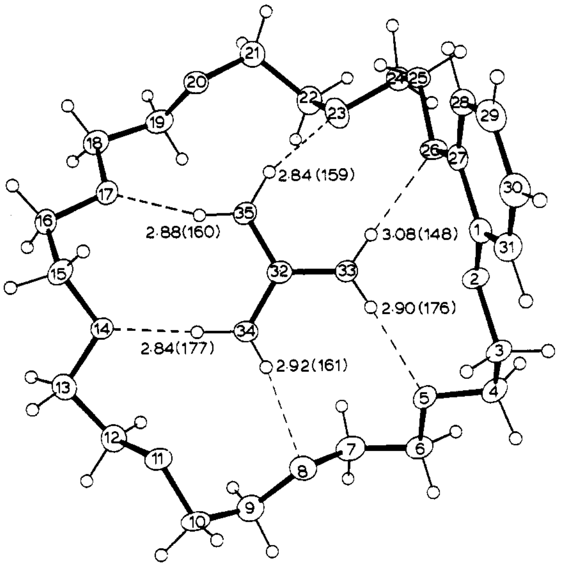

Figure 1. ORTEP[27] view of the complex of the guanidinium cation with the benzo-27-crown-9 molecule showing the atomic numbering. Hydrogen bonds are indicated by broken lines. N(–H)···O distances (Å) and N–H···O angles (°) (between brackets) are indicated.

Table II. Bond Angles[a] Involving Heavy Atoms Only, in the 1:1 Complexes of Guanidinium Perchlorate with (a) Benzo-27-crown-9, (b) Dibenzo-27-crown-9, and (c) Dibenzo-30-crown-10

(a)		(b)		(c)	
O2 - C1 - C27	115.6(4)	O2 - C1 - C27	116.2(4)	O2 - C1 - C30	114.9(4)
O2 - C1 - C31	125.5(4)	O2 - C1 - C31	123.8(5)	O2 - C1 - C34	124.8(4)
C27 - C1 - C31	118.9(5)	C27 - C1 - C31	120.0(5)	C30 - C1 - C34	120.4(5)
C1 - O2 - C3	115.0(4)	C1 - O2 - C3	114.9(4)	C1 - O2 - C3	116.6(4)
O2 - C3 - C4	108.3(4)	O2 - C3 - C4	109.6(4)	O2 - C3 - C4	107.3(4)
C3 - C4 - O5	109.9(4)	C3 - C4 - O5	108.9(4)	C3 - C4 - O5	112.4(4)
C4 - O5 - C6	111.1(4)	C4 - O5 - C6	116.1(4)	C4 - O5 - C6	115.9(4)
O5 - C6 - C7	109.8(4)	O5 - C6 - C7	115.2(4)	O5 - C6 - C7	111.8(3)
C6 - C7 - O8	110.6(4)	O5 - C6 - C32	124.9(5)	C6 - C7 - O8	106.9(3)
C7 - O8 - C9	112.3(4)	C7 - C6 - C32	120.0(5)	C7 - O8 - C9	117.4(3)
O8 - C9 - C10	109.2(4)	C6 - C7 - O8	115.6(4)	O8 - C9 - C10	115.3(3)
C9 - C10 - O11	113.2(4)	C6 - C7 - C35	119.1(5)	O8 - C9 - C35	125.0(4)
C10 - O11 - C12	113.7(4)	O8 - C7 - C35	125.3(5)	C10 - C9 - C35	119.7(4)
O11 - C12 - C13	107.7(4)	C7 - O8 - C9	116.1(4)	C9 - C10 - O11	115.8(3)
C12 - C13 - O14	108.0(3)	O8 - C9 - C10	108.7(4)	C9 - C10 - C38	119.4(4)
C13 - O14 - C15	114.3(3)	C9 - C10 - O11	111.6(4)	O11 - C10 - C38	124.8(4)
O14 - C15 - C16	111.9(4)	C10 - O11 - C12	111.7(5)	C10 - O11 - C12	117.0(4)
C15 - C16 - O17	108.8(4)	O11 - C12 - C13	111.0(5)	O11 - C12 - C13	106.5(4)
C16 - O17 - C18	112.0(4)	C12 - C13 - O14	110.3(5)	C12 - C13 - O14	114.6(4)
O17 - C18 - C19	109.5(4)	C13 - O14 - C15	111.5(5)	C13 - O14 - C15	114.3(5)
C18 - C19 - O20	110.0(4)	O14 - C15 - C16	110.8(6)	O14 - C15 - C16	108.6(4)
C19 - O20 - C21	112.5(4)	C15 - C16 - O17	110.4(5)	C15 - C16 - O17	108.7(4)
O20 - C21 - C22	113.0(4)	C16 - O17 - C18	119.5(7)	C16 - O17 - C18	112.8(4)
C21 - C22 - O23	109.8(4)	O17 - C18 - C19	119.0(9)	O17 - C18 - C19	110.2(4)
C22 - O23 - C24	112.3(4)	C18 - C19 - O20	121(1)	C18 - C19 - O20	109.9(4)
O23 - C24 - C25	109.4(4)	C19 - O20 - C21	118(1)	C19 - O20 - C21	111.9(4)
C24 - C25 - O26	108.7(4)	O20 - C21 - C22	116.3(8)	O20 - C21 - C22	109.0(4)
C25 - O26 - C27	114.5(4)	C21 - C22 - O23	122(1)	C21 - C22 - O23	108.5(4)
C1 - C27 - O26	115.0(4)	C22 - O23 - C24	121.4(7)	C22 - O23 - C24	115.7(4)
C1 - C27 - C28	119.4(4)	O23 - C24 - C25	113.8(5)	O23 - C24 - C25	113.7(4)
O26 - C27 - C28	125.7(5)	C24 - C25 - O26	107.6(5)	C24 - C25 - O26	114.4(4)
C27 - C28 - C29	120.8(5)	C25 - O26 - C27	117.1(4)	C25 - O26 - C27	115.2(5)
C28 - C29 - C30	120.0(5)	C1 - C27 - O26	116.3(4)	O26 - C27 - C28	113.6(4)
C29 - C30 - C31	119.8(5)	C1 - C27 - C28	119.5(5)	C27 - C28 - O29	107.6(4)
C1 - C31 - C30	121.1(5)	O26 - C27 - C28	124.2(5)	C28 - O29 - C30	116.7(4)
N33 - C32 - N34	120.6(4)	C27 - C28 - C29	119.9(6)	C1 - C30 - O29	116.0(4)
N33 - C32 - N35	119.9(4)	C28 - C29 - C30	120.4(6)	C1 - C30 - C31	119.0(4)
N34 - C32 - N35	119.5(4)	C29 - C30 - C31	120.2(7)	O29 - C30 - C31	124.9(5)
O37 -CL36 - O38	109.5(3)	C1 - C31 - C30	120.0(6)	C30 - C31 - C32	120.3(5)
O37 -CL36 - O39	109.2(2)	C6 - C32 - C33	120.3(6)	C31 - C32 - C33	120.1(5)
O37 -CL36 - O40	109.1(2)	C32 - C33 - C34	120.1(6)	C32 - C33 - C34	120.4(5)
O38 -CL36 - O39	109.7(2)	C33 - C34 - C35	119.5(6)	C1 - C34 - C33	119.8(5)
O38 -CL36 - O40	110.1(2)	C7 - C35 - C34	121.0(6)	C9 - C35 - C36	119.8(5)
O39 -CL36 - O40	109.3(3)	N37 - C36 - N38	120.4(5)	C35 - C36 - C37	120.7(5)
		N37 - C36 - N39	119.7(6)	C36 - C37 - C38	120.5(5)
		N38 - C36 - N39	119.9(5)	C10 - C38 - C37	119.9(5)
		O41 -CL40 - O42	107.8(3)	N40 - C39 - N41	120.5(5)
		O41 -CL40 - O43	108.1(3)	N40 - C39 - N42	119.7(5)
		O41 -CL40 - O44	110.5(3)	N41 - C39 - N42	119.7(6)
		O42 -CL40 - O43	111.2(4)	O44 -CL43 - O45	112.1(3)
		O42 -CL40 - O44	109.6(3)	O44 -CL43 - O46	106.5(3)
		O43 -CL40 - O44	109.7(3)	O44 -CL43 - O47	111.5(6)
				O45 -CL43 - O46	98.7(4)
				O45 -CL43 - O47	117.4(7)
				O46 -CL43 - O47	109.3(6)

[a] Estimated standard deviations given in parentheses in units of the least significant digit. The atomic numbering is according to Figures 1, 2, and 3, respectively.

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[26] Kyba et al.[7] reported a 2:3 stoichiometry (crown ether:salt) for the corresponding guanidinium hexafluorophosphate complex.

[27] Johnson, C. K. ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, TN, 1965.

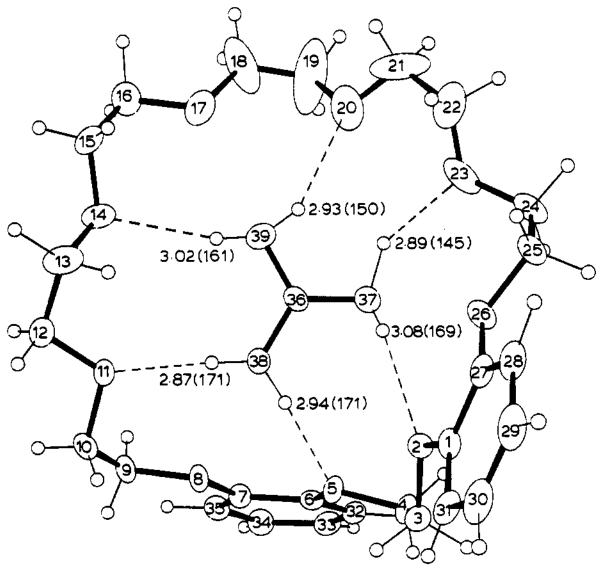

Figure 2. ORTEP[27] view of the complex of the guanidinium cation with the dibenzo-27-crown-9 molecule showing the atomic numbering. Hydrogen bonds are indicated by broken lines. N(-H)···O distances (Å) and N-H···O angles (°) (between brackets) are indicated.

Table III. Torsion Angles[a] in the Macroring for the 1:1 Complexes of Guanidinium Perchlorate with (a) Benzo-27-crown-9, (b) Dibenzo-27-crown-9, and (c) Dibenzo-30-crown-10

(a)		(b)		(c)	
C1 - O2 - C3 - C4	-176.2(3)	C1 - O2 - C3 - C4	-165.9(3)	C1 - O2 - C3 - C4	-175.9(3)
O2 - C3 - C4 - O5	-67.4(3)	O2 - C3 - C4 - O5	-75.4(3)	O2 - C3 - C4 - O5	-63.3(3)
C3 - C4 - O5 - C6	-164.0(3)	C3 - C4 - O5 - C6	-161.6(4)	C3 - C4 - O5 - C6	-80.5(4)
C4 - O5 - C6 - C7	-175.2(3)	C4 - O5 - C6 - C7	166.9(3)	C4 - O5 - C6 - C7	-75.4(3)
O5 - C6 - C7 - O8	-61.2(3)	O5 - C6 - C7 - O8	3.6(4)	O5 - C6 - C7 - O8	-59.0(3)
C6 - C7 - O8 - C9	-144.5(3)	C6 - C7 - O8 - C9	175.8(4)	C6 - C7 - O8 - C9	177.7(3)
C7 - O8 - C9 - C10	-173.1(3)	C7 - O8 - C9 - C10	-178.0(3)	C7 - O8 - C9 - C10	-174.5(3)
O8 - C9 - C10 - O11	68.6(3)	O8 - C9 - C10 - O11	70.3(3)	O8 - C9 - C10 - O11	-0.1(2)
C9 - C10 - O11 - C12	75.4(4)	C9 - C10 - O11 - C12	140.1(4)	C9 - C10 - O11 - C12	-176.9(3)
C10 - O11 - C12 - C13	163.6(3)	C10 - O11 - C12 - C13	166.5(4)	C10 - O11 - C12 - C13	-169.8(3)
O11 - C12 - C13 - O14	60.1(3)	O11 - C12 - C13 - O14	66.2(4)	O11 - C12 - C13 - O14	-62.0(3)
C12 - C13 - O14 - C15	178.6(3)	C12 - C13 - O14 - C15	152.7(5)	C12 - C13 - O14 - C15	-79.4(4)
C13 - O14 - C15 - C16	-92.9(3)	C13 - O14 - C15 - C16	178.1(4)	C13 - O14 - C15 - C16	-166.5(3)
O14 - C15 - C16 - O17	-63.9(3)	O14 - C15 - C16 - O17	-67.4(4)	O14 - C15 - C16 - O17	62.9(3)
C15 - C16 - O17 - C18	-174.1(3)	C15 - C16 - O17 - C18	-168.6(7)	C15 - C16 - O17 - C18	160.7(4)
C16 - O17 - C18 - C19	-172.8(3)	C16 - O17 - C18 - C19	-176.1(8)	C16 - O17 - C18 - C19	-179.8(3)
O17 - C18 - C19 - O20	-70.7(3)	O17 - C18 - C19 - O20	-27(1)	O17 - C18 - C19 - O20	-69.1(3)
C18 - C19 - O20 - C21	-171.7(3)	C18 - C19 - O20 - C21	-117(1)	C18 - C19 - O20 - C21	-176.8(3)
C19 - O20 - C21 - C22	-83.0(3)	C19 - O20 - C21 - C22	-165.3(8)	C19 - O20 - C21 - C22	170.5(3)
O20 - C21 - C22 - O23	-67.5(3)	O20 - C21 - C22 - O23	25.7(9)	O20 - C21 - C22 - O23	-66.2(3)
C21 - C22 - O23 - C24	-105.4(3)	C21 - C22 - O23 - C24	153.2(8)	C21 - C22 - O23 - C24	178.8(3)
C22 - O23 - C24 - C25	164.7(3)	C22 - O23 - C24 - C25	97.3(7)	C22 - O23 - C24 - C25	-90.6(4)
O23 - C24 - C25 - O26	66.9(3)	O23 - C24 - C25 - O26	67.1(4)	O23 - C24 - C25 - O26	63.8(4)
C24 - C25 - O26 - C27	177.5(3)	C24 - C25 - O26 - C27	171.1(4)	C24 - C25 - O26 - C27	76.9(4)
C25 - O26 - C27 - C1	-173.9(3)	C25 - O26 - C27 - C1	-163.3(3)	C25 - O26 - C27 - C28	74.4(3)
O26 - C27 - C1 - O2	1.1(3)	O26 - C27 - C1 - O2	-2.4(4)	O26 - C27 - C28 - O29	68.1(3)
C27 - C1 - O2 - C3	179.9(3)	C27 - C1 - O2 - C3	155.9(3)	C27 - C28 - O29 - C30	-174.6(3)
				C28 - O29 - C30 - C1	-178.0(3)
				O29 - C30 - C1 - O2	-0.2(3)
				C30 - C1 - O2 - C3	176.7(3)

[a] Estimated standard deviations given in parentheses in units of the least significant digit. The atomic numbering is according to Figures 1, 2, and 3, respectively.

Bond distances and bond angles, involving heavy atoms only, are presented in Tables I and II. Torsion angles in the macrocycles are given in Table III. (Complete lists of structural parameters have been deposited as supplementary material.)

As can be seen from the thermal parameters and from the standard deviations in the structural parameters, part of the macroring in the complex of guanidinium perchlorate with 8 exhibits disorder. In particular, the atoms C18, C19, C21, and C22 (Figure 2) show large thermal vibrations. As a result, only one hydrogen attached to C18, one attached to C19, and none of the hydrogens attached to C21 and C22 could be located in a difference Fourier synthesis. In Figure 2 the missing hydrogens have been added at a distance of 1.0 Å with reasonable bond angles, using the algorithm of the GHMC program.[28] As a result of this disorder, the bonding distances in this part of the ring are unrealistically short (Table I), whereas the corresponding bond angles are systematically too large (Table II). It is difficult to indicate the reliability of the torsion angles in this disordered part of the ring, but some of these torsion angles have values which seem rather improbable when compared with "standard" experimental torsion angles in crown ethers.[29] The perchlorate ion in the complex of guanidinium perchlorate with dibenzo-30-crown-10 is also partially disordered, as shown by the structural and thermal parameters and standard deviations in Tables I and II and supplementary material.

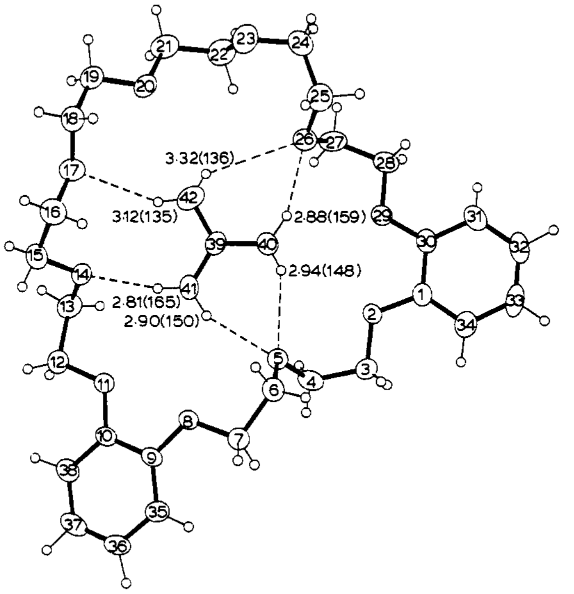

Figure 3. ORTEP[27] view of the complex of the guanidinium cation with the dibenzo-30-crown-10 molecule showing the atomic numbering. Hydrogen bonds are indicated by broken lines. N(-H)···O distances (Å) and N-H···O angles (°) (between brackets) are indicated.

The guanidinium cation is totally encapsulated within the macrocycle in all three complexes. The hydrogen-bonding schemes in the two 27-membered crown ether complexes are the same: each nitrogen atom is hydrogen bonded to two next-neighbor oxygen atoms. The N···O hydrogen-bonding distances vary between 2.84 and 3.08 Å, with N-H···O angles between 145° and 177° (Figures 1 and 2). Furthermore, the crown ether oxygens, which are not involved in hydrogen bonding, seem to have a considerable electrostatic interaction with the nitrogen atoms (N···O distances between 2.79 and 3.14 Å). Although the sequences of the torsion angles in the macrocycles are rather different in both complexes ($ag^{-}a\ ag^{-}a\ ag^{+}g^{+}\ ag^{+}a\ g^{-}g^{-}a\ ag^{-}a\ g^{-}g^{-}g^{-}\ ag^{+}a\ asa$[30] in the complex with benzo-27-crown-9, and $ag^{-}a\ asa\ ag^{+}a\ ag^{+}a\ ag^{-}a\ ag^{-}g^{-}\ ag^{+}a\ g^{+}g^{+}a\ asa$[30] in the complex with dibenzo-27-crown-9, Table III), the structural relations between the guanidinium cation and the hydrogen-bonded crown ether oxygens are quite the same in both complexes.

The longest N-H···O hydrogen bond in both complexes (3.08 Å for both) involves a catecholic crown ether oxygen, reflecting the less basic character of these oxygens. The orientation of the guanidinium cation within the macrocycle is determined by the same fact. If we assume the three NH_2 groups to be identical, there are three different ways in which the guanidinium cation may be oriented within the macrocycle. The different orientations can be obtained by rotations of 40° around the axis, perpendicular to (and passing through the central atom of) the guani-

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(28) Mark, T. C. W.; Mok, F.-C.; Tse, J. S. GHMC, QCPE program no. 345, Indiana.

(29) Goldberg, I. "The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues"; S. Patai, Ed; Wiley: New York, 1980; Supplement E, pp 175-214.

(30) "s" (synperiplanar) denotes an O-C-C-O torsion angle of almost 0° imposed by the benzo substituent.

dinium cation. In the case of the complex with benzo-27-crown-9, two of the three possible orientations involve one catecholic hydrogen-bonded oxygen, whereas in the third orientation both catecholic oxygens are used for hydrogen bonding. In the complex with dibenzo-27-crown-9 two orientations use three out of the four catecholic oxygens, while the third possible orientation shows a hydrogen bonding scheme involving only two of them. It is evident from the X-ray structure determinations that in both cases the orientation of the central cation is such that a minimum of catecholic oxygens is used (Figures 1 and 2). This effect is even more pronounced in the 1:1 complex of **7** with uronium perchlorate[5b] (isoelectronic with the **7**·guanidinium perchlorate complex), with five hydrogen bonds between the central ion and the macrocycle. In this case the nine possible orientations yield an essentially different hydrogen-bonding scheme, using 0,1, or 2 of the catecholic oxygens for hydrogen bonding. The X-ray determination has revealed that the preferred orientation was also the one using as few catecholic oxygens as possible.

The hydrogen-bonding scheme in the 1:1 complex between guanidinium perchlorate and **11** (Figure 3) is rather different. Although each NH_2 group is hydrogen bonded to the macroring via both hydrogens, the bonding is to next-next-neighbor oxygens instead of to next-neighbor oxygens as in the complexes with 27-membered crown ethers. Only four of the ten crown ether oxygens are hydrogen-bonded, because two of them are involved each in two hydrogen bonds (Figure 3). The N···O hydrogen-bonding distances vary between 2.81 and 3.32 Å, with hydrogen-bonding angles between 135° and 165° (Figure 3). These larger distances and larger deviations from linearity for the corresponding angles, compared with the two forementioned complexes with 27-membered crown ethers, are undoubtedly due to the larger ring size of the polyether and the absence of an approximate 3-fold symmetry of the crown oxygen atoms, relative to the central guanidinium ion. The electrostatic interaction between the non-hydrogen-bonded crown ether oxygens and the nitrogen atoms seems to be rather weak (N···O distances between 3.06 and 3.39 Å, thereby neglecting the O(23) atom, which points outwards and has a distance to the nearest nitrogen atom of 4.22 Å). From the view in Figure 3 it can be seen that the macroring, in order to accommodate the guanidinium ion as well as possible, is wrapped around the cation in a fairly irregular way (sequence of torsion angles $ag^-g^-\ g^-g^-a\ asa\ ag^-g^-\ ag^+a\ ag^-a\ ag^-a\ g^-g^+g^+\ g^+g^+a\ asa$,[30] Table III) without, however, reaching the almost perfect complementary hydrogen-bonding scheme of the 27-membered macrorings.

The effect of the catecholic oxygens on the complexation is even more pronounced in this complex than in the two forementioned complexes; none of the four catecholic oxygens is used in hydrogen bonding!

Kinetic Stabilities of the Complexes of the Crown Ethers 7, 8, and 11 with $GuClO_4$. The 500-MHz ^1H NMR spectrum of benzo-27-crown-9 (**7**) in $CDCl_3$ (Figure 4) clearly shows a down-field shift for all the hydrogen atoms of the $-CH_2$ groups upon complexation with $GuClO_4$, especially for the $-CH_2$ groups a, b, and c. The spectrum of a 1:1 mixture of complex and free crown ether in CD_2Cl_2 at room temperature showed average chemical shifts of all hydrogen atoms of the free and the complexed crown ether. This indicates a fast exchange of $GuClO_4$ between free and complexed crown ether. However upon lowering the temperature line broadening of several absorptions was observed indicating that the exchange process is slow on the NMR time scale. Finally both absorptions of the $-CH_2-$ groups a and b corresponding to the free and complexed crown ether are observed separately (Figure 5). The temperature-dependent 500-MHz ^1H NMR spectra of 1:1 mixtures of free and complexed crown ether of dibenzo-27-crown-9 (**8**) and dibenzo-30-crown-10 (**11**) showed the same phenomena. The observed exchange processes consist of two reactions: the association and the decomplexation. The decomplexation process involves breaking the hydrogen bonds and diminishing the electrostatic interactions. The association process involves conformational organization of the macroring of the crown ether prior to complexation. Krane et al.[31] have shown for the 2:1 com-

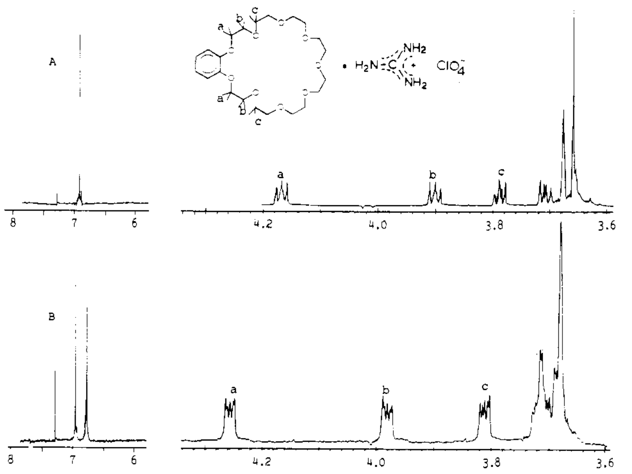

Figure 4. 500-MHz ^1H NMR spectra of benzo-27-crown-9 (A) and benzo-27-crown-9·$GuClO_4$ (B) in $CDCl_3$ at room temperature.

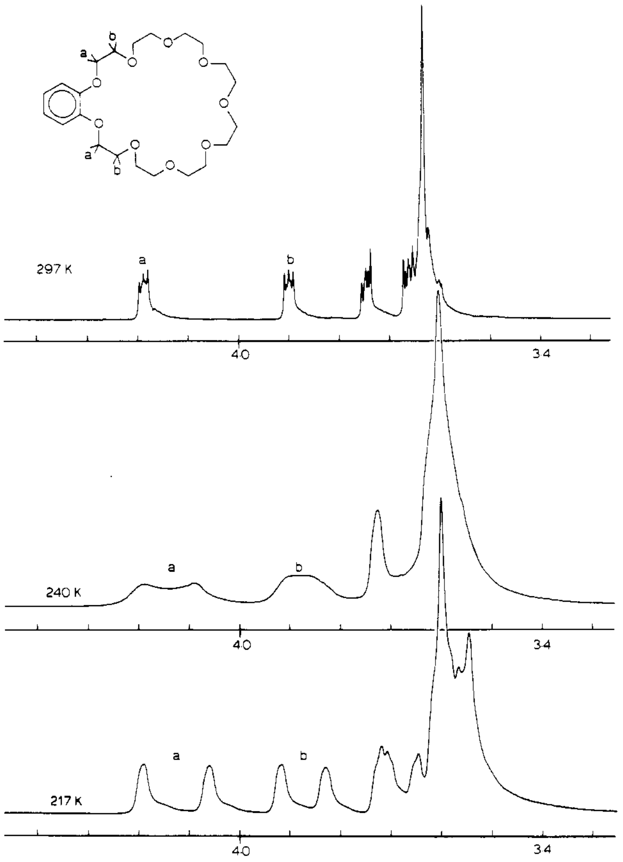

Figure 5. Temperature dependent 500-MHz ^1H NMR spectra of benzo-27-crown-9 and $GuClO_4$ (2:1) in CD_2Cl_2.

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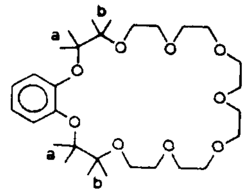
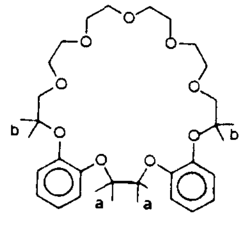
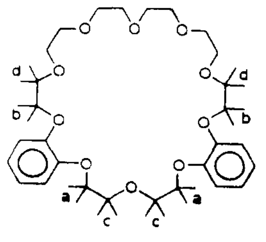
[31] Krane, J.; Amble, E.; Dale, J.; Daasvatn, K. *Acta Chem. Scand. Ser. B* **1980**, *B34*, 255.

Table IV. Free Energy of Activation of Decomplexation of Crown Ether Guanidinium Perchlorate Complexes

compd	H	T_c, °C	k_c, s^{-1}	$\Delta G_d^\ddagger$ (T_c), kcal mol^{-1}
	a	245	135.6	11.6
	b	240	88.1	11.4
	a	233	142.1	11.2
	b	227	69.4	11.2
	d	240	27.8	12.0

plex of 12-crown-4 with NaSCN that activation energies for conformational changes are much lower than the decomplexation barrier. They also showed that the processes of conformational changes occur even when the crown ether is complexed.[32] The observed free energy of activation of the exchange process of complexes of crown ethers can therefore be attributed entirely to the decomplexation of the complex. The rate constants at the coalescence temperature and the corresponding free energies of the decomplexation are summarized in Table IV. For benzo-27-crown-9 (**7**) and dibenzo-27-crown-9 (**8**) it is shown that the $\Delta G_d^\ddagger$ values as calculated from the different signals at their coalescence temperatures agree within experimental error. The three complexes have about the same kinetic stability. From the X-ray determinations one would expect however a lower $\Delta G_d^\ddagger$ value for the dibenzo-30-crown-10·$GuClO_4$ complex, because the macroring seems less suited for the accommodation of the cation. As shown the hydrogen bonds in this complex do not use any of the less basic catecholic oxygens, which may be an explanation of the relatively high observed kinetic stability. The observed $\Delta G_d^\ddagger$ values of the three encapsulated $GuClO_4$ complexes are of the same order of magnitude as reported for perching complexes of alkylammonium salts with 18–21-membered crown ethers.[4,33]

Conclusions

From the above results a number of general conclusions can be drawn about the complexation of the guanidinium cation by crown ethers. The crown ethers can be divided in groups according to their ring size and structure.

Ring Size, Perching vs. Encapsulated Complexes. 18-Crown-6 (**1**) and benzo-18-crown-6 (**2**) hardly extract $GuClO_4$ into the organic phase but form well-defined stoichiometric complexes by precipitation at the interface during extraction. It is assumed that these are perching complexes with the same hydrogen bonding scheme as found by Truter et al.[6] for the 18-crown-6–$GuNO_3$ (1:2) complex. The same holds for dibenzo-18-crown-6 (**3**), but with this compound no complex with a well-defined stoichiometry could be obtained.

Benzo-27-crown-9 (**7**), dibenzo-27-crown-9 (**8**), and dibenzo-30-crown-10 (**11**) extract $GuClO_4$ easily and form 1:1 encapsulated complexes as shown by their X-ray analyses. Also tribenzo-27-crown-9 (**9**), 1,3-xylyldibenzo-30-crown-9 (**12**), and dibenzo-33-crown-11 (**13**) extract $GuClO_4$. Complexes up to a 1:1 stoichiometry can be found and though not proven it is assumed that they also form encapsulated complexes.

Benzo-24-crown-8 (**5**) and dibenzo-24-crown-8 (**6**) hardly extract any $GuClO_4$, probably because the 24-ring is just too small (according to CPK models) to form stable encapsulated complexes. Benzo-24-crown-8 probably has too much conformational freedom to form a perching complex. Dibenzo-24-crown-8 however, which is more rigid because of an extra aromatic ring, can form an approximately 1:2 complex at the interface during extraction with larger salt concentrations.

1,3-Xylyl Unit. If we compare 1,3-xylyldibenzo-27-crown-8 (**10**) with dibenzo-27-crown-9 (**8**) (the C16–O17–C18 group in **8** (Figure 2) is replaced by a 1,3-xylyl unit) it seems strange that the former hardly extracts any $GuClO_4$ to the organic layer. It is obvious from this fact that beside hydrogen bonding the electrostatic interactions of the nitrogens with the oxygen atoms that are not involved in hydrogen bonding play an important role in the complexation. The same explanation applies for 1,3-xylyl-18-crown-5 (**4**) which does not form a complex with $GuClO_4$. However 1,3-xylyldibenzo-30-crown-9 (**12**) does form a complex with $GuClO_4$ of a 1:1 stoichiometry. Therefore a larger ring size can compensate for the disadvantages introduced by the 1,3-xylyl moiety. The destabilizing effect caused by this moiety is also reported for the complexation of *t*-$BuNH_3SCN$ by Cram and co-workers.[19] They found a free energy for association of −8.81 kcal/mol for 18-crown-6 vs. −4.78 kcal/mol for 1,3-xylyl-18-crown-5. The same effect was also found by De Jong et al.[34] who reported *K* values of 2.3×10^7 and 2.2×10^5 L mol^{-1} for the complexation of *t*-$BuNH_3PF_6$ with 18-crown-6 and 1,3-xylyl-18-crown-5, respectively.

Catechol Moiety. The catechol group has a remarkable effect on the complexation of crown ethers with $GuClO_4$. The extraction capability of crown ethers with 27 ring atoms increases in the order tribenzo-27-crown-9 (**9**) < dibenzo-27-crown-9 (**8**) < benzo-27-crown-9 (**7**). Benzo-18-crown-6 (**2**) forms a 1:1 complex, whereas 18-crown-6 forms a 1:2 complex (crown ether:$GuClO_4$). These observations can be explained in terms of the lower basicity of the catechol oxygen atom and was also evident from the orientation of the guanidinium cation in the macrocycles **7**, **8**, and **11**. These findings are also in agreement with the calculated contributions of $(CH_2)_2O\cdots H\text{–}N^+$ and $ArO\cdots HN^+$ interactions to the overall $\Delta G°$ of complexation of crown ethers with *t*-$BuNH_3^+$ salts as reported by Cram and co-workers.[19] It was found that the $ArO\cdots H\text{–}N^+$ interaction is ~0.7 kcal/mol weaker than the $(CH_2)_2O\cdots H\text{–}$

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N^+ interaction. Another consequence of the introduction of catechol units is that it enlarges the rigidity of the crown ether. This effect may render it difficult for the crown ether to adopt the best conformation needed for complexation.

It is clear from this study that crown ethers with 27 and 30 ring atoms have a suitable ring size to form encapsulated complexes with $GuClO_4$. It also explains why the complex of the guanidinium cation with the 27-crown-9-hexacarboxylate macrocycle (K = 9000 L mol^{-1} (H_2O)[8] is much more stable than the corresponding complex with 18-crown-6 (K_a = 45(H_2O)[8] – 50(MeOH)[8, 35] L mol^{-1}). In the latter complex only one O···H–N hydrogen bond occurs, whereas in a 27-crown-9 complex six O···H–N hydrogen bonds (and three O···N interactions) occur. From the X-ray analysis it is obvious that the electrostatic interaction and hydrogen-bonding scheme in the 30-membered ring are not as ideal as in the 27-membered ring. This however is not reflected in the kinetic stability of the complexes, as mentioned before. Aromatic rings (especially 1,3-xylyl) have a negative influence on the complexation of crown ethers with $GuClO_4$. This however might be of great value for the selective properties of these crown ethers.

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 Bruker WM-500 spectrometers in $CDCl_3$, DMSO-d_6, or CD_2Cl_2, and ^{13}C NMR spectra were recorded with a Varian XL-100 spectrometer with Me_4Si as an internal standard. Mass spectra were obtained with a Varian Mat 311A. Elemental analyses were carried out by the Elemental Analytical Section of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands, under the supervision of W. J. Buis and G. J. Rotscheid.

Materials. Dibenzo-24-crown-8 (**6**) refers to Merck reagent. Dibenzo-18-crown-6 (**3**),[12] 1,3-xylyl-18-crown-5 (**4**),[13] benzo-24-crown-8 (**5**),[14] benzo-27-crown-9 (**7**),[7] and tribenzo-2-crown-9 (**9**)[7] were prepared according to the literature. 18-Crown-6 (**1**) was prepared according to Johns et al.[10] The compound was purified by precipitation of the 18-crown-6·nitromethane (1:2) complex[36] with a diethyl ether/nitromethane (10:1/v/v) mixture and then distillation under reduced pressure under nitrogen, yield 30%, mp 38–39 °C. Benzo-18-crown-6 (**2**) was made according to Pedersen.[11] The product was purified by microdistillation with a Büchi GKR-50 apparatus and trituration with diisopropyl ether, yield 30%, mp 43.2–44.4 °C.

Polyethylene glycols and their ditosylates (**14**),[7,16] 2,2′-[1,2-ethanediylbis(oxy)]bisphenol (**15a**),[15] and 2,2′-[oxybis(2,1-ethanediyloxy)]bisphenol (**15b**)[7] were prepared according to the literature.

2,2′-[1,2-Ethanediylbis(oxy-2,1-ethanediyloxy)]bisphenol (15c). To a stirred refluxing solution of 138.0 g (1.25 mol) of catechol and 17.3 g (0.43 mol) of NaOH in 1000 mL of water under nitrogen was added 39.3 g (0.21 mol) of triethylene glycol dichloride. The mixture was refluxed for an additional 72 h and cooled to room temperature. The organic layer was dissolved in ethyl acetate and dried over $MgSO_4$. The ethyl acetate was removed under reduced pressure and the residue was distilled to give 12.5 g of **15c**: yield 18%, bp 224–228 °C (0.07 mm);[37] 80 MHz ^{1}H NMR ($CDCl_3$) δ 6.95–6.80 (m, 10 H, Ar H and Ar OH), 4.23–4.12 (m, 4 H, Ar OCH_2), 3.87–3.81 (m, 8 H, OCH_2CH_2O); mass spectrum, m/e 334.136 (M^+; calcd 334.142).

1,3-Bis((2-(2-hydroxyethoxy)ethoxy)methyl)benzene (16a). To a stirred solution of 9.0 g (0.225 mol) of NaOH in 200 mL of diethylene glycol at 120–125 °C was added dropwise a suspension of 26.4 g (0.1 mol) of 1,3-bis(bromomethyl)benzene in 200 mL of diethylene glycol under nitrogen. After the solution was kept at 120–125 °C for another 10 h, the reaction mixture was poured into water. The organic layer was separated and the water layer extracted with chloroform. The combined organic layers were dried and concentrated in vacuo. Purification was accomplished by distillation: yield, 65%; bp 200–210 °C (0.02 mm); 80 MHz ^{1}H NMR ($CDCl_3$) δ 7.48 (s, 1 H, Ar H), 7.30 (m, 3 H, Ar H), 4.58 (s, 4 H, $ArCH_2$), 3.8–3.5 (m, 16 H, CH_2CH_2), 3.20 (s, 2 H, OH).

The ditosylate of 16a, 16b, was prepared according to the procedure of Pearson et al.:[39] 80 MHz ^{1}H NMR ($CDCl_3$) δ 7.80 and ~7.30 (AB, 4 H, SO_2ARH), 7.2–7.4 (m, 4 H, Ar H), 4.54 (s, 4 H, $ArCH_2$), 4.18 (m, 4 H, $ArOCH_2$), 3.78–3.60 (m, 20 H, CH_2CH_2), 2.42 (s, 6 H, $ArCH_3$).

General Procedure for the Synthesis of Crown Ethers 8, 10, 11, and 12. A suspension of 10.0 mmol of the ditosylate (**14d** or **16b**), 10.0 mmol of the bisphenol (**15a** or **15b**), and 40 mmol of CsF (dried prior to use over P_2O_5 under vacuum at 120 °C) in 100 mL of dry acetonitrile was stirred at reflux temperature for 20 h under nitrogen. The suspension was filtered from salts and concentrated in vacuo.

Dibenzo-27-crown-9 (8) was prepared from bisphenol **15a** and hexa(ethylene glycol) ditosylate (**14d**) according to the general procedure. Purification of the product was accomplished by chromatography on silica gel (ethyl acetate–ethanol, 10%) to give an oil in a yield of 28%: 80 MHz ^{1}H NMR ($CDCl_3$) δ 6.93 (s, 8 H, Ar H), 4.38 (s, 4 H, $ArOCH_2CH_2OAr$), 4.24–4.12 (m, 4 H, $ArOCH_2$), 3.89–3.60 (m, 22 H, CH_2CH_2); ^{13}C NMR δ 149.2 (s) and 148.9 (s) (Ar C-1 and Ar C-2), 121.8, 121.5, 115.6 and 115.3 (d, Ar C-3–Ar C-6), 70.9–68.3 (t, CH_2); mass spectrum, m/e 492.240 (M^+, calcd 492.236). Compound **8** was analyzed as the corresponding guanidinium perchlorate complex.

1,3-Xylyldibenzo-27-crown-8 was prepared according to the general procedure from bisphenol **15a** and ditosylate **16b**. Purification of the product was accomplished by chromatography on silica gel ($CHCl_3$–EtOH, 6%) to give a solid in a yield of 68%: mp 53.0–54.0 °C (diisopropyl ether); 80 MHz ^{1}H NMR ($CDCl_3$) δ 7.39 (s, 1 H, Ar H), 7.35–7.10 (m, 3 H, Ar H), 6.9 (s, 8 H, Ar′ H), 4.51 (s, 4 H, $ArCH_2$), 4.29 (s, 4 H, $Ar'OCH_2CH_2OAr'$) 4.21–4.07 (m, 4 H, $ArOCH_2$), 3.9–3.5 (m, 12 H, CH_2CH_2); ^{13}C NMR δ 149.0 and 148.7 (s, Ar′ C-1 and Ar′ C-2), 138.3 (s, Ar C-1 and Ar C-3), 127.9, 126.8 and 126.6 (d, Ar C-2, Ar C-4–Ar C-6), 121.7, 121.4, 115.5 and 115.0 (d, Ar′ C-3–Ar′ C-6), 72.8–67.6 (t, CH_2); mass spectrum, m/e 524.241 (M^+; calcd 524.241). Anal. Calcd for $C_{30}H_{36}O_8$ (M_r 524.61): C, 68.69; H, 6.92. Found: C, 68.40; H, 6.95.

Dibenzo-30-crown-10 (11) was prepared from the bisphenol **15b** and ditosylate (**14d**) according to the general procedure. Purification of the product was accomplished by chromatography on silica gel (ethyl acetate–ethanol, 10%) to give a solid in a yield of 41%: mp 98–104 °C; 80 MHz ^{1}H NMR ($CDCl_3$) δ 6.90 (s, 8 H, Ar H), 4.25–3.6 (m, 32 H, CH_2CH_2); ^{13}C NMR δ 149.1 and 148.8 (s, Ar C-1 and Ar C-2), 121.6, 121.4, 115.2 and 114.5 (d, Ar C-3–Ar C-6), 70.8–69.0 (t, CH_2); mass spectrum, m/e 536.267 (M^+; calcd 536.262). The compound was analyzed as its guanidinium perchlorate complex.

1,3-Xylyldibenzo-30-crown-9 (12) was prepared according to the general procedure from the bisphenol **15b** and the ditosylate **16b**. Purification of the product was accomplished by chromatography on silica gel ($CHCl_3$–ethyl acetate, 50%) in a yield of 50%: mp 78–80 °C; 80 MHz ^{1}H NMR ($CDCl_3$) δ 7.37 (s, 1 H, Ar H), 7.30–7.13 (m, 3 H, Ar H), 6.90 (s, 8 H, Ar′ H), 4.55 (s, 4 H, $ArCH_2$), 4.16–4.07 (m, 8 H, $ArOCH_2$), 3.9–3.6 (m, 16 H, CH_2CH_2); ^{13}C NMR δ 149.1 and 148.9 (s, Ar′ C-1 and Ar′ C-2), 138.4 (s, Ar C-1 and Ar C-3), 128.1, 126.9 and 126.7 (d, Ar C-2 and Ar C-4–Ar C-6), 121.6, 121.4, 115.6 and 114.5 (d, Ar′ C-3–Ar′ C-6), 73.0–68.8 (t, CH_2); mass spectrum, m/e 568.270 (M^+; calcd 568.267). Anal. Calcd for $C_{32}H_{40}O_9$ (M_r 568.663): C, 67.58; H, 7.09. Found: C, 67.55; H, 7.02.

Dibenzo-33-crown-11 (13). To a stirred refluxing solution of 3.3 g (10 mmol) of bisphenol **15c** and 2.2 g (20 mmol) of KO-*t*-Bu in 100 mL of dry THF under nitrogen was added during

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Table V. Data-Collection Parameters for 1:1 Complexes between Guanidinium Perchlorate and Three Different Crown Ethers

host	benzo-27-crown-9	dibenzo-27-crown-9	dibenzo-30-crown-10
formula	$C_{23}H_{42}O_{13}N_3Cl$	$C_{27}H_{42}O_{13}N_3Cl$	$C_{29}H_{46}O_{14}N_3Cl$
lattice type	orthorhombic	orthorhombic	triclinic
space group	*P*bca	$P2_12_12_1$	$P\bar{1}$
T, K	156	146	218
cell dimensions: *a*, Å	28.397 (5)	24.655 (2)	13.016 (9)
b, Å	8.633 (2)	14.529 (3)	12.741 (4)
c, Å	23.495 (5)	8.633 (2)	10.884 (4)
α, deg	90.0	90.0	91.60 (4)
β, deg	90.0	90.0	93.68 (7)
γ, deg	90.0	90.0	112.88 (4)
V, $Å^3$	5759.83	3092.42	1656.78
Z	8	4	2
D_{calcd}, g cm^{-3}	1.397	1.404	1.399
radiation (graphite monochromated)	Cu Kα	Cu Kα	Mo Kα
μ, cm^{-1}	1.78	1.71	0.20
Θ range, deg	$2 < \Theta < 74.5$	$3 < \Theta < 65$	$3 < \Theta < 25$
no. of unique reflctns measd	5121	2986	5819
no. of reflctns with $I > \sigma(I)$	4373	2807	4517
final no. of variables	530	542[a]	609
final *R*, %	7.5	5.8	6.5
final R_w, %	7.7	6.7	6.8

[a] Six crown hydrogens could not be determined and were not used in refinement.

1 h 5.9 g (10 mmol) of ditosylate **14d** in 50 mL of dry THF. The mixture was stirred and refluxed for another 48 h. Purification was accomplished by chromatography on alumina (ethyl acetate) to give almost pure product in a yield of 40%. An analytical sample was obtained by chromatography on silica gel (ethyl acetate–ethanol, 10%): mp 30–31 °C; ^1H NMR ($CDCl_3$) δ 6.89 (s, 8 H, Ar H), 4.25–4.08 (m, 8 H, $ArOCH_2$), 3.95–3.63 (m, 28 H, CH_2CH_2); ^{13}C NMR δ 148.7 (s, Ar C-1 and Ar C-2), 121.3, 114.6 and 114.3 (d, Ar C-3–Ar C-6), 70.8–68.7 (t, CH_2); mass spectrum, *m/e* 580.283 (M^+; calcd 580.288). Anal. Calcd for $C_{30}H_{44}O_{11}$ (M_r 580.67): C, 62.05; H, 7.64. Found: C, 62.05; H, 7.77.

Extraction Experiments. $CDCl_3$ (1 mL) containing 0.5 mmol of crown ether and 1 mL of an aqueous solution containing 0.5 mmol of guanidinium sulfate and 1.0 mmol of lithium perchlorate were agitated for about 3 h. The $CDCl_3$ layer was separated off and subsequently dried over molecular sieves (4 Å). The ratio of crown ether: guanidinium perchlorate in the chloroform phase was determined from the intensities in the ^1H NMR spectra (chemical shift guanidinium cation ~6.9 ppm). The extraction conditions are stated in a ratio with three numbers: the first number corresponds with the concentration of the crown ether in deuteriochloroform in mmol/mL, the second number corresponds with the concentation of guanidinium cations in water in mmol/mL, and the third number corresponds with the concentration of lithium perchlorate in water in mmol/mL. Conditions A, B, and C refer to ratios of (0.5:1.0:1.0), (0,5:2.0:2.0), and (0.5:4.0:4.0), respectively.

Solid Crown Ether–Guanidinium Perchlorate Complexes. 18-Crown-6–GuClO$_4$ (1:2) crystallized from the aqueous layer after extraction (condition A) in a yield of 20% and at the interface (condition B) during extraction in a yield of 60%: mp 170–171 °C (EtOH); ^1H NMR (Me_2SO-d_6) δ 6.93 (s, 12 H, NH_2), 3.55 (s, 24 H, OCH_2).

Anal. Calcd for $C_{14}H_{36}N_6O_{14}Cl_2$ (M_r 583.376) C, 28.82; H, 6.22; N, 14.41; Cl, 12.15. Found: C, 27.83; H, 6.08; N, 14.52; Cl, 12.00.

Benzo-18-crown-6–GuClO$_4$ (1:1) precipitated at the interface during extraction in a yield of 65%: mp 153–154 °C (EtOH); ^1H NMR (Me_2SO-d_6) δ 6.94 (s, 10 H, Ar H and NH_2), 4.15–4.04 (m, 4 H, $ArOCH_2$), 3.84–3.73 (m, 4 H, $ArOCH_2CH_2$), 3.62 (s, 8 H, OCH_2), 3.56 (s, 4 H, OCH_2).

Anal. Calcd for $C_{17}H_{30}O_{10}N_3Cl$ (M_r 471.891): C, 43.27; H, 6.41; N, 8.90; Cl, 7.51. Found: C, 43.20; H, 6.38; N, 8.90; Cl, 7.55.

Benzo-27-crown-9–GuClO$_4$ (1:1) was obtained in quantitative yield from the organic phase after the solvent was removed under reduced pressure: mp 113–114 °C (EtOH); ^1H NMR ($CDCl_3$) δ 6.94 (s, 4 H, Ar H), 6.76 (s, 6 H, NH_2), 4.35–4.15 (m, 4 H, $ArOCH_2$), 4.01–3.68 (m, 28 H, OCH_2).

Anal. Calcd for $C_{23}H_{42}O_{13}N_3Cl$ (M_r 604.05): C, 45.73; H, 7.01; N, 6.96; Cl, 5.87. Found: C, 45.69; H, 6.97; N, 6.87; Cl, 5.86.

Dibenzo-27-crown-9-GuClO$_4$ (1:1) was obtained in a quantitative yield from the organic phase after the solvent was removed under reduced pressure: mp 140–141 °C (EtOH); ^1H NMR ($CDCl_3$) δ 6.96 (s, 8 H, Ar H), 6.76 (s, 6 H, NH_2), 4.46 (s, 4 H, $ArOCH_2CH_2OAr$), 4.26–4.14 (m, 4 H, $ArOCH_2$), 3.97–3.64 (m, 20 H, OCH_2).

Anal. Calcd for $C_{27}H_{42}O_{13}N_3Cl$ (M_r 652.09): C, 49.73; H, 6.49; N, 6.44; Cl, 5.44. Found: C, 49.75; H, 6.56; N, 6.37; Cl, 5.44.

Dibenzo-30-crown-10-GuClO$_4$ (1:1) was obtained in quantitative yield from the organic phase after the solvent was removed under reduced pressure, mp 122.5–123.5 °C (EtOH/$CHCl_3$ 1%); ^1H NMR ($CDCl_3$) δ 6.92 (s, 8 H, Ar H), 6.64 (s, 6 H, NH_2),4.24–4.14 (m, 8 H, $ArOCH_2$), 4.05–3.65 (m, 24 H, OCH_2).

Anal. Calcd for $C_{29}H_{46}O_{14}N_3Cl$ (M_r 696.15): C, 50.04; H, 6.66; N, 6.04; Cl, 5.09. Found: C, 49.91; H, 6.66; N, 5.92; Cl, 5.01.

X-ray Diffraction. X-ray measurements were performed on a single-crystal diffractometer (Philips PW 1100) using the Θ–2Θ scanning mode. The most important data-collection parameters are presented in Table V. 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[40] and refined by full-matrix least-squares analysis,[41] using reflections having an intensity greater than the estimated standard deviation from counting statistics. For the complexes of guanidinium perchlorate with benzo-27-crown-9 (**7**) and with dibenzo-30-crown-10 (**11**) all hydrogens could unambigiously be located from difference-Fourier maps; for the complex with dibenzo-27-crown-9 (**8**) however, the positions of six crown hydrogens could not be determined, due to partial disorder in the crown ether ring.

Parameters refined were the overall scaling factor, isotropic secondary extinction parameter, positional parameters of all atoms, anisotropic thermal parameters for heavy 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 heavy atoms were taken from International Tables for X-ray Crystallography;[42] for H the scattering factors of Stewart, Davidson, and Simpson[43] were used. No absorption corrections were applied.

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Registry No. **1**, 17455-13-9; **1**–GuClO$_4$ (1:2), 87586-40-1; **2**, 14098-24-9; **2**–GuClO$_4$ (1:1), 87586-41-2; **3**, 14187-32-7; **4**, 53914-83-3; **5**, 72216-45-6; **6**, 14174-09-5; **7**, 63144-76-3; **7**–GuClO$_4$ (1:1), 82243-20-7; **8**, 61260-08-0; **8**–GuClO$_4$ (1:1), 87586-42-3; **9**, 57436-40-5; **10**, 87586-43-4; **11**, 17455-25-3; **11**–GuClO$_4$ (1:1), 87586-44-5; **12**, 87586-45-6; **13**, 87586-46-7; **14a**, 2615-15-8; **14b**, 5617-32-3; **14c**, 5117-19-1; **14d**, 42749-27-9; **14e**, 69502-27-8; **14f**, 57436-38-1; **15a**, 20115-81-5; **15b**, 23116-94-1; **15c**, 68822-97-9; **16a**, 87586-47-8; **16b**, 87597-01-1; CsF, 13400-13-0; triethylene glycol dichloride, 112-26-5; diethylene glycol, 111-46-6; guanidinium sulfate, 594-14-9; guanidinium cation, 25215-10-5; 1,3-bis(bromomethyl)benzene, 626-15-3.

Supplementary Material Available: Lists of anisotropic thermal parameters for heavy atoms and isotropic thermal parameters for hydrogens, positional parameters for all atoms, as well as complete lists of bond lengths, bond angles, and torsion angles (40 pages). Ordering information is given on any current masthead page.

Carbon-13 NMR Spectroscopic Study of Substituted Anthracene Dications[1]

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A series of substituted anthracenes (**2–10** and **20–21**) were oxidized by SbF_5/SO_2ClF at 0 to −30 °C to their dications (**11–19** and **22–23**), which were observed by carbon-13 NMR spectroscopy. In the studied anthracene dications substantial positive charge was found to be localized at C_9 and C_{10} positions. Methyl substitution in these dications was found to deshield the α-carbons as compared to their shielding effect in the corresponding monocations. The proportionality factor of ^{13}C chemical shift to electron density was found to be 174.1–217.0 ppm/e$^-$, clearly proving the dicationic nature of the ions.

Introduction

Polycyclic aromatic hydrocarbons continue to be the subject of extensive research, significantly due to their carcinogenic activity. Experimental evidence for the chemical binding of polycyclic aromatic hydrocarbons to cellular constituents was known as early as the 1940s. In the subsequent years ample evidence has been obtained indicating that polycyclic arenes bind to proteins, DNA, and RNA. A critical problem is to learn what site in the cell is involved in interaction with the carcinogen and the nature of the binding. A number of alternate possibilities are considered including protein binding and nucleic acid binding. Arene oxides have also been postulated as the intermediates in the metabolism of aromatic hydrocarbons. Evidence has been accumulating that most chemical carcinogens act as strongly electrophilic agents or are concerted in vivo to electrophilic agents by metabolic action.[2] This leads to the possibility of involvement of carbocationic reactive intermediates derived from arenes, as potential electrophiles of carcinogenic activity. As part of our continuing investigation of potential biological alkylating agents of carbocationic nature, we continued to study the in vitro chemical conversion of model polyarenes, such as substituted anthracenes to carbocationic species. In the present study we report their two electron oxidation to their related carbodications and the study of their structure by ^{13}C NMR spectroscopy to determine the charge distribution pattern which in turn shows the sites of highest possible electrophilic reactivity.

The ability of superacids to protonate, as well as in certain cases oxidize unsaturated hydrocarbons to produce carbocations and dications is well established.[3] A combination of the nature of the unsaturated hydrocarbon and the superacid used has been found to have a profound effect on the formation of carbocations.[4,5] It is well-known that polynuclear aromatic hydrocarbons such as perylene, naphthacene, and anthracene are oxidized to their monopositive radical ions by strong acids.[6] Dipositive ions of aromatic systems have been observed in electrochemical oxidations[7] and have been implicated as intermediates in reactions of radical cations[8–10] and in ESR studies of stable radical cations.[11] The generation of arene dications from arenes in strong acid media has been reported for naphthacene by SO_3 in dimethyl sulfate[6c] and for naphthacene and 1,2-benzanthracene by $FSO_3H–SbF_5$.[12] The unusual hexachlorobenzene dication[13] has been generated in $SbF_5–Cl_2$ at low temperature. More recently, tetramethylnaphthalene and octamethylnaphthalene were oxidized to their corresponding dications in $SbF_5–SO_2ClF$.[14]

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