Tetrahedron Vol. 34, pp. 2757–2761

0040–4020/78/0915–2757/$02.00/0

CHELATION OF CARBOCATIONS BY POLYETHERS AND POLYAMINES

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(*Received in UK* 2 *August* 1977; *Accepted for publication* 9 *March* 1978)

Abstract—Chelates formed by carbocations and cyclic polyethers and polyamines are studied with semiempirical and *ab initio* MO methods.

Carbon atoms with a coordination number higher than four have received considerable attention.[1–5] A possibility for their formation is provided by the chelation of a carbocation by compounds possessing more than one suitably placed electronegative atom.[6]

Theoretical approaches to chemical structure open the possibility of studying molecules at present not available to the experimentalist, in the hope of uncovering features which might promote their syntheses.[7] In this report we present the results of MO calculations on chelation of carbocations by cyclic polyethers and polyamines.

Methods

While the CNDO/2 method[8] was employed with the full systems, the use of *ab initio* methods[9] was restricted to model systems and to compounds **1** and **2**.

CNDO/2 studies. The reliability of the CNDO/2 results in this particular application was assured by the following facts:

(i) a plot of calculated binding energies vs experimental heats of atomization (obtained from heats of formation)[10,11] of carbocations related structurally to the chelates, gave a linear relationship with a correlation coefficient of 0.995;[a]

(ii) calculations on conformations of cyclohexane, 1,4-dioxane and 1,4-piperazine[12] successfully reproduced experimental trends as well as sophisticated MO and molecular mechanics calculations, and

(iii) CNDO/2 results[5] paralleled sophisticated *ab initio* results[13] for structurally related carbocations such as CH_5^+.

Full geometry optimization[14] was achieved in cyclohexane and cycloheptane derivatives. Geometry optimization in the crown ether compounds however, was carried out after imposing the following symmetry constraints: local C_3 on the Me moiety and local C_n on the crown ether moiety with n equal to the number of O atoms in the ether.

Ab initio *Studies.* Extensive *ab initio* calculations were carried out on positively charged species.[15] It was concluded that geometries and relative energies calculated tended to approach experimental values as the size of the basis set employed was increased and polarization functions were introduced.[15,16] A satisfactory basis set for carbocations was the STO/4-31G one with geometry optimization. The size of our systems however, demanded a less ambitious compromise.

Calculations with the STO-3G basis set and full geometry optimization were carried out on model compounds where the 6-membered rings were replaced by a 4-atom linear chain (compare **1** with **6**, **2** with **7** and **3** with **8**). The energies, relative to the onium compounds (**6** or **1**), from the model calculations were expected to parallel those from calculations on the whole systems, since the former suffered mainly from the exclusion of a fairly constant strain energy due to the bicyclic ring system in the chelates. For some compounds, single calculations at the STO/4-31G level were then performed at the STO-3G optimized geometries.

Compounds **1** and **2** were studied in some detail. First, their geometries were optimized at the STO-3G level, subject only to the constraints of local C_3 symmetry on the Me group and local C_{2h} symmetry in the ring of **1** and C_{2v} in that of **2**. Calculations were then performed with the extended STO/4-31G basis set at the STO-3G optimized geometries, and finally some selected parameters in species **2** were optimized at the 4-31G level.

RESULTS AND DISCUSSION

Cyclohexane derivatives. The most stable conformation of 1-methyl-1,4-dioxanium ion, **1a**, was chosen as reference.

Cation **2a** was shown to correspond to the transition state for Me migration between **5a** and its mirror image. Thus, when the condition that the Me group should lie above the center of the ring was relieved, the molecule fell into the potential of **5a**.

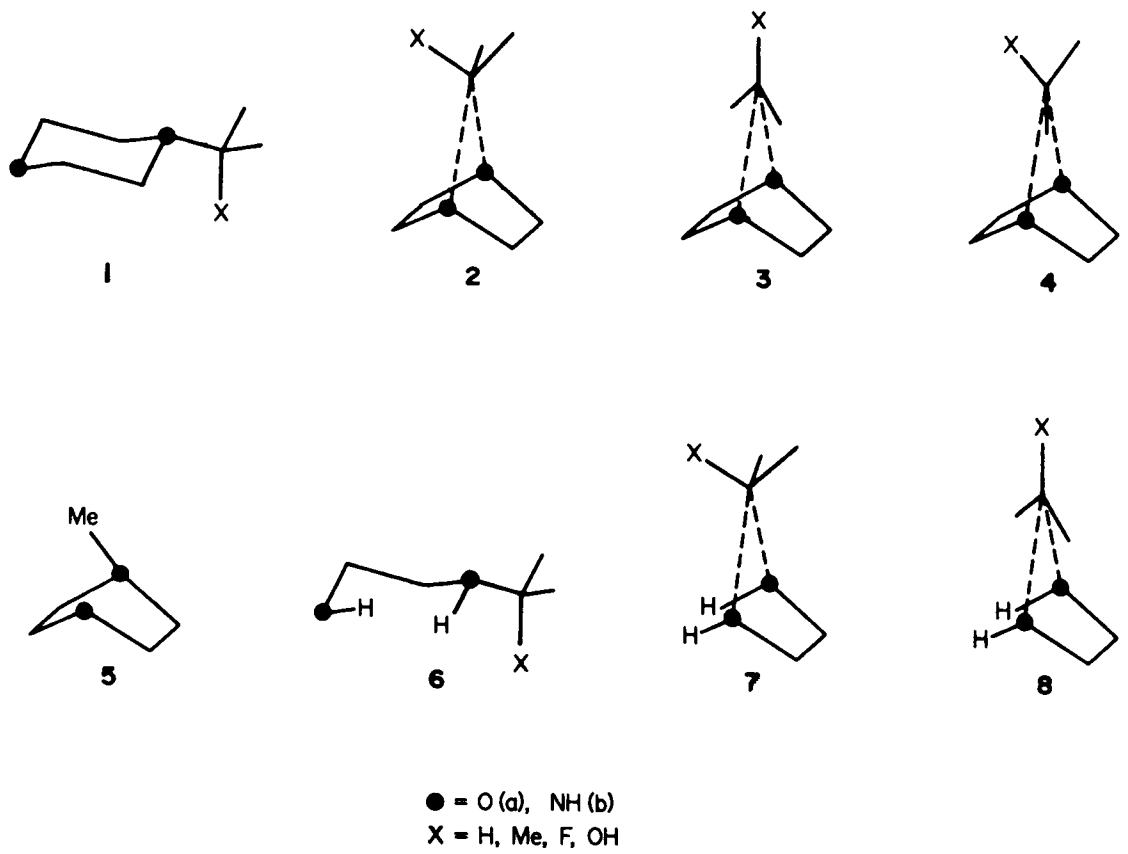
While in **3a** and **4a** the carbocation moiety retained its preferred (in the gas phase) planar conformation, steric repulsions created by the H atoms pointing into the ring and smaller C–O overlap made these species unstable relative to **2a**.

By analogy with cyclohexane, the interconversion of **1a** and **5a** proceeded through a transition state higher in energy than **1a** by about 11 kcal/mol.[b]

The energy difference between chair/equatorial and boat/flagpole methylcyclohexane was calculated to be 5.0 kcal/mol. In the 1,4-dioxane case, the energy difference **5a**–**1a** was only 0.7 kcal/mol, indicating the importance of the interaction between the Me group and the O atom in the 4-position.[18] This effect is presumably the origin of smaller endocyclic angles in the O compound (Fig. 1).

[a]The species included in the plot are Me^+, Et^+, i-Pr^+, t-Bu^+, c-$C_5H_{11}^+$, CH_2F^+, CHF_2^+, $MeOCH_2^+$, $Me_2NCH_2^+$, $(OH)_2CH^+$ and MeO^+. The energies discussed below were extrapolated from this line.

[b]The symmetrical mode of interconversion between chair and boat cyclohexane was calculated by molecular mechanics to be 11.3 kcal/mol.[17] A CNDO/2 calculation gave a value of 9.7 kcal/mol.



The results presented are summarized in Fig. 2.

When the O atoms were replaced by NH groups, the energy difference **2–1** was lowered by 2.2 kcal/mol, reflecting the increased ring puckering of the parent heterocycles[19] which favoured preferentially species with small bonding angles. In addition, the energy difference **5b–1b** was −0.6 kcal/mol, due to the higher basicity of N over O.

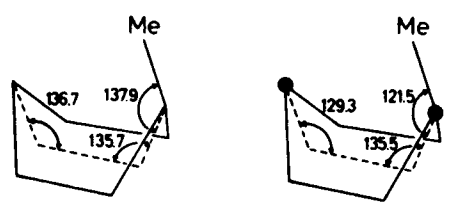


Fig. 1. Comparison between boat/flagpole methylcyclohexane (a) and 1-methyl-1,4-dioxanium ion (b).

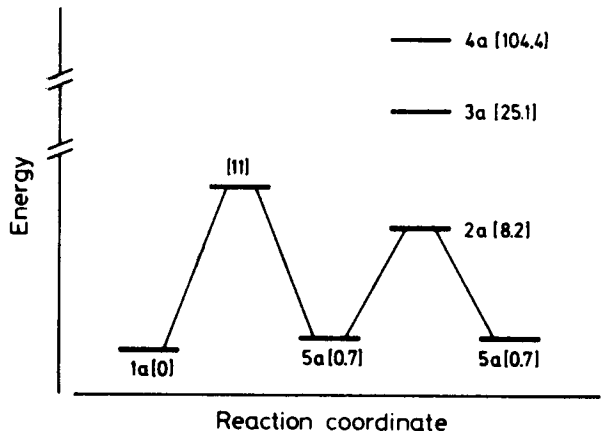


Fig. 2. Energy profile for 1-methyl-1,4-dioxanium ion. Numbers in parentheses are CNDO/2 energies (kcal/mol) relative to **1a**.

Substituent effects were studied through isodesmic reactions.[20] The energies for reaction 1 were calculated

$$CH_2X^+ + CH_4 \xrightarrow{E(1)} CH_3^+ + CH_3X \qquad (1)$$

for a series of groups X.[21] Positive values obtained for Me, F and OH[c] indicated that these substituents stabilized preferentially the cation over the neutral molecule.

In our systems substituent effects could be studied through the isodesmic reaction (2), where species **1** was taken as a model for the hydrocarbon since the charge in it was less concentrated on the Me group (see below).

$$\mathbf{2}(X) + \mathbf{1}(H) \xrightarrow{E(2)} \mathbf{2}(H) + \mathbf{1}(X) \qquad (2)$$

Me, F and OH substituents were found to destabilize **2** relative to **1**.[d] This was due, on one hand, to the absence of resonance effects, which in large part accounted for the greater stability of CH_2X^+ over CH_3^+ in eqn (1), and on the other, from destabilizing inductive and field effects which were greater in **2** than in **1**, as judged from a larger concentration of positive charge in **2** on the C atom bearing the substituent (Fig. 3).

Fluorine substituent effects were studied in model compounds. The STO-3G energy calculated for eqn (3),[e] analogous to

$$\mathbf{7}(F) + \mathbf{6}(H) \xrightarrow{E(3)} \mathbf{7}(H) + \mathbf{6}(F). \qquad (3)$$

Equation (2), was 5.4 kcal/mol, indicating that fluorine stabilized **7** more than **6**. However, small basis sets were shown to overemphasize the stabilizing properties of fluorine towards carbocationic centers.[21] When the STO/4-31G basis set was employed, E(3) reduced to −0.5 kcal/mol, a result qualitatively similar to the CNDO/2 result for the whole system.

[c] E(1) = 30.9, 32.1 and 66.0 kcal/mol respectively with the STO-3G basis set and 29.9, 2.1 and 47.8 kcal/mol with the STO/4-31G basis set.

[d] E(2) = −4.4, −0.2 and −3.0 kcal/mol, respectively.

[e] If the oxygen centers in **7** were made planar, as in **9**, energy decreased by *ca.* 12 kcal/mol, reflecting the π interaction between the O atoms and the adjacent C atoms. These molecules however, did not bear a direct geometrical resemblance to our systems.

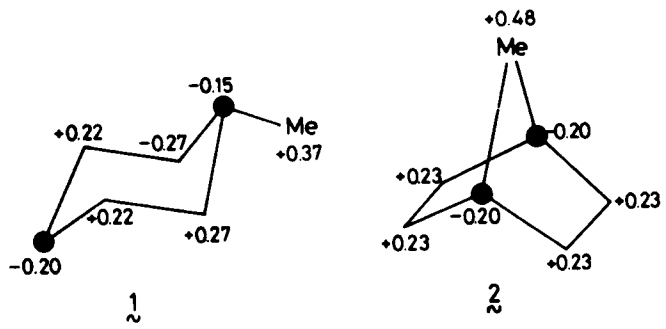


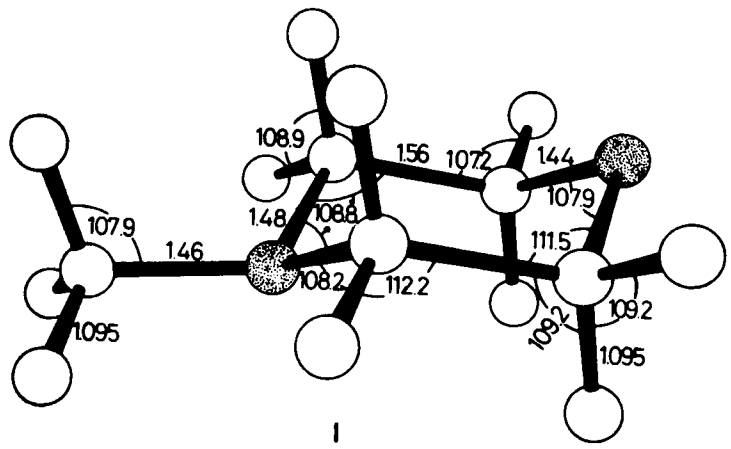
Fig. 3. Charge distributions for the STO-3G optimized structures of **1** and **2**. The figures shown correspond to the summation of charges of the heavy atom and its attached hydrogen atoms.[22]

When eqn (4) was considered, F with both basis sets

$$\mathbf{8}(F) + \mathbf{6}(H) \xrightarrow{E(4)} \mathbf{8}(H) + \mathbf{6}(F) \qquad (4)$$

stabilized **8** relative to **6**.[f] This resulted from the possibility of direct conjugation with the carbocationic center of **8(F)**.

Complete geometry optimization of **1** and **2** at the STO-3G level resulted in structures depicted in Fig. 4. The energy difference **2–1** was 78.7 kcal/mol. However the lack of flexibility of this basis set led to an overestimation of bond angle strain and hence to destabilization



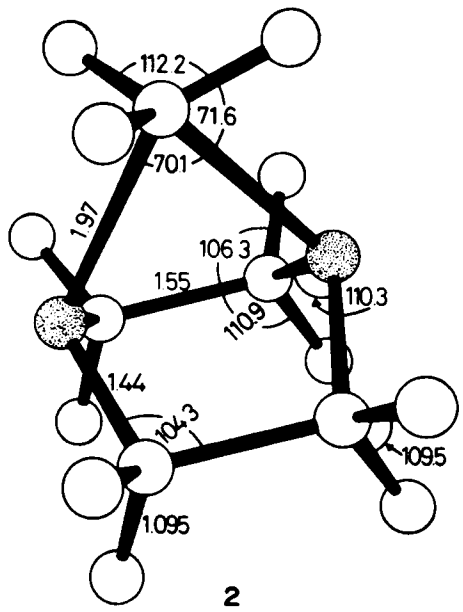


Fig. 4. STO-3G optimized geometries of **1** and **2**.

[f] E(4) = 18.8 kcal/mol (STO-3G); E(4) = 22.6 kcal/mol (STO/4-31G).

[g] The sum of the squares of the coefficients of the carbocationic center in the LUMO of **1** is 0.396, to be compared with 0.960 in **2**. Furthermore, the LUMO of **2** is lower in energy than that of **1** by 0.133 atomic units.

[h] The position of the O atoms was chosen in a way such that Me substitution creates the least steric hindrance.

of **2** relative to **1**.[16] Consequently, when the STO/4-31G basis set was employed at the STO-3G optimized geometries, the energy difference dropped to 56.7 kcal/mol. A further drop of 5.0 kcal/mol occurred when optimization at the STO/4-31G level of some parameters involved in the bond angle strain of **2** (**10**) was performed. Presumably full optimization employing a larger basis set would result in a still smaller **2–1** energy difference.

The strongest interactions between solvent and species **1** and **2** were predicted to occur in the vicinity of the carbocationic center, with the largest share of positive charge (Fig. 3). Ion-dipole interactions, which have been shown to be of predominant importance in the solvation of monoatomic ions,[23,24] were predicted to stabilize **2** more than **1** since the charge was more localized in the former ion (Fig. 3). Charge transfer effects, calculated with a simple PMO model based on the interaction of the LUMO of the carbocation with the HOMO of the solvent, have been shown to account for the solvation energies of a variety of carbocations.[25] This model applied to **1** and **2** also predicts the latter species to be preferentially solvated.[g] The two effects mentioned are partly compensated by the slightly greater steric hindrance to the approach of solvent to the positive center in **2** than in **1**.

The association of triphenylmethyl cation with several linear and cyclic ethers and acetals has recently been studied.[26] Linear correlations were reported between the equilibrium constants and the basicities of the ethers on the one hand and between $\Delta H°$ and $\Delta S°$ on the other. 1,4-Dioxane was found to fit into these correlations thus suggesting a behaviour towards corrdination to the cation similar to that of the other ethers studied. This undoubtedly reflects the bulkiness of the phenyl groups which makes arrangements such as **2–4** improbable.

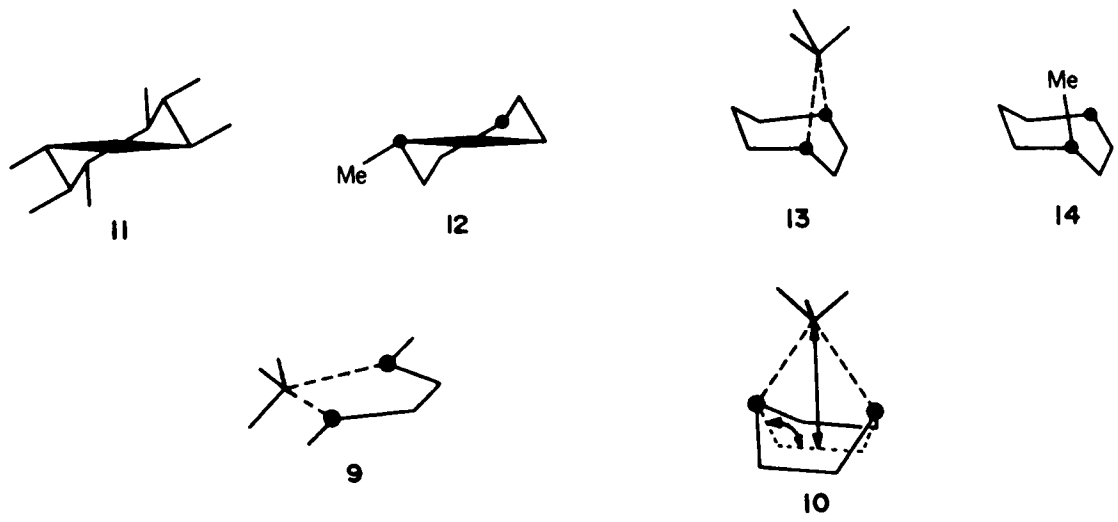
Precedents exist however for the formation of intermediates analogous to **2**. Thus the shift of the chair ⇄ boat equilibrium in 1,4-dioxane towards the boat form in the presence of the field of strong dipoles has been postulated.[27]

Cycloheptane derivatives. The species to be compared are the more stable conformation of 1-Me-1,4-dioxacycloheptane and a species permitting bridging across the O atoms by the Me group. By analogy with cycloheptane, where the C_2 twist-chair form is the more stable[28,29] and where the preferred sites for monosubstitution are the equatorial 2, 3 and 4 positions (**11**),[28,30] species **12** was studied.[h] The bridged species studied was **13**.

The CNDO/2 energy difference **13–12** was 6.9 kcal/mol, which represented a slight improvement over the cyclohexane system. In contrast with the cyclohexane case, there was no high barrier between **12** and **14**, the conformation permitting bridging as in **13**.[28,30]

Crown ethers. The complexation of carbocations by crown ethers has importance from synthetic and mechanistic viewpoints.[31,32] We have studied the interaction of the Me cation with crown ethers by comparing an oxonium species (Me group directly bonded to one O atom) with one in which the Me group lies above the center of the macrocycle (Fig. 5). The crown ethers were constrained to their maxidentate conformation.[33] Results are collected in Table 1.

The macrocycles suffered structural deformations upon complexation which brought the O atoms closer together. Deformations were also observed upon



complexation of simple cations.[36,37] The effect was larger in the smaller cycles where the interactions between the carbocationic center and the O atoms was strongest, as judged from bond order values.

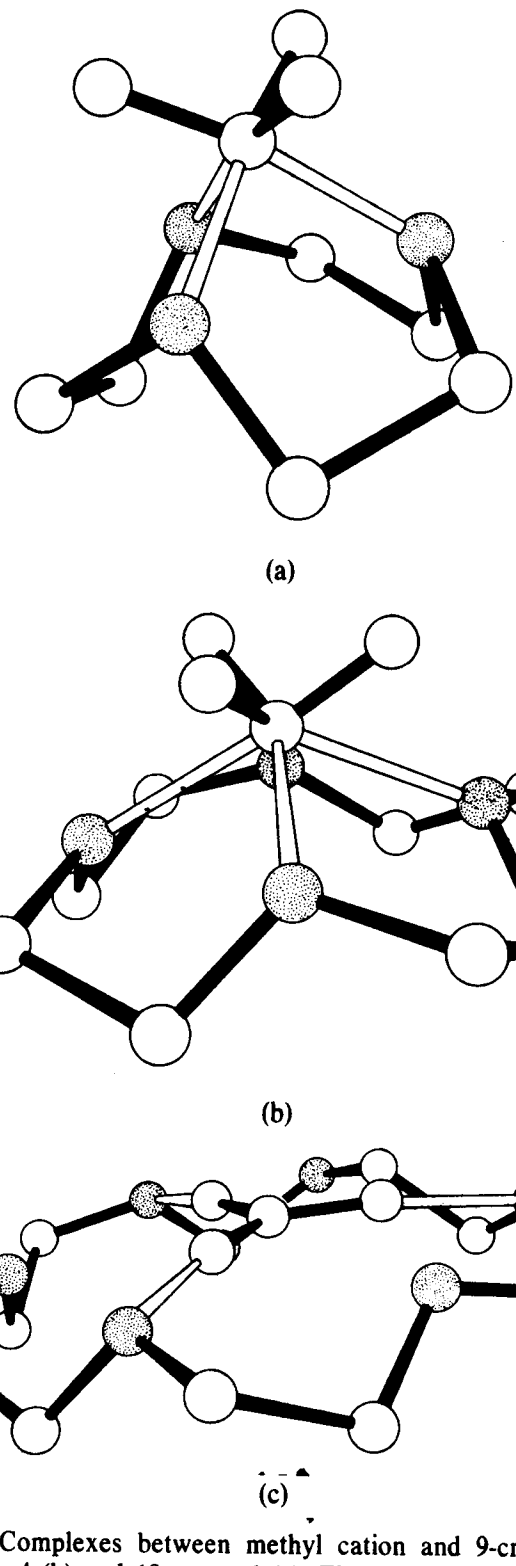


Fig. 5. Complexes between methyl cation and 9-crown-3 (a), 12-crown-4 (b) and 18-crown-6 (c). The oxygen atoms (shaded) share a common plane. The distances from the methyl C atom to any O atom are 1.108 Å (a), 0.811 Å (b) and 0.222 Å (c).

Table 1. Parameters for crown ethers + Me^+ compounds[a]

Crown ether[b]	Center–O[c] Oxonium	Center–O[c] Bridged	ΣC–O_n[d] Bridged	ΔE[e]
9-crown-3	1.559	1.234	1.126	2.3
12-crown-4	1.781	1.543	1.082	36.0
18-crown-6	2.663	2.656	0.018	74.1

[a]Distances in Å, energies in kcal/mol.
[b]For nomenclature, see Ref. 34.
[c]Distance from any O atom to the center of the surface defined by the O atoms.
[d]Summation of bond orders calculated according to Ref. 35.
[e]Energy difference between bridged and oxonium species.

The stronger C–O interactions in smaller rings are reflected in smaller energy differences between bridged and oxonium species. 18-crown-6 is sufficiently large to accomodate within its cavity and without substantial deformations a planar Me cation. The H atoms are then situated at H-bonding distances from O atoms,[38,39] but the species is highly energetic due to the poor electron donation from the O atoms to the carbocationic center.

The results presented suggest that complexation of carbocations in the sense described is favoured by small crown ethers and by substituents in the carbocation which do not create great steric hindrance upon pyramidalization of the central carbon and which do not preferentially stabilize a planar carbocationic species. The use of other electronegative atoms, such as nitrogen, in the crown compound, may also favour complexation.

Acknowledgements—The author wishes to express his gratitude to Prof. H. Dahn for his encouragement and advice, and to Mr. J. Wenger for his invaluable help in the computer programming. The financial support given to Prof. Dahn by the Swiss National Science Foundation (Project No. 2.77272) is gratefully acknowledged.

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