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Complexation of Crown Ethers and Podands with Tropylium Cations: Determination of Stability Constants and Crystal Structure of the Dibenzo-24-Crown-8-Tropylium Cation Complex

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The host–guest complexation of macrocyclic hosts and aromatic carbenium cations has been studied. Three different tropylium tetrafluoroborate compounds were prepared in order to study the interaction between positively charged guests and crown ether hosts. The stability constants of complexes were measured by ^{1}H NMR and UV/Vis spectroscopic methods. Fast atom bombardment mass spectroscopy (FABMS) was used to screen the stoichiometry of complexes. The main interaction force was π–π-stacking and cation–π interaction between aromatic units in benzene-substituted crown ethers and aromatic guests. Additionally, two diphenoxyalkane ligands were prepared to investigate the importance of the macrocyclic ring in the complexation between host and guest.

The X-ray crystal structure of dibenzo-24-crown-8 (2B24C8) with tropylium tetrafluoroborate inclusion complex was determined, giving the following crystal data: 2B24C8–TrBF$_4$ ($C_{31}H_{39}O_8 \cdot 0.5\ CH_3CN \cdot BF_4$), monoclinic, space group $P2_1/n$ (no. 14), $a = 14.158(2)$, $b = 14.791(2)$, $c = 16.384(2)$ Å, $\beta = 93.90(1)$, $Z = 4$. The crystal structure showed that the tropylium ion guest formed an inclusion complex with benzene-substituted crown ethers, and its plane is orientated nearly parallel to the planes of the aromatic nucleus of the host.

Ongoing advances in the development of supramolecular chemistry have stimulated activity in several areas of modern chemistry.[1] The host–guest complexation of macrocyclic compounds has been studied intensively, and the specific binding forces contributing to stable host–guest complexes have attracted considerable interest.[2] Interactions between aromatic units and organic π–π donor–acceptor interactions form a significant type of such forces. They play an important role in molecular recognition, enzyme active sites, ion channels[3,4] and in controlling the conformations and substrate binding properties of nucleic acids and proteins.[5] Recently, the cation–π interaction has received attention as a newly discovered binding force that is important in biological systems.[6] The cation–π interaction is a stabilizing force between a positive charge of the guest and polarizable, electron-rich π-systems of the host.

Our work has focused on host–guest complexation between crown ethers and carbenium ions, especially 1,3,5-cycloheptatrienylium or tropylium ion,[7,8] which is a classical example of an aromatic carbenium cation. It is an effective π-acceptor, as exemplified by the synthesis of many intramolecular charge-transfer complexes.[9] There are also a fairly large number of different double deck phanes and other macrocyclic compounds which have the tropylium unit as a part of their molecular framework.[10–12]

In this work we report the X-ray crystal structure of the host–guest complex of dibenzo-24-crown-8 (2B24C8) with tropylium tetrafluoroborate.[13] The complexation of dibenzo-substituted crown ethers and podands with tropylium ions are studied in solution by ^{1}H NMR and UV/Vis spectroscopic methods and the stability constants for resulting complexes are presented.

Results and discussion

X-Ray crystal structure of the 2B24C8–tropylium complex. We have made efforts to prepare single crystals of several crown ether–tropylium complexes. Unfortunately, only

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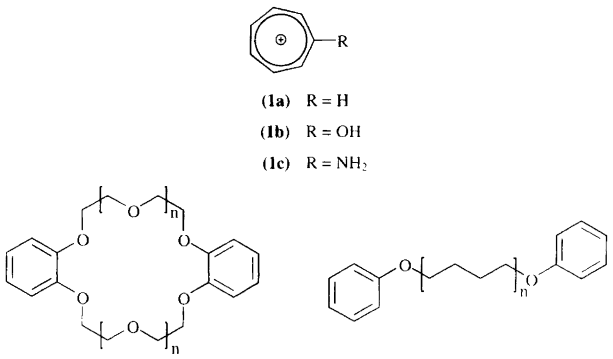

(1a) R = H
(1b) R = OH
(1c) R = NH_2

(2a) n = 1; 2B18C6
(2b) n = 2; 2B24C8

(3a) n = 1
(3b) n = 2

few systems produced suitable crystals for X-ray analysis. The crystal structure of the 2B24C8–tropylium tetrafluoroborate complex is presented in Fig. 1. The benzene rings of crown ether form two planes, and the planar tropylium ion is located between the benzene rings at a van der Waals distance. The plane separation (7.9 Å) between the centroid of two benzene rings corresponds to interplanar separations of about 3.5–4.3 Å between the π-donor and the π-acceptor. The mean mid-point distance between the benzene and the tropylium ring is 4.0 Å. The crystal structure of the 2B24C8–tropylium tetrafluoroborate complex shows that the benzene rings

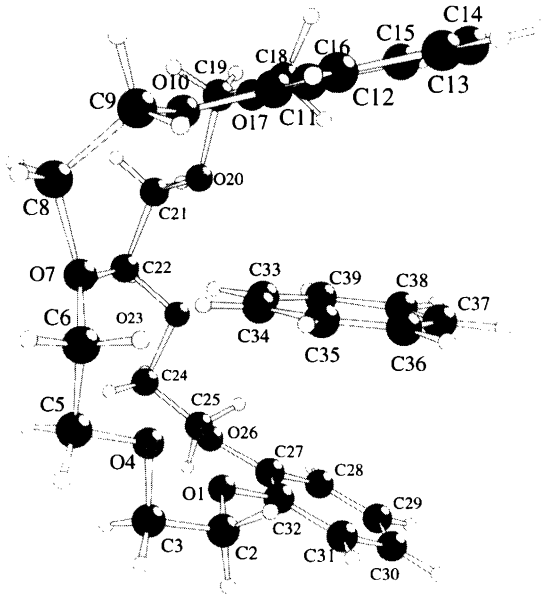

Fig. 1. Ball-and-stick representation of the solid-state structure of the 2B24C8–tropylium cation complex (MeCN and BF_4^- excluded). The distances between the atoms in tropylium and the benzene rings have the following values: C(33)–C(16) 3.525; C(33)–C(27) 5.561; C(39)–C(11) 4.712; C(39)–C(32) 3.617; C(33)–C(16) 3.525; C(34)–C(11) 3.391; C(34)–C(16) 3.378; C(37)–C(13) 4.656; C(37)–C(14) 4.174; C(37)–C(29) 4.644; C(37)C(30) 4.186 Å. The distances between the corresponding atoms in the benzene rings are: C(11)–C(32) 7.155; C(16)–C(27) 7.036; C(13)–C(30) 8.775; C(14)–C(29) 8.732 Å.

are almost parallel with the tropylium ring. The interplanar angles of the electron-deficient and electron-rich rings are 16 and 19°, and the angle between the two benzene rings is 35°. These features are in good accordance with the rules for π–π interactions.[14]

The molecular dimensions of the 2B24C8 ligands are very similar to those expected. The bond lengths of the catechol oxygen atoms are between 1.36 and 1.38 Å, while for the other oxygen atoms the C–O distances are ca. 1.43 Å. The aliphatic CH_2CH_2 bonds are short, 1.46–1.52 Å, but appear to be normal for this type of ligand.[15,16]

The geometry of the tropylium ion in the 2B24C8 complex did not show any localisation of the charge due to complexation. The average value of the seven C–C bond lengths was 1.35 Å, and the bond angles around the seven-membered ring were all close to 128.6° expected for a regular heptagon. X-Ray diffraction studies of tropylium iodide (C_7H_7I) and tropylium perchlorate ($C_7H_7ClO_4$) in the 1960s revealed that both these compounds are ionic and planar with 1.47 Å C–C distances.[17] These experimental C–C bond distances are relatively long, probably due experimental difficulties related to the disorder of the tropylium ion. The bond distance and bond angles of isopropyltropylium hexachloroantimonate and phenyltropylium tetrafluoroborate have also been determined:[18] in both structures the average C–C bond distance in the tropylium rings is 1.38 Å (1.324–1.395 Å) and the angles around the seven-membered rings are all close to 128.6°.

Several attempts have been made to determine the crystal structure of 2B18C6–tropylium tetrafluoroborate complex, which was chemically characterized by elemental analysis, NMR spectra and FABMS spectra (Table 2). The first structure* revealed that the tropylium cation was located symmetrically between the benzene rings. The structure contained no solvent molecule. The tropylium ion was disordered, producing eight electron density peaks instead of seven, and the quality of the structure was low with high *R*-values. The mean mid-point distance between the benzene and tropylium planes was ca. 4.0 Å and the angle 32°. The two facing benzene rings were not parallel, having an angle of ca. 64° between the planes of the rings. Sterical reasons prevented a similar orientation of the benzene rings as in the 2B24C8–tropylium tetrafluoroborate complex (Fig. 1).

Another structure of the 2B24C8–tropylium tetrafluoroborate complex† showed that the π-electron-deficient tropylium ring was not located symmetrically

* Crystal data: 2B18C6–$TrBF_4$ ($C_{27}H_{31}O_6 \cdot BF_4$), formula weight = 538.34, tetragonal, space group $I4$ (no. 79), T = 298 K, a = 13.1260(2), b = 13.1260(2), c = 15.1338(2) Å, β = 90, V = 2607.4 Å^3, Z = 4.

† Crystal data: 2B18C6–$TrBF_4$ ($C_{27}H_{31}O_6 \cdot 2.5\ CH_3CN \cdot BF_4$), formula weight = 620.45, monoclinic, space group $C2/c$ (no. 15), T = 298 K, a = 26.113(3), b = 13.933(1), c = 19.004(2) Å, β = 125.05(2), V = 5590.43 Å^3, Z = 8.

between the benzene rings. The structure contains acetonitrile molecules (disordered) and the cation was partly inserted in the cleft between crown ether benzene rings. The tropylium cation and the other benzene ring were parallel (angle 5°) with an interplanar separation of 3.4 Å and a centroid–centroid distance of 3.7 Å. The second benzene ring formed an angle of ca. 81° with the plane of tropylium ring and the centroid–centroid distance was 5.7 Å. The mean planes of the facing benzene rings were separated by ca. 8.6 Å and they formed an angle of 77°.

Although these structures were unsatisfactory from the crystallographic point of view, the results revealed that large structural variations are possible in the interactions between the cations and benzene rings.

Complexation in solution. NMR spectroscopy has proved to be an efficient technique for the determination of the interactions between macrocyclic hosts and organic guests.[19] The proton spectrum of tropylium tetrafluoroborate consists of a singlet at 9.23 ppm in CD_3CN. When 2B24C8 was added to the solution of tropylium ion in CD_3CN at 25 °C an upfield shift was observed in the resonance of all the seven protons. The chemical shifts of the tropylium protons moved gradually with an increase in the concentration of the crown ether (Fig. 2 is an example). The spectra of substituted tropylium salts are quite complex, with separate multiplets for each pair of hydrogens. The addition of the crown ether shifts these multiplets towards high field. The stability constants for the complexation were calculated directly from the difference in chemical shifts of the H-(1–7) protons (singlet) of tropylium, H-(2/7), H-(3/6) and H-(4/5) protons (multiplet) of substituted tropylium in the crown ether complex and free form, respectively. The stability constants calculated from substituted tropylium H-(2/7), H-(3/6) and H-(4/5) protons corresponded within 5–15%. The largest complexation-induced shift for substituted tropylium was obtained for H-(4/5) protons. The signals of the crown ether did not shift upon complexation. This result was not unexpected, since the concentration of the host was always at least ten times as high as the concentration of the guest. Table 1 presents the stability constants, K, and determined maximum upfield shifts, $\Delta\delta_0$ (i.e. the proton chemical shift difference between free and complexed forms of guest), upon binding in the corresponding crown ether complex.

The substituents of the tropylium ion affected the stability constant. The presence of an electron-withdrawing group in the guest increases the stability of the complex. Substituted tropylium cations form a dipole with a positive charge on the tropylium nucleus in the presence of an electron-withdrawing substituent. The formation of the dipole decreases the electron density in the ring, thus increasing the acceptor ability of the tropylium ring. ^{1}H NMR measurements showed that the tropylium ion formed a complex that was twice as stable with 2B24C8 than with 2B18C6. This confirmed our earlier results[8] that the number of oxygen donors and the size of macrocyclic ring have a significant importance in complex stability.

NMR measurements also afforded useful information about the conformation of the host–guest complexes,

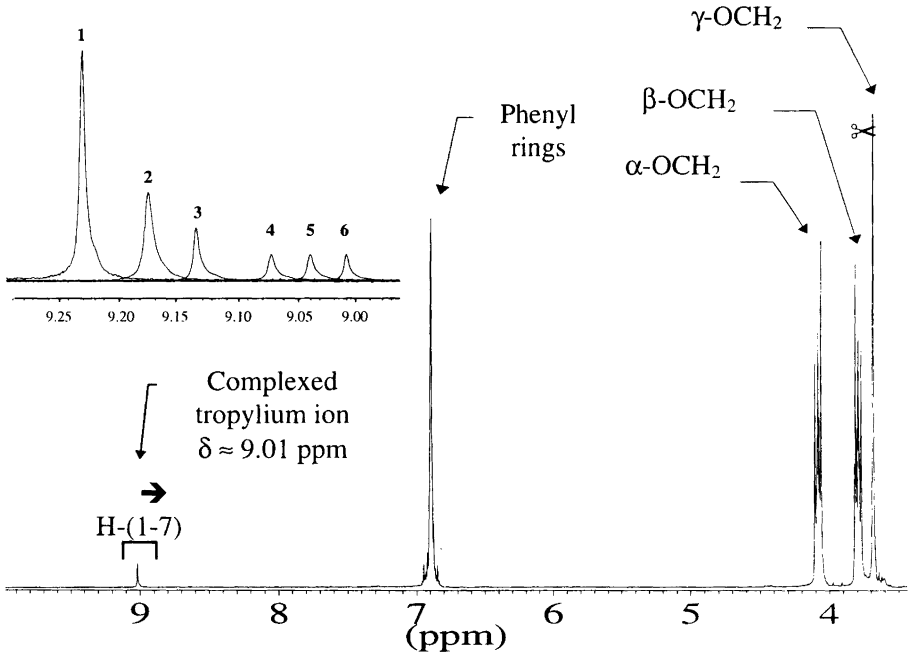

Fig. 2. The ^{1}H NMR spectrum of a mixture of 2B24C8 (0.06 M) and tropylium tetrafluoroborate (4×10^{-4} M) recorded at 200 MHz in CD_3CN at 25 °C. The arrow shows the direction of chemical shift of the tropylium ring protons upon the addition of crown ether {[2B24C8] = (1) 0, (2) 0.01, (3) 0.02, (4) 0.04, (5) 0.05 and (6) 0.06 M} to a solution of tropylium salt (→towards high field). The chemical shift of the uncomplexed tropylium ion is 9.23 ppm.

Table 1. Stability constants (K) and calculated maximum upfield shifts ($\Delta\delta_0$)[a] for the interaction of dibenzo-crown ethers with tropylium ions in CD_3CN solution at 25 °C measured by the ^1H NMR titration method.

Guest	Host	Proton	K/dm^3 mol^{-1}	$\Delta\delta_0$/ppm	r^{2b}
Tropylium [BF_4]	2B24C8	H-(1-7)	10.2 ± 0.3	0.56 ± 0.01	0.9999
	2B18C6	H-(1-7)	5.6 ± 2.8	1.93 ± 1.33[c]	0.9939
Aminotropylium [BF_4]	2B24C8	H-(2/7)	25.2 ± 2.0	0.33 ± 0.02	0.9969
		H-(3/6)	29.8 ± 0.8	0.69 ± 0.01	0.9996
		H-(4/5)	23.0 ± 1.4	0.90 ± 0.04	0.9983
Hydroxytropylium [BF_4]	2B24C8	H-(2/7)	30.4 ± 1.7	0.16 ± 0.01	0.9987
		H-(3/6)	31.8 ± 3.1	0.19 ± 0.01	0.9961
		H-(4/5)	26.4 ± 2.0	0.31 ± 0.01	0.9997

[a] A positive value indicates a shift of the resonance towards high field. [b] Regression correlation (r^2) for the Benesi–Hildebrand plot. [c] The use of eqn. (1) may lead to incorrect values of $\Delta\delta_0$ in systems where the stability constants are small because of an extrapolation.

Table 2. Analytical data and properties of the solid complexes of crown ethers and tropylium ions.

Host–guest (Formulae of complex)	Colour	M.p./°C	λ_{max}/nm (solvent)	Anal. found (required) (%) C	H	N
2B18C6–tropylium [BF_4] ($C_{27}H_{31}O_6BF_4$)	Red	185	340.3, 416.0 (MeCN)	60.24 (61.44)	5.80 (6.31)	
2B24C8–tropylium [BF_4] ($C_{31}H_{39}O_8BF_4$)	Deep red	89 (decomp.)	339.3, 415.5 (MeCN)	59.03 (59.44)	6.46 (6.27)	
2B24C8–hydroxytropylium [BF_4] ($C_{31}H_{39}O_9BF_4$)	Yellow	102	343.2 (MeCN)	57.85 (57.96)	6.26 (6.12)	
2B24C8–aminotropylium [BF_4] ($C_{31}H_{40}O_8NBF_4$)	Orange	54	326.2 (MeCN)	57.68 (58.01)	6.15 (6.29)	1.57 (2.18)

because the induced chemical shift depends mainly on the nearest neighboring interaction. The complexation induces changes in the chemical shifts of the tropylium protons (Table 1), which can be interpreted by the geometry shown in the crystal structure of the 2B24C8–tropylium complex. Recently we have shown that the amino group in the crystal structure of the 2B18C6–aminopyridinium tetrafluoroborate complex was located outside the cleft formed by the benzene rings.[20] This orientation can also be suggested for the aminotropylium complex, since the NH_2 chemical shift showed only a slight change upon complexation.

The electronic spectra of tropylium, hydroxytropylium and aminotropylium tetrafluoroborates in 1,2-dichloroethane (DCE) exhibited absorption maxima at 279, 315 and 328 nm, respectively. The addition of the benzene-substituted crown ethers in the solution of tropylium tetrafluoroborates decreased the absorption at these wavelengths (Table 2). For example, the electronic spectrum of the 2B24C8–tropylium complex (Fig. 3) exhibited a broad long wavelength absorption at 300–450 nm, indicating a charge-transfer interaction between the tropylium ion and the benzene rings in the crown ether. The substantial hypsochromic shift (13 nm) accompanying the change from DCE to MeCN as solvent is in accordance with solvent sensitivity of the charge-transfer

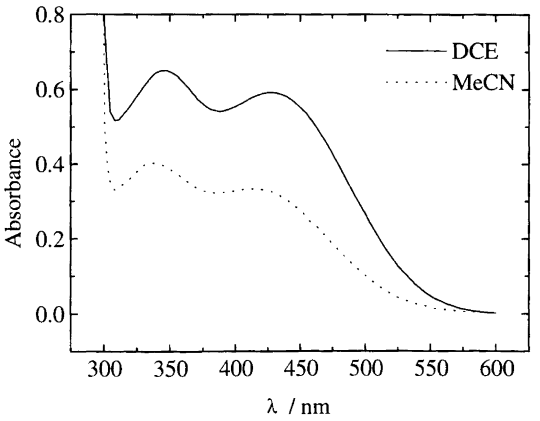

Fig. 3. Absorption spectra of 2B24C8–tropylium tetrafluoroborate complex (6.6×10^{-3} M) in DCE and MeCN solutions at 25 °C.

band.[21] This hypsochromic shift supported the assumption that the absorption is due to an intermolecular charge-transfer transition from the benzene rings to the tropylium ring.

No new absorption bands were observed when benzene-substituted crown ethers were added to the solution of substituted tropylium ion, but the original absorption peak was decreased and broadened towards longer wave-

lengths (Table 2). Because the crown ethers also have very strong absorptions near this region (2B18C6 at 276 nm and 2B24C8 at 277 nm), the NMR titration technique was chosen as the primary method for determining stability constants. However, in many cases the NMR and optical spectroscopic methods support each other, and therefore the stability constants and molar absorptivities were also calculated from UV/Vis spectroscopy data using the method of Rose and Drago.[22] The stability constants for the 2B24C8–tropylium-, –hydroxytropylium and –aminotropylium tetrafluoroborate complexes were 274,[8] 306 and 370 $dm^3 mol^{-1}$ in DCE at 25 °C, respectively. The influence of solvents on the stability constants showed that interactions between crown ethers and tropylium ions were emphasized in a non-polar environment.

The charge-transfer complex between 2B24C8 and 2-dicyanoethylene-1,3-indanedione[23] has a *K*-value of 4.0 $dm^3 mol^{-1}$, and between 2B24C8 and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[24] *K* is 7.5 $dm^3 mol^{-1}$ in dichloromethane (DCM) at 25 °C. The stability constants for the 2B18C6–tetracyanoethylene, –7,7,8,8-tetracyanoquino-dimethane and –chloranil are 3.9, 3.7 and 3.6 $dm^3 mol^{-1}$ in DCM at 25 °C, respectively.[25] A comparison of these values with our present results showed that benzene-substituted crown ethers formed more stable complexes with tropylium ions. The charge-transfer interaction itself between aromatic units, the tropylium ring and benzene substituents was one explanation, and the positive charge of the tropylium ring was another reason for the relatively high values obtained. Furthermore, the cation–π interaction may affect the stability of these host–guest complexes. The major aspect of the cation–π interaction is electrostatic in nature.[6] A complete, quantitative description of the cation–π interaction involves a number of intermolecular forces, such as charge–quadrupole, charge–dipole, charge–induced dipole, charge-transfer and dispersion forces.[6] The cation–π interaction is of enthalpic origin, i.e. the complexation is enthalpically driven.[26] The ^1H NMR measurements of complexation between 2B24C8 and aminotropylium tetrafluoroborate in CD_3CN at three different temperatures revealed similar results. The typical van't Hoff analysis ($R \ln K = -\Delta H^\circ/T + \Delta S^\circ$) gave a value of -11.8 kJ mol^{-1} for ΔH° and -14.5 J mol^{-1} K^{-1} for ΔS°. This was in accordance with our earlier results on complexation of crown ethers with tropylium ion in DCE.[8]

Podands. The influence of macrocyclicity of the ligands on the complexation was studied by preparing two acyclic diphenoxyalkanes, 1,4-diphenoxybutane and 1,8-diphenoxyoctane. The podand-type compounds have two aromatic benzene rings as end-groups connected via oxygen atoms in a flexible carbon chain. 1,8-Diphenoxyoctane was chosen because the length of the carbon chain is the same as half of the macrocycle of 24-crown-8. In spite of several attempts using FABMS, no complex peaks were noticed between the diphenoxy-substituted alkanes and the tropylium ion. Although FAB spectra of diphenoxy-substituted alkanes and tropylium ion did not exhibit corresponding peaks assignable to a complex, solutions of these compounds in DCE and MeCN turned yellow, indicating some interaction between the components.

The stability constants were studied by UV/Vis spectroscopy. The diphenoxyalkanes were found to have essentially zero absorption in the region (over 300 nm) where a new charge-transfer band appeared upon complexation. A double-reciprocal plot ($1/A$ vs. 1/[diphenoxyalkane]) gave a straight line with a good regression correlation, indicating the formation of a 1:1 complex in the concentration range used. The results calculated by the Rose–Drago method gave a *K*-value of 0.7 ± 0.1 $dm^3 mol^{-1}$ ($\varepsilon_C = 1140 \pm 113$ $dm^3 mol^{-1} cm^{-1}$) for the 1,4-diphenoxybutane–tropylium complex and 1.5 ± 0.2 $dm^3 mol^{-1}$ ($\varepsilon_C = 563 \pm 52$ $dm^3 mol^{-1} cm^{-1}$) for 1,8-diphenoxyoctane–tropylium complex in DCE at 25 °C. The uncertainty in *K*-values was quite high (within ±15%). The broad complex peak with a maximum at 450 nm extending to the visible range and the hypsochromic shift together with the magnitude of the stability constants indicated that weak molecular charge-transfer complexes were formed.

The stability constants calculated between podands and the tropylium cation were quite similar to values that have been reported earlier between tropylium ion and aromatic hydrocarbons.[27,28] For example the 1:1 charge-transfer complex between mesitylene and tropylium tetrafluoroborate has a *K*-value of 0.67 $dm^3 mol^{-1}$ in MeCN at 25 °C. The 1,4-diphenoxybutane–tropylium charge-transfer complex in DCE had a similar value, and the 1,8-diphenoxyoctane–tropylium complex had slightly higher *K*-value of 2.3 $dm^3 mol^{-1}$. The higher stability suggested that the two facing benzene rings connected with a longer carbon chain in 1,8-diphenoxyoctane can stabilize the complex by an intermolecular sandwich-type charge-transfer interaction. This was expected in view of the fact that most charge-transfer interactions usually favour an orientation where the donor and the acceptor are parallel to each other.[14] However, the low *K*-values of the acyclic compounds indicated the importance of the macrocyclic, relatively rigid ring in complexation of the carbenium ions.

In summary, we have shown that the aromatic rings of the crown ethers not only form the recognition site but interact directly with the charged carbenium guests, tropylium ions. These binding processes are predominantly driven by attractive charge–charge and cation–π interactions between the molecular host and the cationic guest. In addition, the determined crystal structure contained a rare example of an unsubstituted tropylium ion which was not disordered.

Experimental

General data. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM200 spectrometer. NMR chemical shifts

are reported in ppm downfield from internal tetramethylsilane (TMS). EI and FAB mass spectra (MS) were obtained using a Kratos MS 80 mass spectrometer operating with the DART data system. Ultraviolet/visible (UV/Vis) spectra were recorded with a Philips PU 8740 spectrophotometer. The small amounts of chemicals were accurately weighed with a Perkin–Elmer AD-2 autobalance. Elemental analysis was carried out with a Perkin–Elmer 2400 instrument. Melting points (m.p.) were determined with a Thermopan microscope (Reichert, Vienna) and are uncorrected. Analytical thin layer chromatography (TLC) was conducted using Kieselgel 60 F_{254} (Merck) silica gel precoated plates with fluorescent indicator UV_{254}. Silica gel Kieselgel (particle size 0.05–0.200 mm, 70–325 mesh ASTM, Merck) was used for flash chromatography.

Materials. Acetonitrile (MeCN, Fluka AG), acetonitrile-d_3 (CD_3CN, CEOL C.E.), 1,2-dichloroethane (DCE, Lab-Scan), dichloromethane (DCM, Lab-Scan), diethyl ether (Et_2O, Fluka AG), diethyl acetate (Et_2OAc, Lab-Scan), *n*-hexane (Lab-Scan) and n-pentane (Fluka AG) were dried and distilled according to literature procedures.[29] Dibenzo-24-crown-8 (**2b**, 2B24C8, Fluka AG) was purified by dissolving it in MeOH and precipitated by addition of water (m.p. 104 °C). 18-Crown-6 (18C6, Fluka AG) and dibenzo-18-crown-6 (**2a**, 2B18C6, Parish Chemical Co) were used as received. All other reagents, unless otherwise noted, were obtained from the Fluka AG and used without further purification.

Syntheses. 1,3,5-Cycloheptatrienylium tetrafluoroborate (**1a**). The tropylium salt was prepared according to literature procedures;[30] m.p. 203 °C (decomp.); ^{1}H NMR (CD_3CN, 30 °C) σ 9.24 (7 H, s).

1-Hydroxy-2,4,6-cycloheptatrienylium tetrafluoroborate **(1b).** Tropone: Tropone was prepared by the method of Radlick.[31] ^{1}H NMR (CD_3CN, 25 °C) σ 6.90 (2 H, $H_{2,7}$, m), 6.95 (2 H, $H_{4,5}$, m), 7.02 (2 H, $H_{3,6}$, m). 1-Hydroxy-2,4,6-cycloheptatrienylium tetrafluoroborate was prepared by treatment of tropone with fluoroboric acid in Et_2O. A solution of 45–50% aqueous fluoroboric acid (4.58 g, 0.025 mol) in 50 ml Et_2O was dried with 55 g of SIKKON® ($CaSO_4$) for 12 h. The filtered solution was treated with tropone (2.65 g, 0.025 mol) under nitrogen, and the reaction mixture was stirred for 3 h in room temperature. The solid precipitation was filtered, washed with dry ether and recrystallized from MeCN and Et_2OAc. White microneedles of 7-hydroxy-1,3,5-cycloheptatrienylinium tetrafluoroborate were collected 1.24 g (6.4 mmol, 30%); ^{1}H NMR (CD_3CN, 25 °C) σ 6.61 (1 H, O–H, s), 7.63 (2 H, $H_{2,7}$, m), 7,69 (2 H, $H_{4,5}$, m), 7.79 (2 H, $H_{3,6}$, m); EI MS *m/z* 106 $[C_7H_6OH]^+$ (without counter-anion BF_4^-).

1-Amino-2,4,6-cycloheptatrienylium tetrafluoroborate (**1c**) was prepared by a modification of the method of Doering and Knox.[32] After removal of the solvent the crude product of aminotropylium tetrafluoroborate was chromatographed on silica gel using MeOH–DCE (2:5) as an eluent to give a white residue. Recrystallisation from EtOH–EtOAc (1:4) afforded aminotropylium fluoroborate as white plates, m.p. 197 °C; ^{1}H NMR (CD_3CN, 25 °C) σ 8.15 (2 H, NH_2, s), 7.53 (2 H, $H_{2,7}$, m), 7.59 (2 H, $H_{4,5}$, m), 7.67 (2 H, $H_{3,6}$, m); FABMS (NBA) *m/z* 106 $[C_7H_6NH_2]^+$ (without counter-anion BF_4^-).

1,4-Diphenoxybutane (**3a**). 1,4-Dibromobutane was prepared.[33] Yield 85%; b.p. 74–76 °C at 10 mmHg; ^{1}H NMR ($CDCl_3$, 30 °C) σ 3.44 (2 H), σ 1.04 (2 H); EI MS *m/z* 216 [M^+]. 1,4-Diphenoxybutane was prepared by Williamson synthesis. The solution of NaOH 26% (40 ml) was added dropwise to a mixture of water (150 ml), phenol (24.1 g, 0.256 mol) and 1,4-dibromobutane (27 g, 0.125 mol). The mixture was refluxed for 6 h, then the yellow precipitate formed during the reaction was removed by filtration. The water layer was washed twice with Et_2O. Recrystallisation from warm Et_2O afforded 18.3 g (0.125 mol, 60%) 1,4-diphenoxybutane as white crystal plates: m.p. 99 °C; ^{1}H NMR ($CDCl_3$, 30 °C) σ 7.28 (5 H, aryl, m), 6.91 (5 H, aryl, m), 4.03 (4 H, chain, m), 1.98 (4 H, chain, m); ^{13}C NMR ($CDCl_3$, 30 °C) σ 159.7 (2 C, aryl-O), 130.1 (4 C, aryl), 121.3 (2 C, aryl), 115.3 (4 C, aryl), 68.1 (2 C, O-chain), 26.8 (2 C, chain); EI MS *m/z* 242 [M^+].

1,8-Diphenoxyoctane (**3b**). 1,8-Dibromooctane was prepared from 1,8-octanediole.[33] The yield of 1,4-dibromooctane was 50%; b.p. 94–96 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$, 30 °C) σ 3.41 (8 H), σ 1.86 (4 H); σ 1.36 (4 H); EI MS *m/z* 272 [M^+]. The Williamson synthesis afforded 1,8-diphenoxyoctane as white crystal plates (81%): m.p. 83 °C; ^{1}H NMR ($CDCl_3$, 30 °C) σ 7.27 (5 H, aryl, m), 6.91 (5 H, aryl, m), 3.94 (8 H, chain, t), 1.75 (4 H, chain, m), 1.40 (4 H, chain, m); ^{13}C NMR ($CDCl_3$, 30 °C) σ 159.2 (2 C, aryl–O), 129.4 (4 C, aryl), 120.4 (2 C, aryl), 114.6 (4 C, aryl), 67.8 (2 C, O–chain), 29.3 (2 C, chain); 20.0 (C4, chain); EI MS *m/z* 298 [M^+].

General procedure for the synthesis of solid crown ether–tropylium tetrafluoroborate complex. The appropriate crown ether (0.25 mmol) and tropylium tetrafluoroborate (0.25 mmol) were weighed and dissolved in MeCN (4 ml). Et_2O was used to precipitate the solid complex, which was collected by filtration. The physical properties of the complexes are collected in Table 2.

Complexation studies. Fast atom bombardment mass spectroscopy (FABMS). The atom gun was operated at 8 keV, and argon was employed as the bombarding gas with a pressure of ca. 1×10^{-6} Torr in the collision region. Samples were mixed with a small amount of 3-nitrobenzyl alcohol (NBA, Aldrich-Chemie) matrix on a stainless-steel probe. Spectra were recorded in the positive-ion mode. Only the main peaks were collected: crown ethers and $Tr^+BF_4^-$ see Refs. 7 and 8, 2B24C8–1-NH_2–$Tr^+BF_4^-$; *m/z* 106 ($TrNH_2^+$, 100%), 488

([2B24C8]$^+$, 2.9), 554 ([2B24C8–TrNH$_2$]$^+$, 2.2); 2B24C8–1-OH–Tr$^+$BF$_4^-$; 107 [TrOH$^+$ (and from NBA), 100], 489 ([2B18C6+H]$^+$, 8.4), 555 ([2B24C8–TrOH]$^+$, 0.6); 1,4-diphenoxybutane–Tr$^+$BF$_4^-$; 91 (Tr$^+$, 100), 242 ([1,4-DiOPhBu]$^+$, 3.5), no complex peak; 1,8-diphenoxyoctane–Tr$^+$BF$_4^-$; 91 (Tr$^+$, 100.0), 298 ([1,8-DiOPhOc]$^+$, 9.8), no complex peak. The spectra contain peaks of *m/z* values at 154, 136 and 107 originating from the NBA matrix and the cleavage ions at *m/z* 45, 89, 133, 177, etc. due to $(C_2H_4O)_n$ fragmentation of crown ether. In all spectra well detectable different tropylium ions have their peaks at *m/z* 91 [Tr$^+$], *m/z* 106 [TrNH$_2^+$] and *m/z* 106 [TrOH$^+$]. The absence of higher peaks than the 1:1 complex in all FABMS spectra measured indicated preferential 1:1 complex formation in the gas phase.

Stability constant determination by ^1H NMR titration. A standard solution of acceptor in CD_3CN was prepared with a concentration of acceptor [$(10–4)\times10^{-4}$ M] just sufficient to give an observable NMR line. A small amount of tetramethylsilane (Aldrich-Chemie) was added as an internal standard. A series of donor solutions was made by weighing out an appropriate amount of donor (0.1–0.02 M). A 3–5 ml portion of the standard solution was then added, and the flask was reweighed. After preparation of the samples a portion was transferred to a sample tube (5 mm). The tube was capped and the spectrum was measured immediately to avoid evaporation. The temperature was held constant within ±0.3 °C. The stability constant K for 1:1 complexation was calculated from the NMR chemical shifts and the Benesi–Hildebrand equation, eqn. (1)[34]

$$\frac{1}{\Delta\delta_{obs}} = \frac{1}{K\Delta\delta_0}\times\frac{1}{C_D} + \frac{1}{\Delta\delta_0} \qquad (1)$$

where $\Delta\delta_{obs}=\delta_{obs}-\delta_A$, $\Delta\delta_0=\delta_{AD}-\delta_A$ and δ_{obs} is the observed NMR shift of the specific acceptor proton (or an equivalent set) in the equilibrium solution, δ_A is the shift of the free acceptor proton and δ_{AD} is the shift of the acceptor proton in the pure complex. C_D and C_A are the initial analytical concentrations of donor and acceptor.

Stability constant determination by UV/Vis spectroscopy. The stability constant for 1:1 complexation was defined by a method previously described in detail elsewhere.[8] The Rose–Drago equation,[24] eqn. (2), is

$$\frac{1}{K} = \frac{A-A_0}{\varepsilon_C-\varepsilon_A} - C_A - C_D + \frac{C_D C_A(\varepsilon_C-\varepsilon_A)}{A-A_0} \qquad (2)$$

where A_0 is the absorbance of pure acceptor solution, A is the absorbance of acceptor–donor solution, and ε_C and ε_A are the molar absorptivities of complex and acceptor in solution, respectively.

X-Ray crystal structure of the 2B24C8–tropylium tetrafluoroborate complex. The complex formed between 2B24C8 and tropylium crystallized with 1:1 stoichiometry when an equimolar mixture of the two components was dissolved in MeCN and precipitated with Et_2O. Single crystals suitable for X-ray analysis were crystallized from MeCN:DCE. The structure also contains the BF_4^- counteranion and the MeCN solvent molecule (with a population parameter of 0.5).

The following crystal data were determined: $C_{31}H_{39}O_8\cdot0.5\ CH_3CN\cdot BF_4$, $M=646.97$, monoclinic, space group $P2_1/n$ (no. 14), $a=14.158(2)$, $b=14.791(2)$, $c=16.384(2)$ Å, $\beta=93.90(1)$, $V=3423.2(8)$ Å^{-3}, $Z=4$, $D_C=1.255$ g cm^{-3}, $F(000)=1360$, $T=296\pm1$ K.

Data were collected from a deep red crystal $0.25\times0.45\times0.45$ mm. 4744 unique reflections were recorded with an Enraf-Nonius CAD4 diffractometer using graphite monochromatized Mo K_α radiation [λ(Mo K_α)=0.7107 Å] and the $\omega/2\theta$ scan mode (scan width in degrees: $0.70+0.35\tan\theta$) to $2\theta=46°$ ($h=0\rightarrow15$, $k=0\rightarrow16$ and $l=-18\rightarrow18$), 2727 reflections with $I>3\sigma I$ were used for refinement. An empirical absorption correction[35] [μ(Mo K_α)=0.272 mm^{-1}] was applied to the data with minimum and maximum correction coefficients of 0.902 and 1.090, respectively.

The structure was solved by direct methods (SHELXS)[36] and subjected to full-matrix refinement (CRYSTALS).[37] The structure solution revealed extensive disorder in the BF_4 group, in MeCN and also in the crown ether skeleton. A new crystal was measured in order to reduce the extent of the disorder. After several attempts it came evident that all crystals measured gave the same disorder. The refinement without any restraints gave an *R*-value of ca. 0.15 with very unreasonable bond distances and angles. However, the refinements gave information that the disorder was caused by two or more overlapping orientations of the BF_4 group. The disordered parts [BF_4, MeCN and atoms C8 (C81), C22 (C221) and O23 (O231) in the 24C8 chain] were refined with 29 geometrical restraints in order to prevent anomalous bond distances and angles. The population parameters in the BF_4 molecule were kept at 1.0, which gave a reasonable result, but caused a large thermal movement of the F atoms. The population parameters for MeCN were kept at 0.5 and for atoms C8, C22, O23 were kept at 0.6 (relative to 0.4 for C81, C221, O231). The restrained refinement caused a decrease in the final *R*-values and improved the ΔF-map. Also more reasonable bond distances and angles were obtained.

All non-H atoms were refined anisotropically. The hydrogen atoms were put at their idealised positions and were refined as riding atoms with fixed isotropic temperature factors ($U=0.08$ Å^2). The F_o/parameter ratio was 6.03, the final *R*-value was 0.1169 and R_w was 0.1025 for 452 parameters: $w=w'[1.0-(\Delta F/6\sigma F)^2]^2$, where $w'=$ Chebychev polynomial for F_c with five coefficients (1.26, −13.9, −8.21, −8.96, −5.43).[38] On convergence the maximum shift/error was <0.12. The highest peak in the final difference map was 0.79 e Å^{-3}, located near the disordered BF_4^-.

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge

Crystallographic Center (CCDC). Any request to the CCDC for this material should quote the full literature citation (Ref. 13) and the reference number 182/93.

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