Crystal structure of an inclusion complex between dibenzo-24-crown-8 and tropylium tetrafluoroborate

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The dibenzo-24-crown-8 encapsulates the non-disordered tropylium ion ($C_7H_7^+$) with charge-transfer type π–π-interactions with average bond distances of 1.35 Å and C–C–C angles of 129° confirming a regular delocalised heptagon structure.

Macrocyclic polyethers or crown ethers can form complexes with inorganic and organic cations and with neutral molecules.[1] Much interest has been focused on characterising the structure of crown ether complexes and evaluating the thermodynamics of cation–ligand interactions. Numerous investigations on the binding of a metal, ammonium, diazonium, hydronium, acylium and hydrazinium ions to macrocyclic polyethers have been reported.[2] By contrast, papers describing the complexation of carbocations by crown ethers are relatively few.[3,4] One of the most stable carbenium ions is the 1,3,5-cycloheptatrienylium or tropylium ion ($C_7H_7^+$) with a pK_a value[5] of 4.75. The high pK_a value reflects the high stability of the carbenium ion. Feldman and Winstein[6] found that the tropylium ion forms a 1 : 1 charge-transfer complex with various aromatic hydrocarbons, in addition Komatsu *et al.*[7] have reported a transannular stabilisation of a tropylium moiety *via* charge transfer interactions. The tropylium ion has been later found to be an effective π-acceptor as exemplified by the synthesis of many intramolecular charge-transfer complexes.[8] There is a large number of tropyliophanes[9] which have the tropylium ion as a part of the molecular skeleton. In addition similar tropylium ions containing macrocyclic compounds have been synthesized.[10,11]

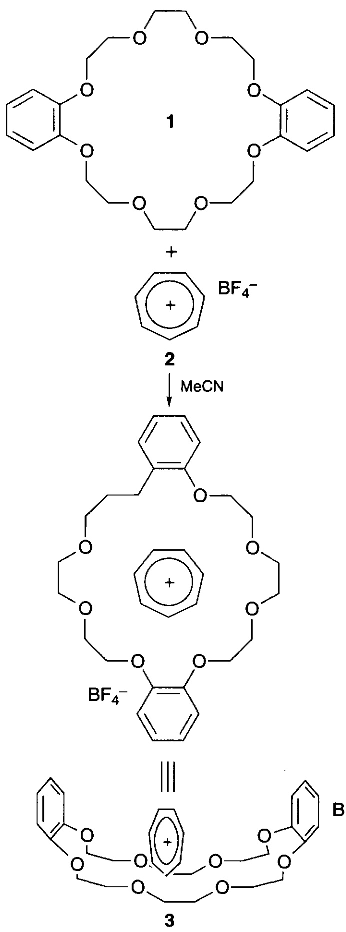
We have recently studied molecular complexation between cyclic polyethers and tropylium ions in the gas phase and in solution.[3] As a sequel to our studies on the interactions between crown ethers and stable organic cations, we report here the crystal structure of the dibenzo-24-crown-8-tropylium tetrafluoroborate inclusion complex. The X-ray structures of many dibenzocrown ethers and their metal complexes have now been determined, including dibenzo-24-crown-8.[12,13] However, structural characterisation of supramolecular inclusion complexation between cyclophanes or crown ethers and tropylium ions has not been reported earlier.

The dibenzo-24-crown-8-tropylium tetrafluoroborate complex **3** (Scheme 1) was prepared§ in acetonitrile and crystallised from acetonitrile–1,2-dichloroethane for an X-ray diffraction study.¶

The X-ray structure of **3** does not show anomalous bond distances or angles but does show that the tropylium ring is encapsulated by the crown ether (Fig. 1). Our previous study[3] shows that benzene substituted crown ethers form 1 : 1 molecular complexes with tropylium ions. Since the molecular diameter of the tropylium ion is too large to fit into the cavity of the smaller polyethers studied, no inclusion complexes were observed. The stability constant values increase with the ring size of the crown ether. The dibenzo-24-crown-8 was found to have the smallest cavity which can fully encapsulate the tropylium ion. The relatively high values of the stability constants (dibenzo-24-crown-8-tropylium tetrafluoroborate complex has a pK_a value of 2.44) together with the colour formation in 1,2-dichloroethane solution and the non-bonded contact distances (Fig. 1) indicate that the complexation is most likely of a charge-transfer nature.[3]

X-ray diffraction studies of C_7H_7I and $C_7H_7ClO_4$ in the 1960's revealed that both compounds are ionic, planar and have C–C distances of 1.47 Å.[14] In both cases the C_7H_7 ion was found to be disordered around the axis perpendicular to the ring plane. The experimental C–C bond distances determined from data for $C_7H_7ClO_4$ are obviously too long and are associated with experimental difficulties due to the disorder. In the present inclusion complex the tropylium ion is not disordered and the average value for the seven C–C bond lengths is 1.35 Å. The bond angles in the seven-membered ring are all close to the 128.6° expected for a regular heptagon.

Our results shows that supramolecular inclusion complexes between crown ethers (and analogues cyclophanes) and stable carbenium ions can be prepared and isolated in crystalline form and used in a detailed structural study. The encapsulation of the



Scheme 1

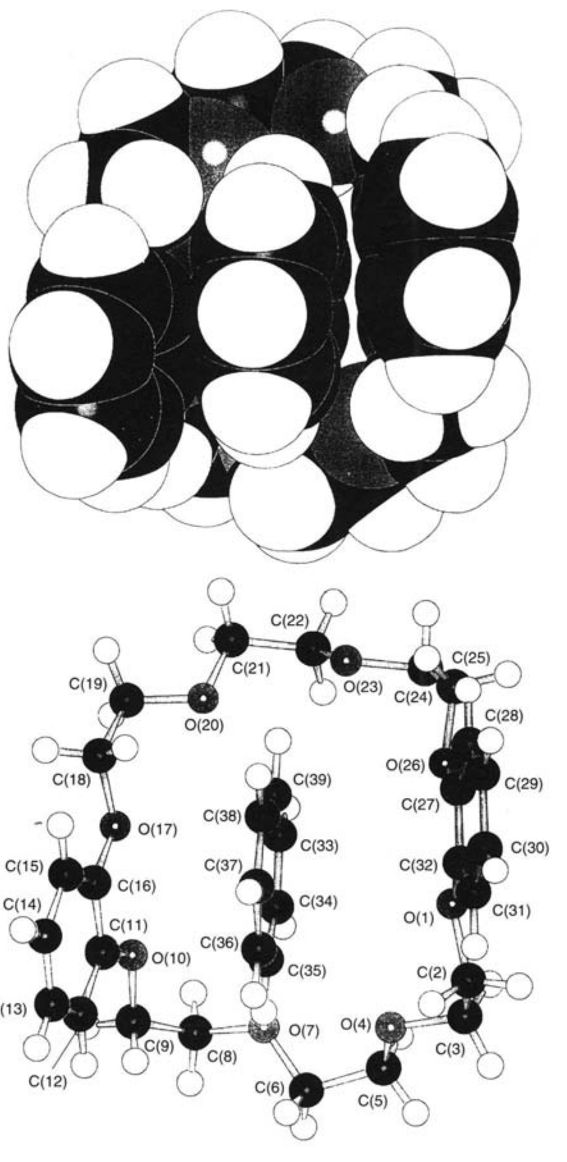


Fig. 1 A SCHAKAL[15] plot for **3** based on X-ray studies (MeCN and BF_4^- excluded, only the major conformation of 24-C-8 is shown). The distances between the tropylium and benzene rings in **3** are between 3.5–4.3 Å [C(11)–C(35); 3.50(1), C(12)–C(35); 3.69(1), C(13)–C(32); 3.56(1), C(14)–C(32); 3.73(1), C(15)–C(35); 3.98(1), C(16)–C(33); 3.67(1), C(27)–C(33); 3.56(1), C(28)–C(38); 3.88(1), C(29)–C(38); 4.22(1), C(30)–C(37); 4.28(2), C(31)–C(37); 3.94(1), C(32)–C(39) 3.62(1) Å].

carbenium ion into a large cavity can be used to fix the ion orientation and therefore prevent the structurally unfavourable disorder.

Footnotes

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§ *Experimental procedure and selected spectroscopic data* for **3**: Dibenzo-24-crown-8 **1** (0.22 g, 0.5 mmol) was dissolved in acetonitrile (20 ml) and tropylium tetrafluoroborate **2** (89.1 mg, 0.5 mmol) was added with stirring. The solvent was removed by evaporation and a crude oil crystallised on cooling. The oil was recrystallised from acetonitrile to yield a dibenzo-24-crown-8-tropylium salt complex as red crystals which were washed with cold ether (2 × 10 ml) and dried *in vacuo* at room temp., mp 99–100 °C. The 1 : 1 complex between dibenzo-24-crown-8 and the tropylium ion was identified by fast atom bombardment mass spectrometry (FAB-MS). Positive ion FAB-MS: m/z 539 [dibenzo-24-crown-8-C_7H_7]$^+$. ^{1}H NMR (CD_3CN, 303 K): δ 3.72 (s, OCH_2, 8 H), 3.80 (m, OCH_2, 8 H), 4.03 (m, OCH_2, 8 H), 6.81 (s, aryl, 8 H) and 9.15 (s, C_7H_7, 7 H). Free tropylium ion ^{1}H NMR (CD_3CN, 303 K) δ 9.24 (s, 7 H).

¶ *Crystal data* for **3**: [$C_{24}H_{32}O_8 \cdot C_7H_7^+$] $BF_4^- \cdot 0.5$ MeCN, $M = 646.97$, 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}, $F(000) = 1360$, $T = 296 \pm 1°$ K, crystal dimensions 0.25 × 0.45 × 0.45 mm, deep red, 4744 unique reflections were recorded with an Enraf-Nonius CAD4 diffractometer using graphite monochromatized Mo-Kα radiation [λ(Mo-Kα) = 0.7107 Å] and ω/2θ scan mode (scan width in degrees: $0.70 + 0.35 \tan\theta$) to $2\theta = 46°$ (h: $0 \rightarrow 15$, k: $0 \rightarrow 16$ and l: $-18 \rightarrow 18$), 2727 reflections with $I > 3\sigma I$ were used for refinement. An empirical absorption correction (DIFABS, N.Walker, and D. Stuart, *Acta Crystallogr., Sect. A39* (1983) 158) [μ (Mo-Kα) = 0.272 mm^{-1}] was applied to the data with minimum and maximum correction coefficients 0.902 and 1.090, respectively. Structure solution and refinement: the structure was solved by Direct Methods[16] and subjected to full-matrix refinement.[17]

The structure solution revealed disorder in the BF_4 anion and also in crown ether skeleton. All non-H atoms were refined anisotropically. The hydrogen atoms were calculated to their idealised positions and were refined as riding atoms with fixed isotropic temperature factors ($U = 0.08$ Å^2). F_o/parameter ratio = 6.03 and the final R value was 0.117 and $R_w = 0.103$ for 452 parameters: $w = w' \cdot [1.0 - (\Delta F/6 \cdot \sigma F)^2]^2$, where w' = Chebychev polynomial for F_c with five coefficients (1.26, −13.9, −8.21, −8.96, −5.43). Convergence, max. shift/error < 0.12 Å final difference map displayed no electron density higher than 0.79 e Å^{-3}, which locates near the disordered $BF^-{}_4$. Suitable crystals for X-ray study of dibenzo-24-crown-8-tropylium tetrafluoroborate complex were obtained by slow evaporation of a 1,2-dichloroethane–acetonitrile solution.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/93.

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