Polar crystals with one-dimensional arrays from achiral components: crystal structures of 2 : 2 complexes of dibenzo-18-crown-6–imidazolium and pyrazolium perchlorates

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Biologically important planar five-ring aromatic bases as their imidazolium and pyrazolium cations form crystalline 2 : 2 complexes with dibenzo-18-crown-6, creating one-dimensional arrays in a polar crystal lattice.

Supramolecular complexation, where the main binding force is π-stacking or charge-transfer interaction between two aromatic units, has recently attracted increasing attention.[1] These interactions have been utilised for example in the preparation of catenanes and rotaxanes and their precursor complexes.[2] Carbocations such as tropylium ion also form supramolecular complexes, where the charge-transfer interaction is the dominant binding force.[3] The biologically important nitrogen-containing heterocycle imidazole and its isomer pyrazole form planar five-membered organic cations when treated with the proper acid. The cations are bis-functional and can interact with crown ether type host structures both by hydrogen bonding to the ether oxygen atoms and/or by charge-transfer interactions to the electron rich phenyl rings of the crown ether.[4] In this work we have prepared and characterised such complexes and found out that dibenzo-18-crown-6 (DB18C6) complexes form polar crystal lattices with very interesting structural features.

The DB18C6·imidazolium complex **6**† is much more stable (NMR titration in CD_3CN solution, Table 1) than the corresponding π–π tropylium complex (5.6 $dm^3\ mol^{-1}$),[3] indicating additional H-bonding in the former compound. For the imidazolium perchlorate the highest stability constant was measured for 18-crown-6 (18C6) owing to the H-bonding to the ether oxygen atoms. The stability constants for the benzo and dibenzo crown ethers were, however, nearly 50% lower. This implies a competing complexation behaviour between H-bonding and π-stacking/charge-transfer interactions for the imidazolium complex. The stability constant of DB24C8 was close to the corresponding value of tropylium cation[3] (10.2 $dm^3\ mol^{-1}$) and manifests complexation predominantly *via* π–π interactions. The aromatic ring in the crown ether decreases electron density in the adjacent oxygen atoms, which seems to result in higher stability of the 18C6·imidazolium complex. The stability constant of the DB18C6·pyrazolium complex **7** is much higher than that for the DB18C6·imidazolium complex. This can be rationalised by the suitable stereochemistry of two simultaneously-acting intracomplex (Scheme 1) hydrogen bonds.

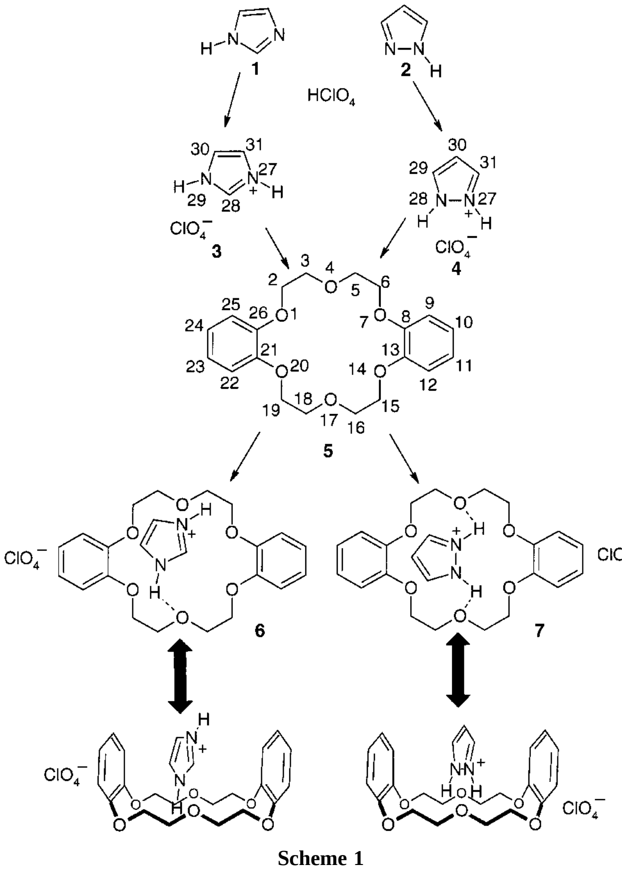
Table 1 Stability constants and limiting shifts for the interaction of crown ethers with imidazolium and pyrazolium ions in CD_3CN at 303 K

Host	K_a/dm³ mol⁻¹	$\Delta\delta_C$/ppm	$r^{2\ a}$
Imidazolium perchlorate			
DB24C8	8 ± 1	0.36 ± 0.04	0.993
DB18C6	27 ± 5	0.50 ± 0.06	0.977
B18C6	25 ± 1	0.62 ± 0.01	0.999
18C6	40 ± 1	0.563 ± 0.004	0.999
Pyrazolium perchlorate			
DB18C6	113 ± 6	0.197 ± 0.003 (H-3,5)	0.995
	65 ± 1	0.463 ± 0.004 (H-4)	0.999

[a] Regression correlation for Benesi–Hildebrandt plot.

In the crystalline state,‡ however, the structures of **6** and **7** are surprisingly similar. In both cases the complexes crystallised out in an acentric monoclinic space group (*Cc*) due to a spontaneous resolution. The crown ether offers two interaction sites, a structurally minor site that is formed by the OCH_2CH_2O chains of the crown and a structurally major site situated between the phenyl rings. These two sites, both capable of inclusion of a planar guest, have a 90° angle towards each other and are facing opposite directions (Fig. 1). The simultaneous inclusion of a guest into the both sites during the packing creates a one-dimensional array of host–guest complexes with a 90° turn between the adjacent DB18C6 molecules.

Although formally complexes are 1 : 1 complexes in solution, the crystal packing can only be described as a 2 : 2 complex. The



Scheme 1

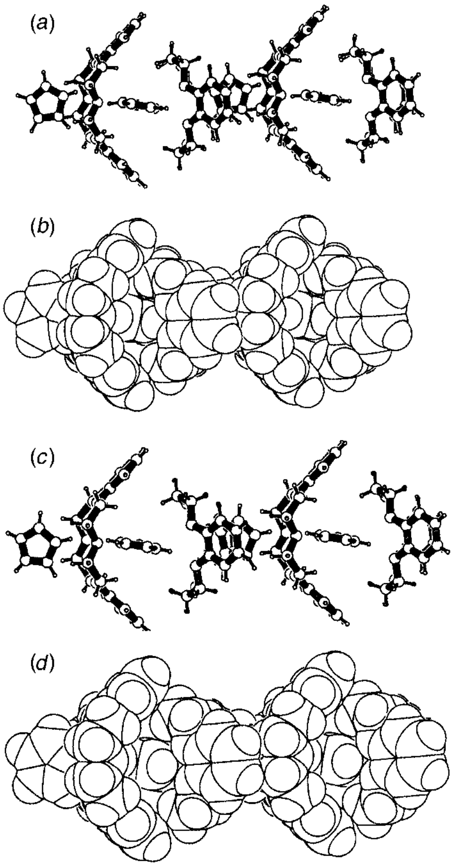


Fig. 1 PLATON (ref. 8) plot for the packing of complexes **6** and **7** into one-dimensional arrays. Four adjacent complexes are shown as ball-and-stick and VDW presentations: (*a*) and (*b*) for **6** and (*c*) and (*d*) for **7**.

polarity of the crystal is caused by the interaction of the adjacent one-dimensional arrays. The arrays all pack in the same direction, thus creating a polar axis in the crystal lattice. The existence of the H-bonding and the weak charge transfer interaction is evident for both structures. The imidazolium cation in **6** has one intracomplex H-bond to the major site of its host [N27···O4 = 2.823(7), H27···O4 = 1.99(9) Å and angle 148(7)°] and two weaker intercomplex H-bonds to the minor site of the adjacent host [N29···O1′ = 3.022(7), H27···O1′ = 2.28(8) Å and angle 132(6)°; N29···O20′ = 3.048(7), H27···O20′ = 2.19(8) Å and angle 144(6)°]. The distance between the centroids of the cation and the nearest phenyl ring is 4.12(1) Å, indicating a weak charge-transfer interaction. The pyrazolium cation in **7** is more strongly bound into the major site of its host by two H-bonds [N27···O17 = 2.71(1), H27···O17 = 1.88 Å and angle 155(1)°; N28···O4 = 2.79(1), H28···O14 = 1.91(12) Å and angle 174(1)°]. The charge-transfer interaction is similar to that in complex **6** [distance between closest centroids is 4.04(1) Å]. The interaction in complex **7** to the minor site of the adjacent host is much weaker (H···O′ distances vary from 2.59 to 3.45 Å) than in the case of complex **6**. The adjacent guests inside the arrays of **6** and **7** are surprising close to each other, the non-bonded contact distance between the closest adjacent H-atoms are 2.82 Å for **6** (H31···H29′) and 2.83 and 2.96 Å for **7** (H30···H27′ and H30···H28′, respectively).

The structures presented here are interesting from the crystal engineering[5] and supramolecular technology[6] points of view. This type of tightly packed one-dimensional molecular arry could form a matrix for (photo)chemical reactions leading to advanced molecular wires and similar new materials. The close proximity of the guests inside the array is a feature not frequently encountered in crystal lattices and could, with the use of larger crown ethers and functionalised guests, lead to new tailor-made polymers or polyrotaxanes.

Notes and references

† *Synthesis and characterisation*: The imidazolium and pyrazolium salts were prepared according to a published procedure (ref. 7). The complexes were prepared by mixing equimolar amounts of the above salt and DB18C6 MeCN solutions. The complexes **6** and **7** precipitated soon after mixing of the components or after addition of anhydrous Et_2O.

Selected data for **6**: 54%, mp 215–220 °C; *m/z* (FAB, NBA matrix) 429 [$DB18C6{\cdot}C_3N_2H_5 - ClO_4]^+$; δ_H(200 MHz, CD_3CN, 25 °C) 3.8 (m, OCH_2, 8H), 4.1 (m, OCH_2, 8H), 6.9 (s, aryl, 8H) 7.4 (d, imidazolium, 2H), 8.8 (t, imidazolium, 1H) ($C_{23}N_2H_{29}ClO_{10}$ (528.93): calc. C, 52.23; H, 5.53; N, 5.30; found C, 52.70; H, 5.50; N, 5.31%). For **7**: 62%, mp 210–215 °C; *m/z* (FAB, NBA matrix) 429 [$DB18C6{\cdot}C_3N_2H_5 - ClO_4]^+$; δ_H(200 MHz, CD_3CN, 25 °C) 3.9 (m, OCH_2, 8H), 4.1 (m, OCH_2, 8H), 6.6 (t, pyrazolium, 1H), 6.9 (s, aryl, 8H), 8.1 (d, pyrazolium, 2H) ($C_{23}N_2H_{29}ClO_{10}$ (528.93): calc. C, 52.23; H, 5.53; N, 5.30; found C, 52.14; H, 5.10; N, 5.36%).

‡ The data were recorded with Enraf-Nonius CAD4 (**6**) or Kappa CCD (**7**) diffractometers using graphite monochromatised Mo-Kα radiation [λ(Mo-Kα) = 0.71073 Å]. The data was processed with Denzo-SMN ver. 0.93.0 (Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, in *Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A*, ed. C. W. Carter, Jr. and R. M. Sweet, Academic Press, 1997, pp. 307–326). The structures were solved by direct methods [SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467] and refinements, based on F^2, were made by full-matrix least-squares techniques [SHELXL-97 (G. M. Sheldrick, SHELXL-97—A program for crystal structure refinement, 1997, University of Göettingen, Germany)]. H-atoms calculated and refined as riding atoms, absolute structure could not be reliably determined. *Crystal data* for **6**: colourless, 0.20 × 0.20 × 0.40 mm, $C_2H_{24}O_6{\cdot}C_3H_5N_2{}^+ClO_4{}^-$, from MeCN, M_r = 528.93, monoclinic, space group *Cc* (no. 9), a = 17.802(4), b = 14.225(4), c = 12.199(3) Å, β = 129.34(2)°, V = 2394(1) Å^3, F(000) = 1112, T = 173.0 ± 0.1 K, Z = 4, D_c = 1.467 g cm^{-3}, 2184 reflections were recorded in the range $2.06 \leqslant \theta \leqslant 24.97°$ (h: 0 → 21, k: 0 → 16, l: −14 → 11). Reflections were corrected for Lorentz polarisation effects and the ψ-scan method was used for absorption correction [μ(Mo-Kα) = 0.221 mm^{-1}, maximum transmission 0.9571 and minimum transmission 0.9167]. The final residuals were $R1$ = 0.0433 and $wR2$ = 0.1201 for 1887 unique data with $I > 2\sigma(I)$ and $R1$ = 0.0596, $wR2$ = 0.1259 for all data and for 325 parameters: $w = 1/[\sigma^2(F_o{}^2) + (0.0405P)^2 + 7.62P]$, where P [Max ($F_o{}^2$, 0) + 2 $F_c{}^2$]/3 and GooF = 1.193. The final difference map displayed no electron density higher than 0.24 e Å^{-3}. For **7**: colourless, 0.15 × 0.20 × 0.45 mm, $C_{20}H_{24}O_6{\cdot}C_3H_5N_2{}^+ClO_4{}^-$, from MeCN, M_r = 528.93, monoclinic, space group *Cc* (no. 9), a = 17.804(1), b = 14.131(1), c = 12.317(1) Å, β = 129.00(1)°, V = 2408.1(3) Å^3, F(000) = 1112, T = 173.0 ± 0.1 K, Z = 4, D_c = 1.459 g cm^{-3}, 2828 reflections were recorded in the range $2.94 \leqslant \theta \leqslant 27.87°$ (h: 0 → 23, k: 0 → 18, 1: −16 → 12). Reflections were corrected for Lorentz polarisation effects and no absorption correction was applied. [μ(Mo-Kα) = 0.220 mm^{-1}). The final residuals were $R1$ = 0.0887 and $wR2$ = 0.2290 for 1953 unique data with $I > 2\sigma(I)$ and $R1$ = 0.1319, $wR2$ = 0.2536 for all data and for 326 parameters: $w = 1/[\sigma^2(F_o{}^2) + (0.0588P)^2 + 10.71P]$ where P = [Max ($F_o{}^2$, 0) + 2$F_c{}^2$]/3 and GooF = 1.125. The final difference map displayed no electron density higher than 0.78 e Å^{-3}. CCDC 182/1221. See http://www.rsc.org/suppdata/cc/1999/897/ for crystallographic files in .cif format.

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