PAPER

NJC
www.rsc.org/njc

Cation–π interaction: a case for macrocycle–cation π-interaction by its ureidoarene counteranion

Carole Arnal-Herault, Mihail Barboiu,* Eddy Petit, Mathieu Michau and Arie van der Lee

Institut Européen des Membranes - UMR-CNRS 5635, Place Eugène Bataillon, CC 047, F-34095 Montpellier Cedex 5, France. E-mail: mihai.barboiu@iemm.univ-montp2.fr; Fax: +33 467 149 119; Tel: +33 467 149 195

Received (in St Louis, MO, USA) 30th June 2005, Accepted 10th October 2005
First published as an Advance Article on the web 28th October 2005

We report the solid state structures of homocomplex $[\mathbf{1}\cdot K]^+[I]^-$ and of heterocomplexes $[\mathbf{1}\cdot K]^+[\mathbf{3}\cdot I]^-$ and $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]$. In the $[\mathbf{1}\cdot K]^+[I]^-$ complex the apical position of the K^+ in the macrocycle is occupied by a $-CH_2-$ moiety of a neighboring 18-crown-6, consistent with a close contact and corresponding to 'agostic' interactions between K^+ and $-CH_2-$ moieties. In the $[\mathbf{1}\cdot K]^+[\mathbf{3}\cdot I]^-$ complex the second apical site of the cation is coordinated by a bridging water molecule which is simultaneously H-bonded to both the phenol hydroxyl and the iodide anion. In the $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$ complex the second apical site of the cation is occupied by the indole moiety. Moreover, the new heterocomplex system $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$ presented here, despite the multiple possibilities of K^+–π contacts with the sterically available phenyl, phenyl-indole and pyrrole-indole rings of **4**, shows that the pyrrolo C2=C3 double bond is a versatile π-donor. ^{1}H NMR results led us to conclude that the complexes adopt similar conformations in solution to those observed in the solid state.

Introduction

Intermolecular interactions involving aromatic rings are key processes in both chemical and biological recognition. Among these interactions, cation–π interactions between positively charged species (alkali, ammonium and metal ions) and aromatic systems with delocalized π-electrons are now recognized as important non-covalent binding forces of increasing relevance.[1] The importance of interactions between alkali cations and the side chains of aromatic amino acids has been known for many years and they are of particular biological significance.[1,2]

Structural evidence for alkali cation–aromatic interactions may be found in the literature and it was best revealed by computational, solution (ES-MS, NMR) and solid state studies of different ion–molecule complexes.[2–12] Most of the first pioneering examples include aromatics, organic anions or solvent molecules.[2b] The development of different homo- and heteroditopic receptors like calixarenes,[3a] salophens,[3b] or metallic complexes[3c] showed cation–π interactions based on ion-pairing interactions in solution and in solid state.[8] Gokel and co-workers made crucial advances during the last decade and provided useful insights in this field.[4] Their studies were confined to macrocyclic equatorially-bound alkali-cations.[4–9] Different crown-ethers were chosen as well known Na^+ and K^+ complexants and were decorated with one or two identical covalently-attached arene sidearms of four essential aromatic amino acids.[5] They were connected by flexible sidearms, long enough to permit the arene to occupy the vacant apical coordination sites (Scheme 1a). The direct bonding of the aromatic moieties in a specific position with respect to the crown molecule imposes a spatially limited, but optimized position of the arene. Particular success has been encountered using only 2-carbon linker arms and no conclusive or negative results have been obtained for other linker lengths.[4b,c]

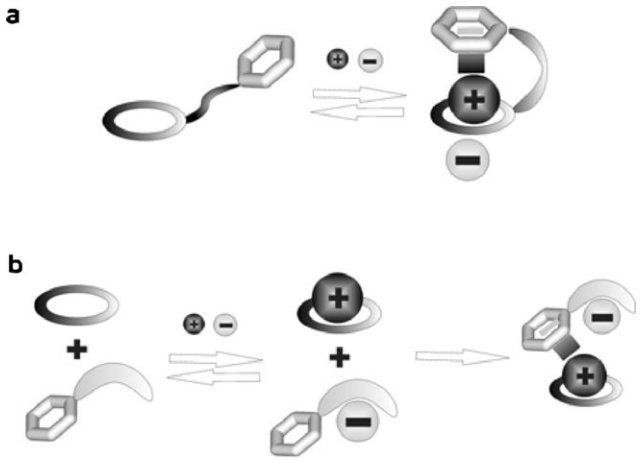
Our strategy was to use 18-crown-6, **1** and phenylureidoarene (PhNHCONHAr) **2–4** compounds (Scheme 2) as well-recognized macrocyclic- and urea-receptors of K^+ and of I^-, respectively.[10] We have examined these systems as synergetic individual cation and anion receptors for the co-extraction of potassium salts from water to an organic phase and we have observed anomalous π-interactions in solution between the resulting cationic $[\mathbf{1}\cdot K]^+$ and the anionic-arene $[\mathbf{2–4}\cdot I]^-$ individual species. In many known K^+–crown complexes, the cation is bound equatorially by the 18-crown-6 macroring and the counteranion, solvent (water) and aromatic moieties occupy the cation's apical positions.[2,4] Although the membrane transport chemistry remains under investigation, the exciting implication that the crown–K^+ cation and the non-covalently bound π-donor residues of the discrete benzoureidoarene anion receptors **2–4** could present cation–π contacts, despite the entropically unfavourable conditions (Scheme 1b), led us to study these systems in solution and in the solid state.

Results and discussions

Three phenylureidoarene anion receptors **2–4** were prepared for studies described here. We restricted our studies to benzene **2**, phenol **3**, and indole **4** as the arene (Ar) termini of phenylalanine, tyrosine and tryptophan, three aromatic essential amino acids (Scheme 2). The imidazole derivative could not be employed for this study due to its low solubility. The phenyl isocyanate was treated with the corresponding aromatic amine (CH_3CN, Δ, 5 h) to afford, after crystallization, **2–4** as white powders (90%). The heteroditopic systems were obtained by dissolving **1**:KI (1:1, mol:mol) and **1**:**2**/**3**/**4**:KI (1:1:1, mol:mol:mol), respectively, in acetone-d_6. Layering these solutions with isopropyl ether resulted in the formation of colorless single crystals of homocomplex $[\mathbf{1}\cdot K]^+[I]^-$ and of heterocomplexes $[\mathbf{1}\cdot K]^+[\mathbf{3}\cdot I]^-$ and $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$. Attempts to crystallize the heterocomplex $[\mathbf{1}\cdot K]^+[\mathbf{2}\cdot I]^-$ failed until now and only tiny single crystals, too small for X-ray analysis, could be obtained from different solution-diffusion experiments.

In the solid state structures of $[\mathbf{1}\cdot K]^+[I]^-$ (Fig. 1), $[\mathbf{1}\cdot K]^+[\mathbf{3}\cdot I]^-$ (Fig. 2a) and $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$ (Fig. 2b) the 18-crown-6 ring is nearly planar and in the D_{3d} conformation. The distances between the oxygen donors and the bound K^+ are as expected (average $d_{K\cdots O}$ of 2.80 Å). Generally, one apical position of K^+ is

DOI: 10.1039/b509240j

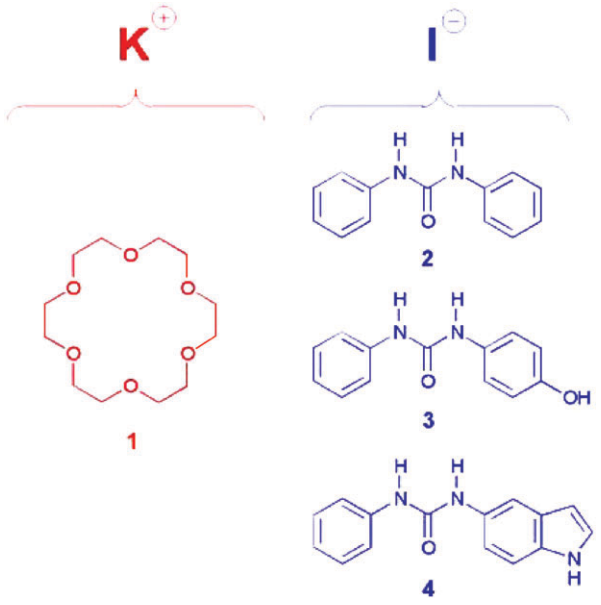


Scheme 1

occupied by the I^- anion ($d_{K\cdots I}$ of 3.40 Å). In the heterocomplex structures $[\mathbf{1}\cdot K]^+[\mathbf{3}\cdot I]^-$ and $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$ the I^- anion is hydrogen-bonded to the urea N–H residues (average $d_{H\cdots I}$ 2.75 Å).

We have found in the Cambridge Structural Database (April 2005)[11a] only the poly-iodide structures of $[\mathbf{1}\cdot K]^+[I_3]^-$ [11b] and $[\mathbf{1}\cdot K]^+[I_5]^-$,[11c] but surprisingly, not the crystal structure of $[\mathbf{1}\cdot K]^+[I]^-$, which is very different from the previous ones. In the solid state structure of $[\mathbf{1}\cdot K]^+[I]^-$ two I^- anions are H-bonded by a bridging water molecule (average $d_{O\cdots I}$ of 3.75 Å) leading to a layered water–iodide network (Fig. 1a). These layers are stratified with adjacent macrocyclic layers of $[\mathbf{1}\cdot K]^+$ and are in close contact by $K^+\cdot I^-$ apical ionic interactions. The second apical position of the K^+ in the macrocyclic layer is occupied by a $-CH_2-$ moiety of a neighboring 18-crown-6 (Fig. 1b). The ionic radius of K^+ is 1.4–1.5 Å[11d] and the half-thickness of a $-CH_2-$ moiety is about 2.00 Å; adding these values, the contact values are in the range of 3.4–3.5 Å. In $[\mathbf{1}\cdot K]^+[I]^-$ the distance $d_{K\cdots C}$ is 3.50 Å, consistent with a close contact and corresponding to "agostic" interactions[12] between K^+ and $-CH_2-$ moieties. To our knowledge, the present system is the first example of a macrocyclic complex where the $K^+\cdots H-C-$ "agostic" interactions and an apical contact might in principle be associated.

In the $[\mathbf{1}\cdot K]^+[\mathbf{3}\cdot I]^-$ complex the second apical site of the cation is coordinated by one water molecule ($d_{O\cdots K+}$ of 2.71 Å) which plays a critical role in organizing the partners in the network. In contrast with previously reported solid state



Scheme 2 Structure of K^+ (**1**) and I^- (**2–4**) cation and anion, respectively, receptors.

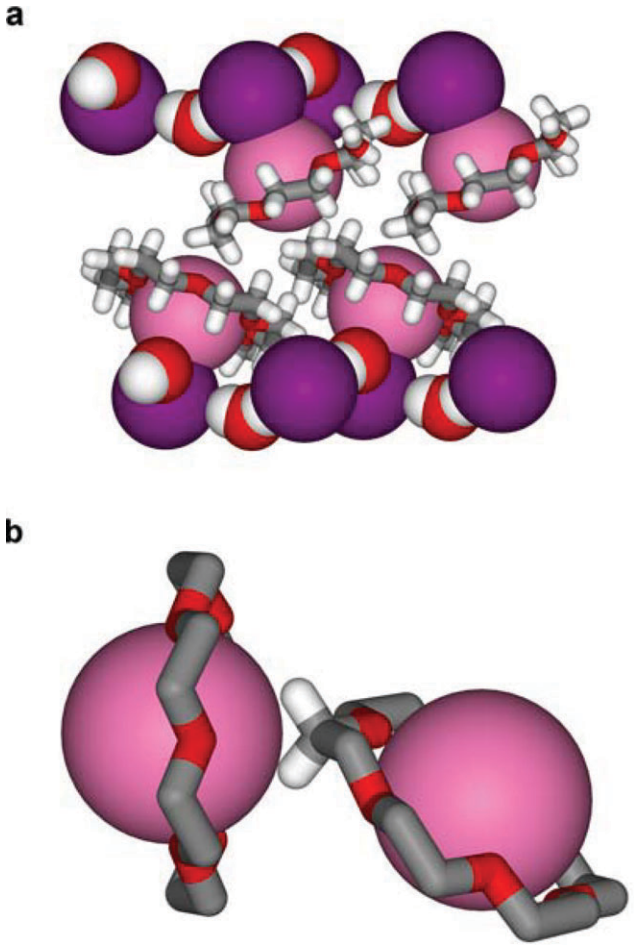
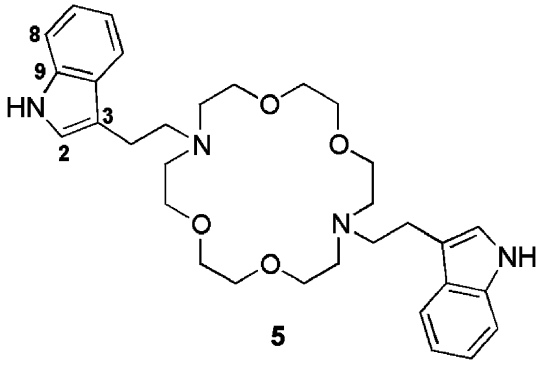


Fig. 1 Crystal structure (stick representation) of (a) $[\mathbf{1}\cdot K]^+[I]^-$. (b) Apical "agostic" $K^+\cdots H-C$-interactions. K^+ magenta, water molecules red and I^- violet spheres.

structures of K^+ [5] and Ca^{2+} [6] lariat-ether complexes, the second apical position is coordinated by a bridging water molecule which is simultaneously H-bonded to both the phenol hydroxyl ($d_{O\cdots O}$ of 2.83 Å) and the iodide anion ($d_{O\cdots I}$ of 3.56 Å). Moreover the phenol hydroxyl is H-bonded to the urea oxygen ($d_{O\cdots O}$ of 2.66 Å) of the neighboring receptor **3**.

In $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$ the second apical site of the cation is occupied by the indole moiety. As in most of the previously reported structures we observed a close π-contact between indole and the bound K^+ cation at the pyrrolo-subunit.[7–9] Selected distances and the relative orientation of the K^+ with respect to the indole are shown in Table 1 and Fig. 3, respectively. The NH indole moiety is H-bonded with the urea oxygen ($d_{N\cdots O}$ of 2.80 Å) of a vicinal phenylureidoindole **4** molecule. This influences the relative interaction between the indole-ring and the bound K^+, inducing a lateral contact between the C2═C3 double bond and the cation (Fig. 3).



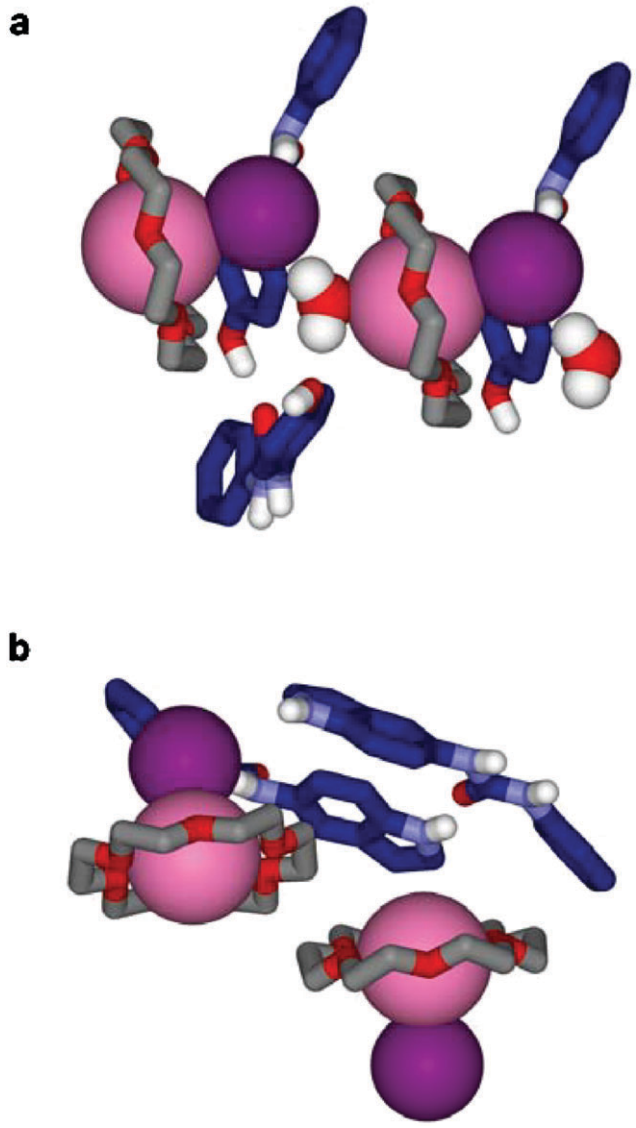


Fig. 2 Crystal structure (stick representation) of (a) $[\mathbf{1}\cdot K]^+[\mathbf{3}\cdot I]^-$ and (b) $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$. K^+ magenta and I^- violet spheres.

In $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$ the distance between K^+ and the C2═C3 centroid is 3.24 Å, indicating rather strong K^+–π contacts. This new interaction is geometrically different from most of the cation–π interactions observed in the solid state structure of the lariat-crown complex $[\mathbf{5}\cdot K]^+[I]^-$ reported by Gokel *et al.* (Table 1, Fig. 3), where the cation is centered to the pyrrole ring and is closely situated to the C2 atom.[7,8]

In nature either aromatic subunit of the indole ring, the arene terminus of tryptophan, may be available for cation complexation. Moreover, the new heterocomplex system $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$ presented here, despite the multiple possibilities of K^+–π contacts with the sterically available phenyl, phenyl-indole and pyrrole-indole rings of **4** (the ligand could turn/translate around/with the I^- anion), shows that the pyrrolo C2═C3 double bond is a versatile π-donor.

^{1}H NMR experiments were performed on solutions of phenylureidoarene anion receptors **2–4** and of heterocomplexes $[\mathbf{1}\cdot K]^+[\mathbf{2}\cdot I]^-$, $[\mathbf{1}\cdot K]^+[\mathbf{3}\cdot I]^-$ and $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$ in acetone-d_6 at 25 °C (Fig. 4).

^{1}H NMR dilution experiments on solutions of 0.04 to 0.16 mol L^{-1} of $[\mathbf{1}\cdot K]^+[\mathbf{2}\cdot I]^-$, $[\mathbf{1}\cdot K]^+[\mathbf{3}\cdot I]^-$ and $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]$ showed an invariant shift of all ^{1}H NMR signals upon increasing concentration, which is indicative of a strong self-association through the anion hydrogen bonding, cation complexation and ion-pairing of resulted species in solution.

Table 1 Geometry of the K^+–indole π-interaction. A comparison between Gokel's lariat complex[7,8] $[\mathbf{5}\cdot K]^+[I]^-$ and the $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$ heterocomplex

	K^+–R distance (Å)	
R	**5**	$[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$
K^+–N_{indole}	3.51	4.43
K^+–$C2_{indole}$	3.32	3.34
K^+–$C3_{indole}$	3.57	3.27
K^+–$C8_{indole}$	3.89	4.40
K^+–$C9_{indole}$	3.91	4.97
K^+–pyrrolocentroid	3.50	3.96
K^+–benzocentroid	4.77	5.63

The urea NH protons and the adjacent aromatic protons (H3, H4, H5) showed typical downfield shifts of 1.01 to 1.25 ppm and 0.15 ppm, respectively, which is indicative of strong H-bonding with the I^- anion. The other hydrogen atoms H1, H5, H7 and H8, non-adjacent to the urea moiety, were upfield shifted ($\Delta\delta = -0.07$ to -0.15 ppm) and suggesting their close proximity with the bound cation. Similar effects have been reported for alkali metal cation–indole π complexation in solution and in all cases the arene residue is predicted to coordinate the cation.[7,8] Hydrogens of the indole NH and the phenol OH exhibited modest shifts and seem practically unaffected by complexation: $\Delta\delta = -0.02$ and -0.1 ppm, respectively. The expected deshielding, consistent with the H-bonding observed in the solid state structures, is probably accompanied by a shielding phenomenon due to the close proximity of the cation. We therefore conclude that the complexes adopt similar conformations in solution to those observed in the solid state. This could be argued by strong ion-pairing interactions and favorable hydrogen bonding in a solvent like acetone.

Conclusion

In summary, we present here solid state and solution study evidence that demonstrates alkali metal cation–π and $K^+\cdots$H–C- "agostic" interactions for a family of macrocyclic heterocomplexes. We have emphasized the macrocycle–cation π-interaction by its ureidoarene counteranion in solution and in the solid state. Other similar systems include inorganic anions, such as tetraphenylborate, or solvent molecules, such as toluene or benzene, forming the cation–π complexes with alkali cations.[3b] In our case, two distinct entities, the aromatic residue of the anion receptor and the crown–cation, could interact apically as constituents of geometrically discrete ion-pair receptors. Theoretical treatments and most solid state

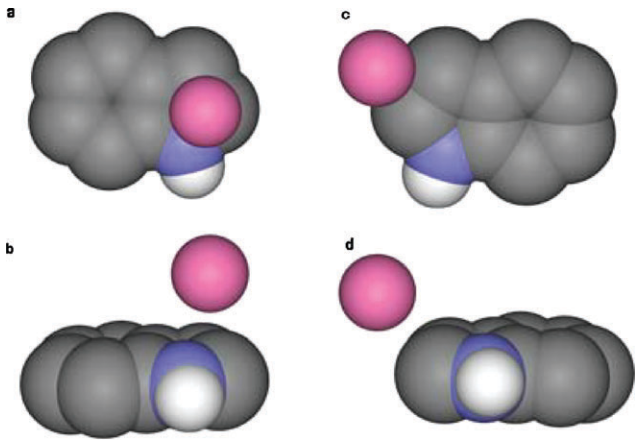


Fig. 3 Top and side-view CPK representation of K^+–indole cation–π interactions for the complexes (a), (b) $[\mathbf{5}\cdot K]^+[I]^-$ [7,8] and (c), (d) $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$. K^+ represented as magenta scaled spheres.

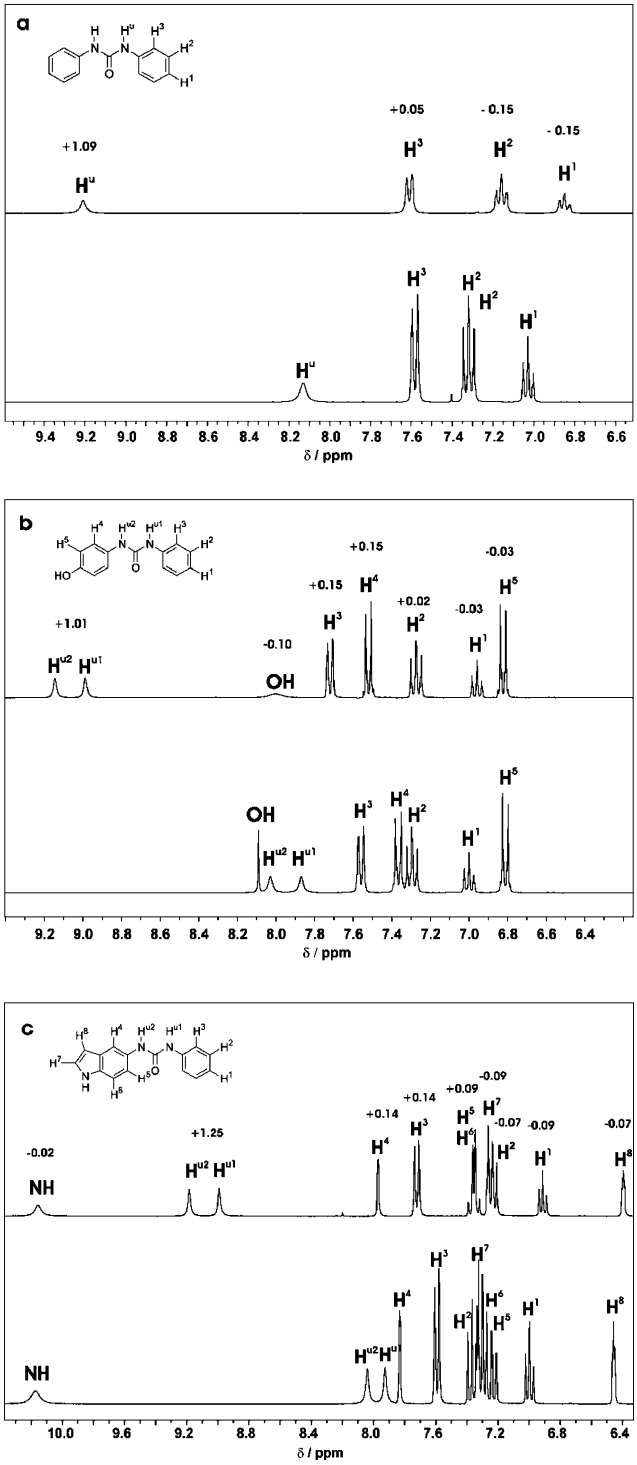


Fig. 4 ^{1}H NMR spectra of phenylureidoarene anion receptors (a, bottom) **2**, (b, bottom) **3**, (c, bottom) **4** and of heterocomplexes (a, top) $[\mathbf{1}\cdot\mathrm{K}]^+[\mathbf{2}\cdot\mathrm{I}]^-$, (b, top) $[\mathbf{1}\cdot\mathrm{K}]^+[\mathbf{3}\cdot\mathrm{I}]^-$ and (c, top) $[\mathbf{1}\cdot\mathrm{K}]^+[\mathbf{4}\cdot\mathrm{I}]^-$ in acetone-d_6 at 25 °C.

structures predict that indole should bind to an alkali metal with the benzocentroid.[2] In terms of dynamic diversity the heteroduplex complex $[\mathbf{1}\cdot\mathrm{K}]^+[\mathbf{4}\cdot\mathrm{I}]^-$ represents an attractive illustration of the self-selection, based on specific cation–pyrrole π-interactions in competition with two other benzene rings, of a unique solid state component. Once again, and without any constraining steric impediment in the $[\mathbf{1}\cdot\mathrm{K}]^+[\mathbf{4}\cdot\mathrm{I}]^-$ complex, the pyrrolo subunit of the indole (*i.e.* the C2═C3 bond) is a strong π-donor group.

These systems may be used in principle for comparative membrane transport experiments, leading to more subtle analyses of these interactions, and such studies are under way.

Experimental

Methods and materials

All reagents were obtained from commercial suppliers and used without further purification. All organic solutions were routinely dried by using sodium sulfate (Na_2SO_4). ^{1}H NMR spectra were recorded on an ARX 300 MHz Bruker spectrometer in acetone-d_6, with the use of the residual solvent peak as reference. Mass spectrometric studies were performed in the negative and the positive ion mode using a quadrupole mass spectrometer (Micromass, Platform 2+). Samples were dissolved in acetonitrile and were continuously introduced into the mass spectrometer at a flow rate of 10 mL min^{-1} through a Waters 616HPLC pump. The temperature (60 °C) and the extraction cone voltage (V_c = 5–10 V) were usually set to avoid fragmentations.

General procedure for the synthesis of compounds 2–4 and heterocomplexes $[\mathbf{1}\cdot\mathrm{K}]^+[\mathbf{2}\cdot\mathrm{I}]^-$, $[\mathbf{1}\cdot\mathrm{K}]^+[\mathbf{3}\cdot\mathrm{I}]^-$ and $[\mathbf{1}\cdot\mathrm{K}]^+[\mathbf{4}\cdot\mathrm{I}]^-$

2–4 were prepared by adding phenyl isocyanate to the corresponding amino derivative in acetonitrile and the reaction was refluxed under argon for 5 h. After removal of the solvent, the residue was subjected to recrystallization from acetonitrile to afford **2–4**.

The numerations used for the assignments of the ^{1}H NMR signals (according to the corresponding COSY spectra) are shown in Fig. 4.

1,3-Diphenylurea, 2. ^{1}H NMR (300 MHz, acetone-d_6): δ(ppm) 8.13 (s, 2H, NH); 7.59 (dd, 4H, H^3, J = 7.91 Hz); 7.32 (t, 4H, H^2, J = 8.44 Hz); 7.03 (t, 2H, H^1, J = 7.42 Hz).

$[\mathbf{1}\cdot\mathrm{K}]^+[\mathbf{2}\cdot\mathrm{I}]^-$. ^{1}H NMR (300 MHz, acetone-d_6): δ(ppm) 9.22 (s, 2H, NH); 7.63 (dd, 4H, H^3, J = 8.58 Hz); 7.18 (t, 4H, H^2, J = 8.32 Hz); 6.87 (t, 2H, H^1, J = 7.68 Hz); 3.55 (m, 24H, CH_2–O). ESI-MS (CH_3CN) m/z: 339.2 $[\mathbf{2}\cdot\mathrm{I}]^-$; 551.7 $[(\mathbf{2})_2\mathrm{I} - \mathrm{H}]^-$; 763.70 $[(\mathbf{2})_3\mathrm{I} - \mathrm{H}]^-$.

1-(4-Hydroxyphenyl)-3-phenylurea. 3 ^{1}H NMR (300 MHz, acetone-d_6): δ(ppm) 8.09 (s, 1H, OH); 8.03 (s, 1H, NH^{u2}); 7.87 (s, 1H, NH^{u1}); 7.56 (dd, 2H, H^3, J = 3.07 Hz); 7.37 (dd, 2H, H^4, J = 4.61 Hz); 7.30 (t, 2H, H^2, J = 16 Hz); 7.00 (t, 1H, H^1, J = 7.3 Hz); 6.82 (dd, 2H, H^5, J = 4.48 Hz).

$[\mathbf{1}\cdot\mathrm{K}]^+[\mathbf{3}\cdot\mathrm{I}]^-$. ^{1}H NMR (300 MHz, acetone-d_6): δ(ppm) 9.14 (s, 1H, NH^{u2}); 9.98 (s, 1H, NH^{u1}); 8.00 (b, 1H, OH); 7.71 (dd, 4H, H^3, J = 6.66 Hz); 7.52 (dd, 2H, H^4, J = 8.96 Hz); 7.27 (t, 2H, H^2, J = 8.33 Hz); 6.95 (t, 1H, H^1, J = 7.3 Hz); 6.81 (dd, 2H, H^5, J = 8.96 Hz); 3.60 (m, 24H, CH_2–O). ESI-MS (CH_3CN) m/z: 355.5 $[\mathbf{3}\cdot\mathrm{I}]^-$; 582.8 $[(\mathbf{3})_2\mathrm{I} - \mathrm{H}]^-$; 811.27 $[(\mathbf{3})_3\mathrm{I} - \mathrm{H}]^-$; ESI+MS ($CH_3CN$) m/z: 267.7 $[\mathbf{3}\cdot\mathrm{K}]^+$; 495.7 $[(\mathbf{3})_2\mathrm{K} + \mathrm{H}]^+$; 723.7 $[(\mathbf{3})_3\mathrm{K} + \mathrm{H}]^+$; 952.2 $[(\mathbf{3})_4\mathrm{K} + \mathrm{H}]^+$; 1180.5 $[(\mathbf{3})_5\mathrm{K} + \mathrm{H}]^+$; 1408.1 $[(\mathbf{3})_6\mathrm{K} + \mathrm{H}]^+$.

1-(1*H*-Indol-5-yl)-3-phenylurea. 4 ^{1}H NMR (300 MHz, acetone-d_6): δ(ppm) 10.17 (s, 1H, NH); 8.04 (s, 1H, H^{u2}); 7.92 (s, 1H, H^{u1}); 7.83 (s, 1H, H^4); 7.60 (dd, 2H, H^3, J = 9 Hz); 7.21–7.40 (m, 5H, H^2, H^5, H^6, H^7); 7.00 (t, 1H, H^1, J = 7.29 Hz); 6.45–6.47 (t, 1H, H^8, J = 4.23 Hz).

$[\mathbf{1}\mathrm{K}]^+[\mathbf{4}\mathrm{I}]^-$. ^{1}H NMR (300 MHz, acetone-d_6): δ(ppm) 10.16 (s, 1H, NH); 9.18 (s, 1H, H^{u2}); 8.99 (s, 1H, H^{u1}); 7.97 (s, 1H, H^4); 7.73 (dd, 2H, H^3, J = 7.56 Hz); 7.32–7.36 (m, 2H, H^5, H^7); 7.21–7.27 (m, 3H, H^2, H^6); 6.91 (t, 1H, H^1, J = 8.45 Hz); 6.40 (d, 1H, H^8, J = 4.48 Hz); 3.68 (m, 24H, CH_2–O). ESI+MS (CH_3CN) m/z: 290.4 $[\mathbf{4}\cdot\mathrm{K}]^+$; 541.5 $[(\mathbf{4})_2\mathrm{K} + \mathrm{H}]^+$. ESI-MS

(CH_3CN) m/z: 378.7 $[3I]^-$; 629.9 $[(\mathbf{4})_2I - H]^-$; 881.2 $[(\mathbf{4})_3I - H]^-$.

Crystallographic details

$[\mathbf{1}\cdot K]^+[I]^-\cdot H_2O$, $C_{12}H_{26}IKO_7$, orthorhombic, space group $P2_12_12_1$, $a = 8.230(3)$ Å, $b = 12.890(7)$ Å, $c = 7.337(7)$ Å, $V = 839.2(14)$ Å^3, $Z = 4$, $D_c = 1.619$ g cm^{-3}, $R_1 = 0.0746$, w$R_2 = 0.0769$ for 4541 $[I > 2\sigma(I)]$ data, 199 parameters refined.

$[\mathbf{1}\cdot K]^+[\mathbf{3}\cdot I]^-\cdot H_2O$, $C_{25}H_{38}IKN_2O_9$, orthorhombic, space group $P2_12_12_1$, $a = 8.2770(11)$ Å, $b = 10.5760(13)$ Å, $c = 34.165(5)$ Å, $V = 2990.7(7)$ Å^3, $Z = 4$, $D_c = 1.503$ g cm^{-3}, $R_1 = 0.0243$, w$R_2 = 0.0219$ for 7772 $[I > 2\sigma(I)]$ data, 344 parameters refined.

$[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$, $C_{27}H_{37}IKN_3O_7$, orthorhombic, space group $P2_12_12_1$, $a = 8.7154(9)$ Å, $b = 10.7550(10)$ Å, $c = 32.742(3)$ Å, $V = 3069.0(5)$ Å^3, $Z = 4$, $D_c = 1.475$ g cm^{-3}, $R_1 = 0.0317$, w$R_2 = 0.0299$ for 4266 $[I > 2\sigma(I)]$ data, 353 parameters refined.

The diffraction intensities for $[\mathbf{1}\cdot K]^+[I]^-$ and $[\mathbf{1}\cdot K]^+[\mathbf{3}\cdot I]^-$ were collected at the ID11 beamline of the European Synchrotron Radiation Facility in Grenoble, France, using a Bruker Smart CCD Camera at 120 K. The diffraction intensities for $[\mathbf{1}\cdot K]^+[\mathbf{4}\cdot I]^-$ were collected at the X-ray Scattering Service of the Institut Européen des Membranes and the Institut Charles Gerhardt of the Université de Montpellier II, France, at 175 K using an Oxford Diffraction Xcalibur I diffractometer. All three structure were solved by direct methods using SIR2002[13] and refined by least-squares methods on F using CRYSTALS.[14] $[I]^-$ in $[\mathbf{1}\cdot K]^+[I]^-$ was found to be disordered over three different sites with site occupancy factors (s.o.f.) 0.15, 0.8, and 0.05, respectively. This disorder could not be satisfactorily modelled using anisotropic ADP's; the s.o.f.'s were determined – and fixed – as to have approximately equal and reasonable isotropic ADP's for the three atoms. A largest electron density hole of -5.83 Å^3 was found at about 1 Å from the $[I]^-$ ion in the space between crown ether moieties; it can be probably be considered as a spurious hole due to a – still – inadequate modelling of the electron density distribution of the $[I]^-$ ion. CCDC reference numbers 284056–284058. For crystallographic data in CIF or other electronic format and detailed information about the crystal structure refinements see DOI: 10.1039/b509240j

Acknowledgements

This research was supported by the European Science Foundation (EURYI Award 2004), by the "Ministère de la Recherche et de la Technologie" (ACI Jeunes Chercheurs 2002) and by the CNRS. G. Vaughan is kindly thanked for assistance during the measurements at the ID11, ESRF, Grenoble. R. Astier is kindly thanked for the X-ray data collection in Montpellier.

References

1 (*a*) R. MacKinnon, *Angew. Chem., Int. Ed.*, 2004, **43**, 4265–4277; (*b*) A. M. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem., Int. Ed.*, 2003, **42**, 1210–1250; (*c*) J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303–1324.
2 (*a*) E. S. Meadows, S. L. De Wall and G. W. Gokel, *Eur. J. Org. Chem.*, 2000, 2967–2978, and references therein; (*b*) see ref. 49–56 in ref. 6.
3 (*a*) P. Lhotak and S. Shinkai, *J. Phys. Org. Chem.*, 1997, **10**, 273–285; (*b*) M. Cametti, M. Nissinen, A. Dalla Cort, L. Mandolini and K. Rissanen, *J. Am. Chem. Soc.*, 2005, **127**, 3831–3837, and references therein; (*c*) S. D. Zaric, *Eur. J. Inorg. Chem.*, 2003, 2197–2209.
4 (*a*) G. W. Gokel, L. A. Barbour, S. L. De Wall and E. S. Meadows, *Coord. Chem. Rev.*, 2001, **222**, 127–154; (*b*) G. W. Gokel, L. A. Barbour, R. Ferdani and J. Hu, *Acc. Chem. Res.*, 2002, **35**, 878–886; (*c*) G. W. Gokel, *Chem. Commun.*, 2003, 2847–2852; (*d*) G. W. Gokel and A. Mukhopadhyay, *Chem. Soc. Rev.*, 2001, **30**, 274–286.
5 S. L. De Wall, L. J. Barbour and G. W. Gokel, *J. Am. Chem. Soc.*, 1999, **121**, 8405–8406.
6 J. Hu, L. A. Barbour, R. Ferdani and G. W Gokel, *Chem. Commun.*, 2002, 1806–1807.
7 S. L. De Wall, E. S. Meadows, L. J. Barbour and G. W. Gokel, *J. Am. Chem. Soc.*, 1999, **121**, 5613–5614.
8 E. S. Meadows, S. L. De Wall, L. J. Barbour and G. W. Gokel, *J. Am. Chem. Soc.*, 2001, **123**, 3092–3107.
9 J. Hu, L. J. Barbour and G. W. Gokel, *J. Am. Chem. Soc.*, 2002, **124**, 10940–10941.
10 (*a*) M. Barboiu, G. Vaughan and A. van der Lee, *Org. Lett.*, 2003, **5**, 3073–3076; (*b*) M. Barboiu, S. Cerneaux, G. Vaughan and A. van der Lee, *J. Am. Chem. Soc.*, 2004, **126**, 3545–3550.
11 (*a*) F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **B58**, 380–38; (*b*) M. Sievert, V. Krenzel and H. Bock, *Z. Kristallogr.*, 1996, **211**, 794–797; (*c*) I. Patenburg and I. Muller, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2003, **59**, m427–m428; (*d*) R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Cryst.*, 1976, **A32**, 751–767.
12 G. C. Forbes, A. R. Kennedy, R. E. Mulvey, B. A. Roberts and R. B. Rowlings, *Organometallics*, 2002, **21**, 5155–5121.
13 M. C. Burla, M. B. Camalli, G. L. Carrozzini, R. Cascarano, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 2003, **36**, 1103.
14 P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487.