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PAPER

Benzimidazole-based anion receptors: tautomeric switching and selectivity†

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Tautomeric switching is observed in a series of benzimidazole-based anion receptors upon addition of basic anions. An *N*-methylbenzimidazole based receptor selectively interacts with dihydrogen phosphate over a variety of other putative anionic guests *via* a combination of donated and accepted hydrogen bonds.

Introduction

Anion complexation processes[1–3] can often be more complex than they first appear. For example, we have found examples of deprotonation of receptors by basic anions[4,5] (as have other groups),[6] deprotonation of bound anions by free anions in solution,[7,8] and studied the effect of anions on tautomerism processes in acridinone-based anion receptors.[9]

Imidazole and benzimidazole groups have been used in a variety of anion receptors. Often these receptors contain an imidazolium or benzimidazolium group in which the imidazole nitrogen atoms are both covalently bound to sp^3 hybridized carbon atoms. In these systems the positively charged imidazolium CH group functions as a hydrogen bond donor with guests bound by a combination of hydrogen bonding and electrostatic interactions.[10–21]

Less common are systems in which neutral imidazole or benzimidazole units are employed as NH hydrogen bond donors. In these systems, as noted by Causey and Allen in their 2002 report on the anion complexation properties of fluorescent biimidazole diamides,[22] tautomerism processes may affect the nature of the hydrogen bonding array presented to an anionic guest. Several receptors containing 2-aminobenzimidazole have been reported which act as effective receptors for anions.[23–28] Imidazoles, benzimidazoles and related compounds have also been employed in colorimetric,[29–31] fluorescent[32] and electrochemically active[33,34] anion sensors. Imidazoles have also been employed by Merschky and Schmuck as an intramolecular buffer in low-weight organocatalysts for phosphate hydrolysis in water.[35] We have previously explored benzimidazole moieties in receptors designed on complex ureas.[36] We wished to study the effect of anions on a series of simple benzimidazole urea-based anion receptors. These systems were based on our diindolylurea scaffold[37] that has proven highly effective as a receptor for phosphate anions. In the benzimidazole derivatives the urea group will donate a hydrogen bond to the benzimidazole nitrogen. We wished to ascertain the effect of anions on these systems and in particular whether the receptors would tautomerise to offer a convergent array of urea and imidazole NH hydrogen bond donors to particular anions – potentially the most basic anionic guests, increasing the selectivity for these guests over other anionic species (Scheme 1).

Results and discussion

Compounds **1** and **2** were synthesised by the reaction of 4-aminobenzimidazole with either pentafluorophenylisocyanate or hexylisocyanate in pyridine, with the pure product obtained *via* recrystallisation from methanol or ethyl acetate affording yields of 76% and 46% for compounds **1** and **2** respectively. Compound **3** was synthesised by the formation in dichloromethane of the carbonyldiimidazole-activated derivative of 4-aminobenzimidazole which was then reacted with a second equivalent of the amine in pyridine. The product precipitated from the reaction solution in 45% yield.

Compound **4** was synthesised by coupling 1-methyl-4-aminobenzimidazole with triphosgene in a mixture of dichloromethane and a saturated aqueous solution of $NaHCO_3$. Two crops of the product were isolated, the first by precipitation from the reaction mixture. The remaining solution was reduced *in vacuo* and the residue recrystallised from methanol affording the product as a white crystalline material in 42% overall yield.

Compound **5** was synthesised *via* the formation of an activated carbonyldiimidazole derivative of 7-aminoindole. This compound was reacted with 1-methyl-4-aminobenzimidazole in a chloroform, triethylamine and dimethylformamide solution. The product was isolated by precipitation with water and hexane in a yield of 27%.

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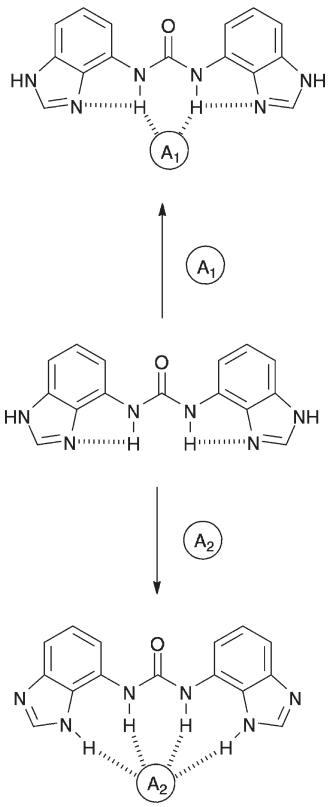
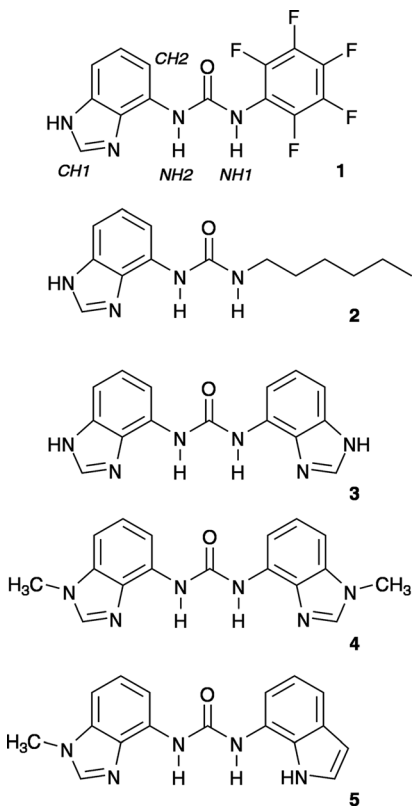
†Electronic supplementary information (ESI) available: Experimental details and characterisation data. CCDC reference numbers 851118–851121. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob06800h



Scheme 1 A dibenzoimidazoleurea compound binds anion A_1 *via* two hydrogen bonds but anion A_2 *via* four. The tautomerism triggered by A_2 increases the number of hydrogen bond donors offered to the anion and directs the lone pairs on the benzimidazole nitrogen atoms away from the anion-binding site so increasing the affinity of the receptor for A_2 over that of A_1.



The interactions of compounds **1–5** with various anionic guests were studied by ^{1}H NMR titration techniques in DMSO-d_6/0.5% water solution. Compound **1** was studied with a variety of anions added as tetrabutylammonium salts. Upon addition of chloride, continuous downfield shifts of one of the urea NH resonances and the benzimidazole NH were observed whilst the signal from the second urea NH group does not shift (Fig. 1). This is evidence that leads us to suggest that the receptor adopts a conformation in which the urea *NH2* forms an intramolecular hydrogen bond to the benzimidazole nitrogen atom leaving the other NH groups to interact weakly *via* a single hydrogen bond with added chloride (Fig. 2).

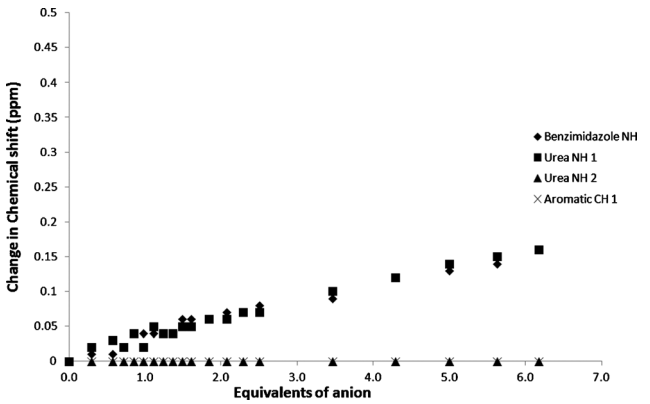


Fig. 1 ^{1}H NMR titration of compound **1** with tetrabutylammonium chloride.

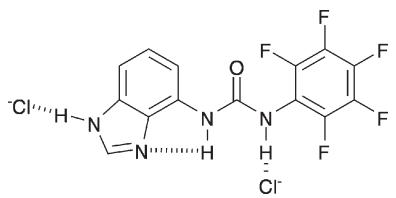


Fig. 2 The conformation of compound **1** in the presence of chloride.

HMBC NMR solution studies of compound **1** in DMSO/0.5% water provide further evidence that this conformation is adopted in solution. In the absence of anionic guests the benzimidazole NH proton (12.5 ppm) and the urea *NH1* proton (9.3 ppm) appear as broad resonances which do not couple to any carbon nuclei. This is evidence that these NH groups are freely exchanging. However the urea *NH2* proton (9.2 ppm) appears as a sharp resonance that couples to various carbon nuclei. This indicates that this NH is not freely exchanging. The most likely reason for this is the formation of an intramolecular hydrogen bond from the urea NH to the adjacent benzimidazole nitrogen (analogous to that shown in Scheme 1). Upon addition of one equivalent of tetrabutylammonium sulfate, significant changes are observed in the HMBC spectrum (see ESI†). Both urea NH resonances have shifted downfield, broadened and resonate at the same chemical shift (11.7 ppm). The urea *NH2* no longer couples to any carbon signals and the benzimidazole NH resonance has also shifted downfield (14.2 ppm). Taken together, this is evidence that leads us to suggest all three of the NH groups are involved in hydrogen bonding to sulfate with the broad

resonances indicating that there is no longer any intramolecular hydrogen bonding.

By increasing the temperature at which the NMR experiments with compound **1** were performed, larger shifts of the NH resonances were observed upon addition of chloride. This is presumably due to a change of binding mode. The ^{1}H NMR spectra of compound **1** in a DMSO-d_6/H_2O 0.5% solution at various temperatures are shown in Fig. 3. As the temperature is increased a broadening is observed with all three NH signals (9.0–13.0 ppm), which may be indicative of the intramolecular hydrogen bonds breaking and the NH groups consequently freely exchanging. To test this theory the ^{1}H NMR titration with tetrabutylammonium chloride was repeated at 333 K. In this case the urea *NH1* proton resonance broadens out and cannot be followed however both the benzimidazole and urea *NH2* proton resonances can be followed during the titration. This time unlike the room temperature experiments shown in Fig. 1 the urea *NH2* proton shifts downfield at the same rate as the benzimidazole NH proton. This is evidence that both NH groups are involved in forming the receptor : anion hydrogen bonded complex and that intramolecular hydrogen bonding and the tautomeric event have a limited effect on the anion binding process at this temperature (see ESI†).

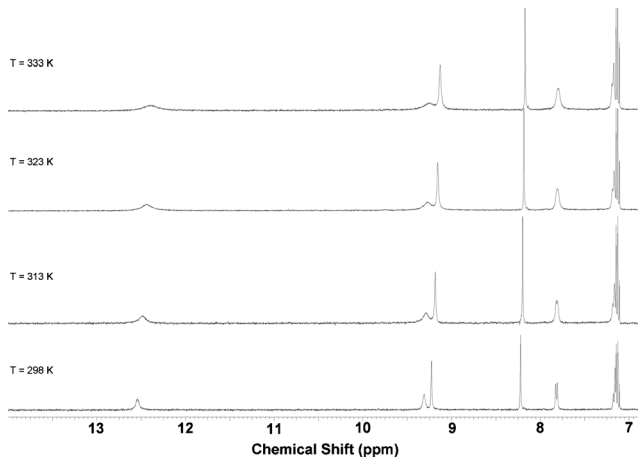


Fig. 3 ^{1}H NMR spectra of compound **1** in DMSO-d_6/H_2O 0.5% at variable temperatures.

A single crystal X-ray structure of receptor **1** was obtained from a crystal grown from a solution of the compound in DMSO.‡ It shows that in the solid state in the absence of anions the receptor adopts a conformation with the benzimidazole NH group oriented away from the urea group (Fig. 4). This compound forms a dimer, held together by the formation of intermolecular hydrogen bonds N1···O11 2.825(2) Å; N12···O11 3.037(2) Å; N13···N24 2.881(3) Å; N21···O21 2.956(2) Å; N22···O21 2.752(2) Å; N23···O11 2.821(2) Å. Thus the

‡ Crystal data for compound **1**: M = 342.24, Monoclinic, a = 16.627(4), b = 8.9654(18), c = 17.878(4) Å, α = 90.00°, β = 93.051(4)°, γ = 90.00°, U = 2661.3(10) Å^3, T = 100(2)K, space group $P21/n$, Z = 8, μ(Mo K\α) = 0.160 mm^{-1}, 18 568 reflections measured, 6004 unique reflections (R_{int} = 0.0351). The final R_1 values were 0.0571 ($I > 2\sigma(I)$). The final $wR(F_2)$ values were 0.1081 ($I > 2\sigma(I)$). The final R_1 values were 0.0680 (all data). The final $wR(F_2)$ values were 0.1130 (all data). The goodness of fit on F_2 was 1.143.

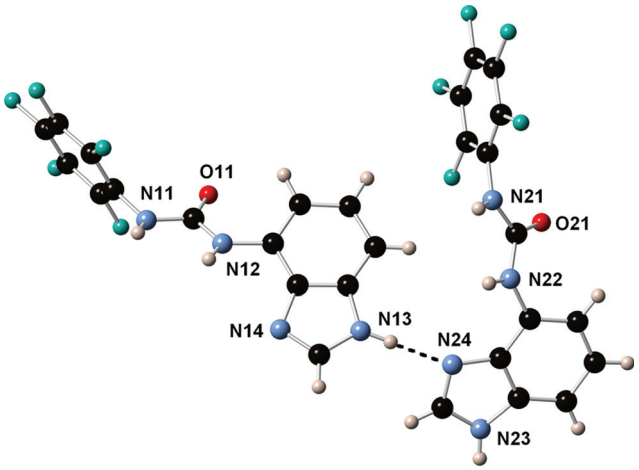


Fig. 4 The single crystal X-ray structure of compound **1**. Non-acidic hydrogen atoms have been omitted for clarity. Data were collected on a Rigaku AFC12 and Saturn724+ mounted at the window of RA-FRE+ HFM with Varimax optics; standard structure solution and refinement procedures were followed.[37]

conformation adopted in the solid state matches the conformation of the compound in solution in the absence of anions.

Upon addition of acetate to the NMR solution of the receptor, all three of the NH resonances broaden. After the addition of one equivalent of acetate a single NH peak begins to reappear and sharpens with further equivalents of anion. Although this makes it impossible to follow the NH resonances it is possible to follow the aromatic CH resonances of the benzimidazolium group as can been seen from the stack plot in Fig. 5. This shows a typical titration profile for the formation of a 1 : 1 complex and is also supported by the Job plot analysis. This is evidence that a different mode of binding occurs upon addition of acetate than was observed with the addition of the chloride anion. This could be due to the more basic acetate anion binding favourably to the other tautomer of the receptor in which all three hydrogen bonds are directed to form a single anion-binding site (Fig. 6).

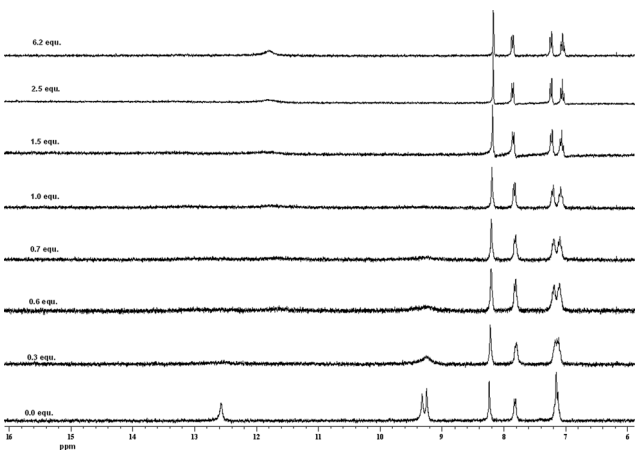


Fig. 5 ^{1}H NMR stack plot of compound **1** *vs.* tetrabutylammonium acetate in DMSO-d_6/H_2O 0.5%.

Addition of benzoate under the same conditions resulted in a slow exchange process on the NMR timescale with resonances for the free ligand broadening and disappearing and new broad

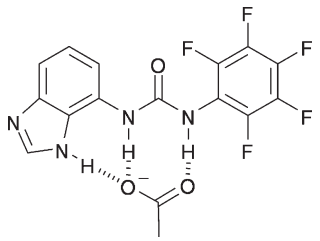


Fig. 6 Proposed mode of binding of acetate in DMSO-d_6/H_2O 0.5% solution.

resonances for the benzoate complex appearing over the course of the titration. In this case all three of the NH groups had shifted downfield and hence we believe that the same binding mode observed with acetate occurs in this case.

Crystals of the benzoate complex of compound **1** were grown by slow evaporation of a methanol solution of the receptor in the presence of excess tetrabutylammonium benzoate.§ The structure (Fig. 7) reveals that in the solid-state benzoate is bound to the tautomer in which the benzimidazole NH is convergently directed with the urea NH groups N1···O3 2.799(5); N2···O3 2.795(6); N3···O2 2.768(5); N3···O3 3.397(6) Å. Two of these complexes are held together by hydrogen bonding interactions with water molecules to create a dimer containing receptor : anion : water 2 : 2 : 2 O4···N4 2.903(6); O4···O2 2.878(5) Å.

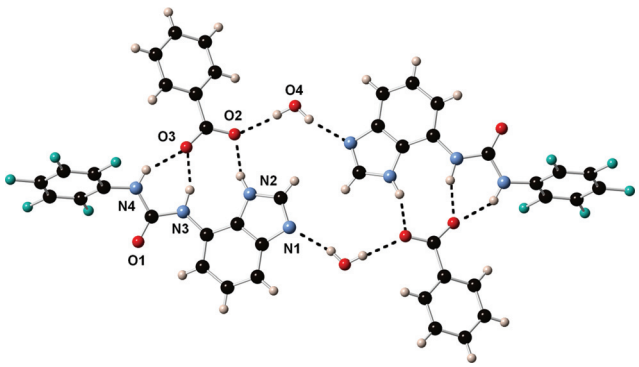


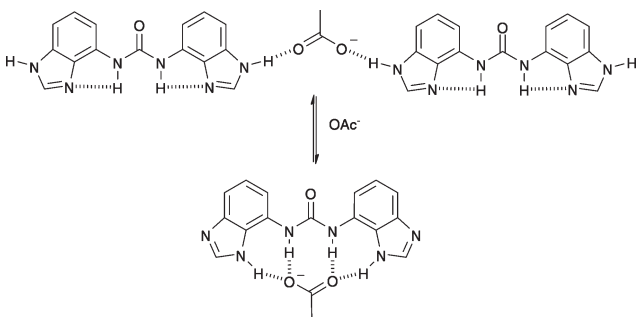
Fig. 7 The single crystal X-ray structure of the benzoate complex of compound **1**. Non-acidic hydrogen atoms and the tetrabutylammonium counter cation have been omitted for clarity. Data were collected on a Rigaku AFC12 and Saturn724+ mounted at the window of RA-FRE+ HFM with Varimax optics; standard structure solution and refinement procedures were followed.[37]

Proton NMR titration studies show that tetrahedral or pseudo-tetrahedral anions such as sulfate or dihydrogen phosphate bind to the three NH groups, presumably in the convergent hydrogen bond donor tautomer. The proton NMR titration curves are sigmoidal in these cases. This is presumably related to the tautomerism processes occurring within the receptor. Although these sigmoidal curves can be seen more clearly with these particular anions the sigmoidal binding curves are also observed with acetate and benzoate and to some extent bicarbonate with the remaining compounds **2–5**. Sigmoidal curves are not observed with anions that have a lower affinity for the receptors such as hydrogen sulfate, nitrate and chloride. Presumably these less basic anions do not induce the tautomeric switch. Additionally, slow exchange processes occur most commonly with dihydrogen phosphate, sulfate and benzoate anions with compounds **1–4**. Some of these examples such as compound **2** and sulfate show several different processes reflected in a combination of slow and fast exchange in the ^{1}H NMR titration experiments.

Compound **2** contains a hexyl chain instead of a pentafluorophenyl group. The interaction of this receptor with chloride was very similar to that of compound **1**. In general the interaction with the other anions was similar to that of compound **1** however in a number of cases more significant broadening of the NH resonances and signal overlap of the urea NH and aromatic CH resonances made it impossible to follow these resonances throughout parts of the titration experiments.

Compound **3** again showed a similar interaction with chloride although in this case as both urea NH groups are involved in intramolecular hydrogen bonding, the anion was observed to only interact with the benzimidazole NH groups (*i.e.* continuous downfield shifts of the benzimidazole NH groups were observed upon addition of chloride whilst the urea NH group resonance was not perturbed).

Upon addition of acetate the benzimidazole NH resonances broaden immediately but do not shift. Between one and two equivalents of acetate the urea NH resonances also broaden into the baseline and then re-appear shifted downfield as 2 equivalents of acetate are added. This may be indicative of initial complexation to the benzimidazole NH groups which at a certain tipping point switches over to a 1 : 1 complex with the anion bound to the urea NH groups and the benzimidazole NH groups (Scheme 2). Interestingly, benzoate behaves in a similar fashion to chloride in this case with interactions only with the benzimidazole NH groups.



Scheme 2 An equilibrium between acetate complexed to the benzimidazole NH groups and acetate bound in a convergent array of four hydrogen bond donors by the alternate tautomer.

Addition of sulfate or dihydrogen phosphate results in a slow exchange complexation process on the NMR timescale indicative of the formation of a 1 : 1 complex. The ^{1}H NMR spectra for the sulfate titration are shown in Fig. 8.

§ Crystal data for the benzoate complex of compound **1**: M = 723.82, Monoclinic, a = 21.464(15), b = 8.350(6), c = 20.873(14) Å, α = 90.00°, β = 98.375(12)°, γ = 90.00°, U = 3701(4) Å^3, T = 100(2)K, space group $P21/c$, Z = 4, μ(Mo K\α) = 0.102 mm^{-1}, 24 627 reflections measured, 6506 unique reflections (R_{int} = 0.0982). The final R_1 values were 0.1173 ($I > 2\sigma(I)$). The final $wR(F_2)$ values were 0.1791 ($I > 2\sigma(I)$). The final R_1 values were 0.1445 (all data). The final $wR(F_2)$ values were 0.1917 (all data). The goodness of fit on F_2 was 1.269.

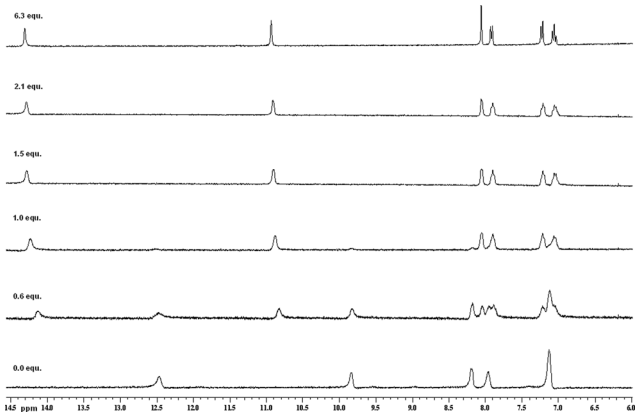


Fig. 8 ^{1}H NMR titration with compound **3** *vs.* tetrabutylammonium sulfate shows slow exchange on the NMR timescale.

By adding two equivalents of HPF_6 to the NMR titration solution and then repeating the NMR titrations a contrasting set of results were obtained. The now diprotonated receptor binds chloride more strongly *via* the urea NH groups (and presumably the benzimidazole NH groups) and anions such as nitrate which do not interact with the other receptors now form weak complexes with the protonated system. More complex ^{1}H NMR titration profiles are obtained with more basic anions possibly due to proton transfer from the protonated receptor to the added anion.

Compound **4** is analogous to compound **3** except that the benzimidazole groups are methylated. This removes the possibility of these groups donating hydrogen bonds. Proton NMR titrations with a variety of anionic guests shows remarkably high selectivity for dihydrogen phosphate (Fig. 9). Presumably the anion donates two hydrogen bonds to the benzimidazole groups as shown in Fig. 10.

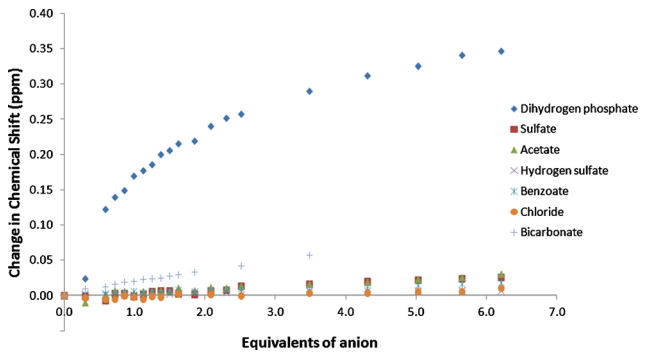


Fig. 9 ^{1}H NMR titrations with compound **4** and a variety of anionic guests added as the tetrabutyl/tetraethyl ammonium salts following the urea NH.

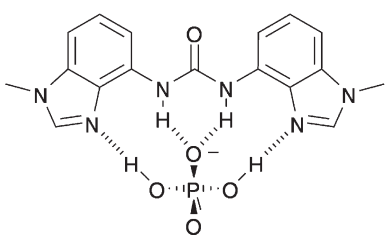


Fig. 10 The proposed binding mode of compound **4** with dihydrogen phosphate.

Crystals of a methanol solvate of compound **4** were grown by slow evaporation of a methanol solution containing compound **4**.¶ The structure (Fig. 11) reveals that in the solid-state the methanol molecules are bound to the receptor through both the hydrogen bond donating and accepting groups within the receptor's cleft, this produces a dimer supported by the formation of CH hydrogen bonds N3···O2B 2.850(3); N3···O2A 2.986(3); N4···O2B 2.856(3); N4···O2A 2.970(3); O2A···N5 2.825(3); O2B···N5 2.767(3); C16···N2 3.402(2) Å.

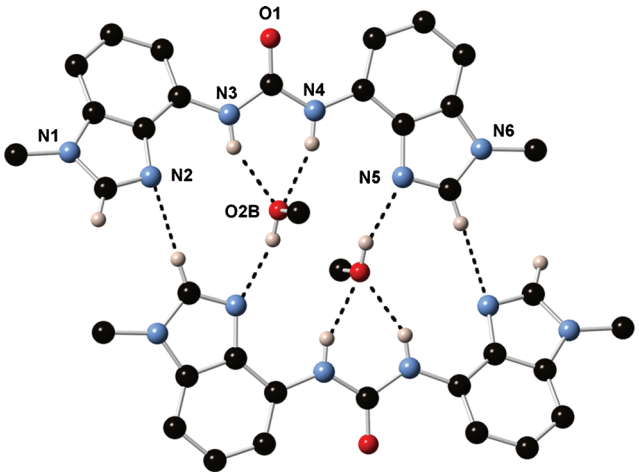


Fig. 11 The single crystal X-ray structure of the methanol complex of compound **4**. Non-acidic hydrogen atoms and parts of the disordered methanol molecule have been omitted for clarity. Data were collected on a Bruker Nonius KappaCCD with a Mo rotating anode generator, standard structure solution and refinement procedures were followed.

A second crystal structure containing a pentameric water cluster was obtained by slow evaporation of a DMSO solution containing compound **4**.‖ This water cluster was found to be supported by intermolecular hydrogen bond formation between the water molecules themselves and two receptor molecules N5···O2W 2.822(2); N6···O2W 3.254(2); O1W···O3W 2.792(2); O3W···N2 2.896(2); O1W···N3 3.086(3); O2W···O1W 2.825 (3); O2W···N2 3.084(2) Å. Fig. 12 shows this pentameric water cluster while Fig. 13 shows a bottom view of the structure.

Compound **5** contains one benzimidazole and one indole group and was found to bind anions with 1 : 1 stoichiometry. The titration curves that were obtained with this receptor and various anionic guests are more typical of simple 1 : 1

¶Crystal data for the methanol solvate of compound **4**: M = 352.40, Monoclinic, a = 7.2914(2), b = 13.7723(3), c = 17.2777(4) Å, α = 90.00°, β = 99.684(2)°, γ = 90.00°, U = 1710.29(7) Å^3, T = 120(2)K, space group $P2_1/c$, Z = 4, μ(MoKα) = 0.094 mm^{-1}, 18 453 reflections measured, 3025 unique reflections (R_{int} = 0.0426). The final R_1 values were 0.0444 ($I > 2\sigma(I)$). The final $wR(F_2)$ values were 0.1151 ($I > 2\sigma(I)$). The final R_1 values were 0.0523 (all data). The final $wR(F_2)$ values were 0.1222 (all data). The goodness of fit on F_2 was 1.024.

‖Crystal data for the water solvate of compound **4**: M = 730.8, monoclinic, a = 29.489(5), b = 7.2109(11), c = 18.264(3) Å, α = 90.00°, β = 119.114(8)°, γ = 90.00°, U = 3392.9(9) Å^3, T = 120(2)K, space group C 2/c, Z = 4, μ(MoKα) = 0.104 mm^{-1}, 9118 reflections measured, 3888 unique reflections (R_{int} = 0.0365). The final R_1 values were 0.0567 ($I > 2\sigma(I)$). The final $wR(F_2)$ values were 0.1514 ($I > 2\sigma(I)$). The final R_1 values were 0.0693 (all data). The final $wR(F_2)$ values were 0.1606 (all data). The goodness of fit on F_2 was 1.080.

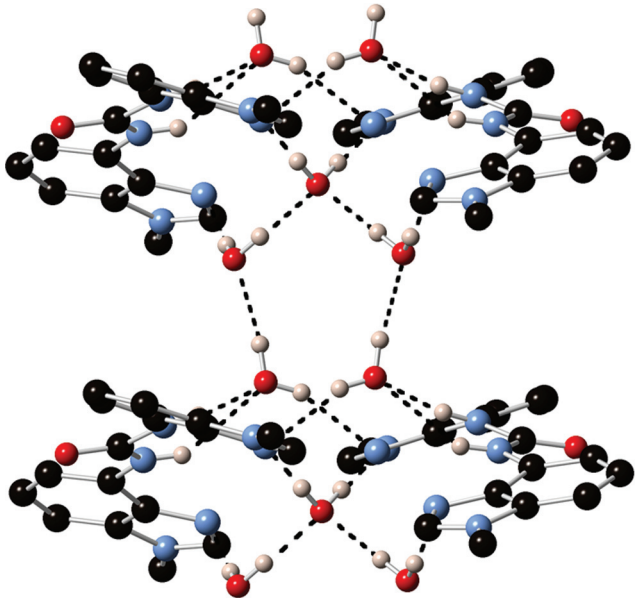


Fig. 12 The single crystal X-ray structure of compound **4**. Non-acidic hydrogen atoms have been omitted for clarity. Data were collected on a Rigaku AFC12 and Saturn724+ mounted at the window of RA-FRE+ HFM with Varimax optics; standard structure solution and refinement procedures were followed.[37]

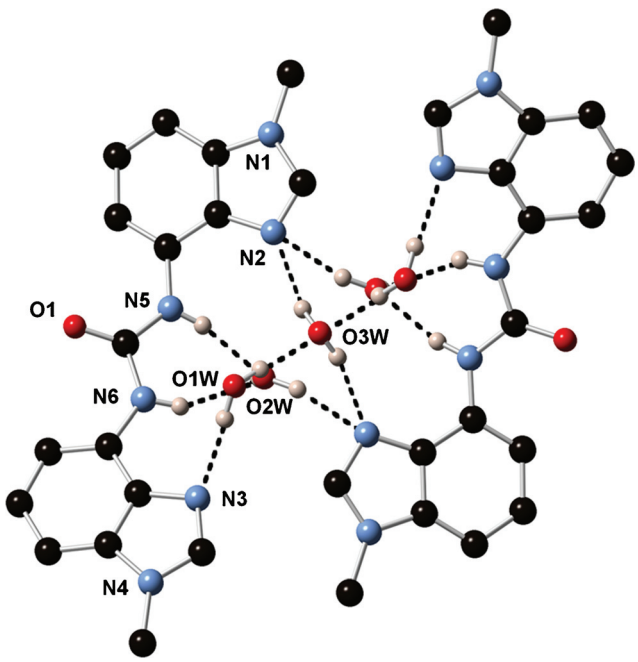


Fig. 13 The single crystal X-ray structure of compound **4** (bottom view). Non-acidic hydrogen atoms have been omitted for clarity. Data were collected on a Rigaku AFC12 and Saturn724+ mounted at the window of RA-FRE+ HFM with Varimax optics; standard structure solution and refinement procedures were followed.[37]

receptor : anion complex formation and are comparable to the titration curves obtained from studies on our previously reported diindolylurea compounds.[38] However the sigmoidal nature of the curve is still apparent upon the addition of dihydrogen phosphate, sulfate, acetate and benzoate anions to the receptor solutions, indicative of the tautomeric switch. However this is not observed with the addition of chloride or nitrate anions which have a weaker affinity to the receptor and therefore do not initiate the switch. Interestingly there is no evidence of this event in the titration curve of **5** with bicarbonate. As with compound **4** and dihydrogen phosphate this is most likely due to both the receptor and the anion being able to form a combination of hydrogen bond donating and accepting interactions. This may also be the case for compound **2** with the addition of this anion. It is because of these more simplistic results that we have found it acceptable to calculate binding constants from these two sets of titration data to give binding constants of 130 M^{-1} and 422 M^{-1} for compounds **2** and **5** respectively.[39]

Conclusions

Tautomeric switching of this type of benzimidazole-based anion receptor offers a method of reducing the affinity for certain anionic guests which do not trigger the switch whilst still strongly interacting with more basic anions which do bind to the alternate tautomer. Methylation of these systems provides receptors that cannot switch and consequently show selectivity towards anions which can both accept and donate hydrogen bonds. We are continuing to explore the chemistry of these interesting receptor systems.

Acknowledgements

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Notes and references

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