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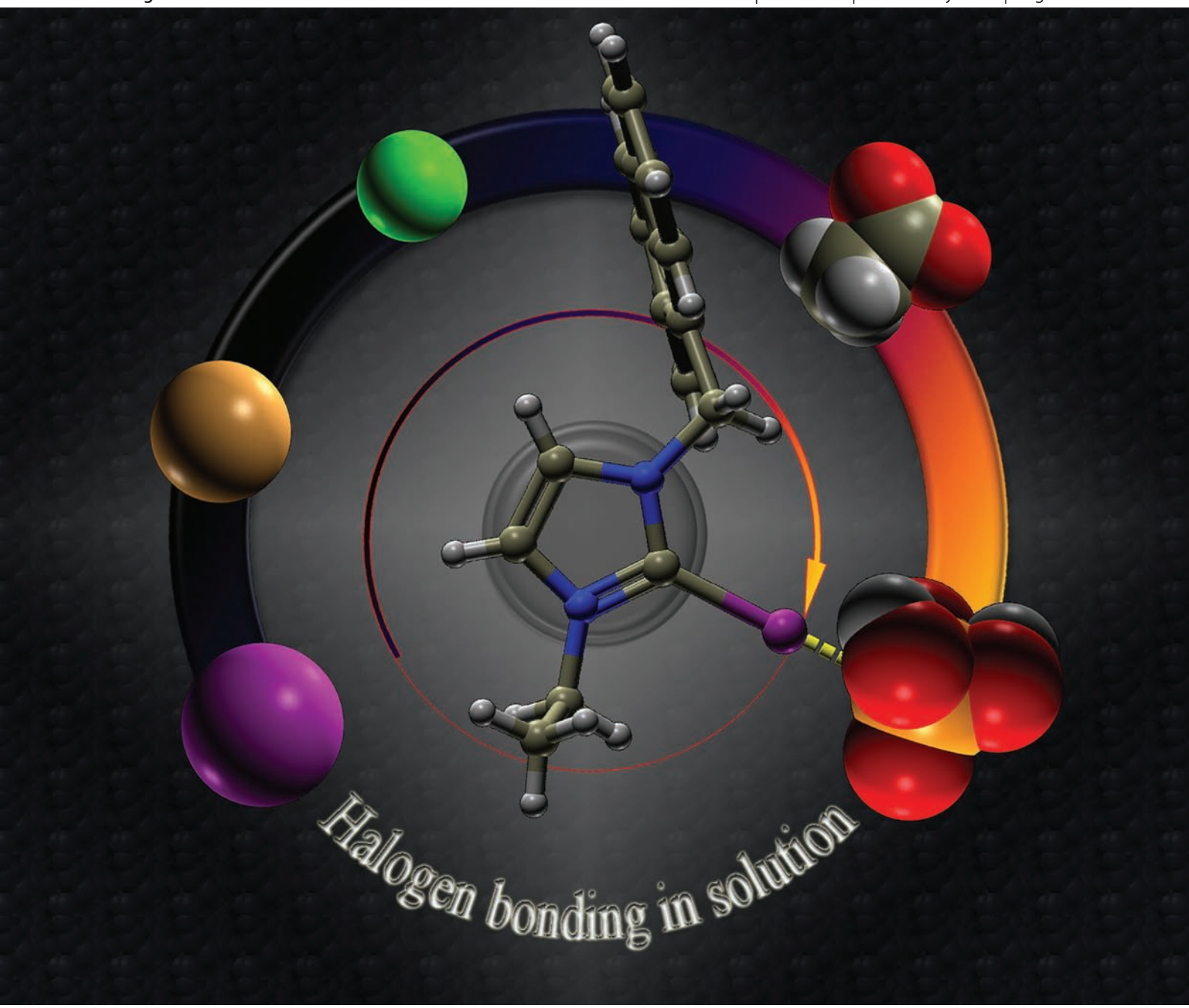

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PAPER

2-Iodo-imidazolium receptor binds oxoanions *via* charge-assisted halogen bonding†

Massimo Cametti,[a] Kari Raatikainen,[a] Pierangelo Metrangolo,*[a,b] Tullio Pilati,[a] Giancarlo Terraneo[a,b] and Giuseppe Resnati*[a,b]

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A detailed ^{1}H-NMR study of the anion binding properties of the 2-iodo-imidazolium receptor **1** in DMSO allows to fully attribute the observed affinities to strong charge-assisted C–I···X$^-$ halogen bonding (XB). Stronger binding was observed for oxoanions over halides. Phosphate, in particular, binds to **1** with an association constant of *ca.* 10^3 M^{-1}, which is particularly high for a single X-bond. A remarkably short C–I···O$^-$ contact is observed in the structure of the salt **1**·$H_2PO_4^-$.

Anion recognition is one of the classical themes in supramolecular chemistry since its early age, and still a flourishing area of research.[1] In particular, recognition of oxoanions, such as phosphate and acetate, is of particular interest due to their biological interest.[2] In the search of efficient ways to capture negatively charged species, the use of many different noncovalent forces has been explored, such as Coulombic interactions, metal coordination, hydrogen bonding (HB), anion···π[3] and, only recently, halogen bonding (XB). The latter is, nowadays, a well-recognized form of noncovalent interaction that generally arises between the positive region of the electrostatic potential surface of halogen atoms and negative sites.[4] Herein we report on a receptor that exploits charge-assisted XB for the strong binding of inorganic phosphate in DMSO solution.

Investigations on X-bonded systems have sharply increased in recent years and nowadays encompass both experimental and theoretical studies. The overwhelming majority of the experimental studies on XB are related to crystal engineering[5] and supramolecular materials.[6] In marked contrast with such an abundance of solid state investigations, studies on anion binding by XB in solution are surprisingly scanty.[7] Only recently, new data on molecular associations of anionic species driven by XB in solution have appeared,[8–11] drawing attention to the huge potential of this interaction in the field.

Notably, the 2-Br-imidazolium unit has been employed by Beer *et al.* as the binding site on the axle molecule of a pseudo-rotaxane system,[9] and also in a bidentate [2 + 2] macrocycle.[10] In the first case, the anion binding event, occurring in $CDCl_3$, acts in favour of the formation of a rotaxane. The XB is only one of several interactions involved in the three-body assembly and results in a two-fold increase of the association constant compared to the HB-based analogue. In the case of the macrocyclic imidazoliophane bis PF_6^- salt, X-bonds are proposed by the authors to be present in a strongly competing solvent (9 : 1 CD_3OD:D_2O mixture), and to be responsible for the observed association constants for the halide anions, measured by ^{1}H-NMR titration experiments. Bromide was found to bind with a K of *ca.* 10^3 M^{-1}, while iodide displayed an approximately 4-fold decrease in binding affinity and chloride was practically not bound. Finally, Taylor *et al.* reported on dipodal and tripodal receptors,[11] some of which were capable of high-affinity anion recognition by XB alone.[11a,b] The authors suggested the possibility of a difference in the intrinsic selectivities of HB and XB for anions, and proposed that the observed preference for halides over oxoanions could be due to greater charge-transfer and/or dispersion contributions in XB.

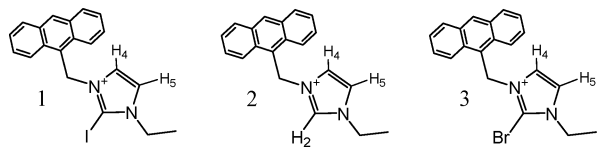
These remarkable examples show that XB can be used for anion binding and in the formation of supramolecular assemblies, and they justify the renewed trust in XB for solution studies. Given the dearth of knowledge on this topic, there is a strong necessity for studies on simple systems in solution. These would provide easier data interpretation, which is essential, especially in cases where the occurrence and selectivity of a given interaction has to be verified and its magnitude evaluated.

This work focused on the study of the anion recognition properties of the 2-iodo-imidazolium derivative **1**·I$^-$ towards a series of anions in DMSO solutions. Our main interest was to evaluate unequivocally the magnitude of XB in solution and its preferential selectivity for oxoanions over halides by using a very simple receptor system. ^{1}H-NMR was found to be a very informative technique which aided the discrimination of various possible binding contributions (HB *versus* XB) in an easy and reliable manner. Relevant comparisons were made with the

[a]*NFMLab Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, via Mancinelli 7, I-20131, Milan, Italy. E-mail: pierangelo.metrangolo@polimi.it, giuseppe.resnati@polimi.it*
[b]*Center for Nano Science and Technology@Polimi, Istituto Italiano di Tecnologia, via Pascoli 70/3, I-20133, Milano, Italy*

† Electronic supplementary information (ESI) available: Experimental procedures and syntheses of compounds; NMR titration experiments; Titration plots; Crystallographic data and CIF files for the structures of **1**·I$^-$, **2**·Cl$^-$, **1**·Br$^-$, **1**·Cl$^-$, and **1**·$H_2PO_4^-$. CCDC reference numbers 828713–828715 and 828717. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob06524f

2-H and 2-Br derivatives, **2**·I^- and **3**·I^-, respectively, in order to assess the relative strength of the XB with respect to the HB in the analogous 2-H derivative and the decrease of the XB strength with the halogen atom polarizability (Scheme 1). The anthracenyl substituent was chosen with the purpose of facilitating the obtainment of suitable crystalline materials for X-ray characterization of the anion–receptor complexes in the solid state, since behaviour of alkyl imidazolium salts as ionic liquids is well known. Iodide salts of **1** and **2** were obtained in good yields by adapting published procedures.[12] The salt **3**·I^- was obtained by the direct bromination of **2**·I^- with *N*-bromosuccinimide (see ESI†).



Scheme 1 Molecular formulae of the studied imidazolium compounds.

Slow evaporation of a concentrated solution of **1**·I^- in DMF produced good quality single crystals of the salt (Fig. 1a). We also obtained single crystals of the salts **1**·Br^- and **1**·Cl^- (Fig. 1b,c) by slow evaporation of receptor **1**·I^- solutions in $CHCl_3$/acetone and acetone, respectively, in the presence of a 10-fold excess of the corresponding tetrabutyl ammonium (TBA) halide salt. As anticipated, the iodine atom on the positively charged imidazolium ring functioned as an efficient XB-donor site, and displays short C–I···X^- distances in all of the three obtained structures (X = I, Br, and Cl). The observed C–I···X^- distances are 3.2828(6) Å (X = I), 3.0994(5) Å (X = Br), and 3.0233(5) Å (X = Cl), which roughly correspond to a 20% reduction with respect to the sum of the van der Waals and ionic radii of the atoms involved.[13] The C–I···X^- angles are 171.93(18)° in **1**·I^-, 178.46(8)° in **1**·Br^-, and 174.14(5)° in **1**·Cl^-, and are perfectly in line with similar X-bonds already described in the literature.[14] Adventitious water molecules are entrapped in the crystal lattice of **1**·Cl^- where they are involved in a rectangular-shaped HB-pattern with Cl^-. The anion is further coordinated *via* weak HB with one proton on the imidazolium ring (H5). In **1**·Br^-, a molecule of $CHCl_3$, crystallization solvent, is weakly H-bonded to the bromide anion, which further interacts with another hydrogen atom on the anthracenyl moiety. Despite the structural differences among the three structures, the occurrence of strong X-bonds is a common feature. For comparison purposes, we also crystallized the chloride salt of the non-halogenated imidazolium derivative **2** (see ESI†).

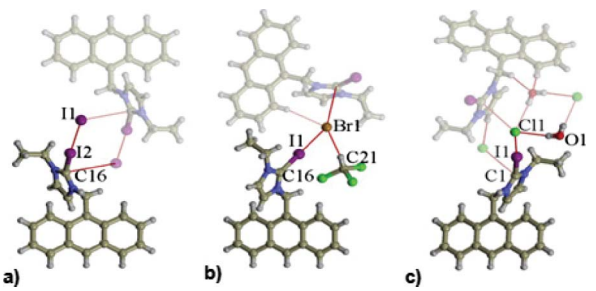


Fig. 1 Single crystal X-ray structures of the 2-iodo-imidazolium (**1**) iodide (a), bromide (b), and chloride (c) salts shown as ball and stick models. Color code: gray, C; light gray, H; purple, I; blue, N; light brown, Br; green, Cl; red, O. Short contacts involving anions are shown as solid red lines.

Noticeably, the slow evaporation of a solution of **1**·I^- in DMF in the presence of a large excess of (TBA)H_2PO_4 led to the precipitation of crystals of the salt **1**·$H_2PO_4^-$ (Fig. 2). The asymmetric unit is composed of the ion pair and one molecule of DMF. The ion pair is tightly bound by strong and directional XB between the I atom of the imidazolium cation and the O3 phosphate oxygen atom. The XB distance (O3···I1) is 2.6024(23) Å and the angle is 177.84(17)°. The detected distance is surprisingly short, representing a 30% reduction with respect to the sum of the van der Waals and ionic radii of I and O, respectively.[13] This indicates a remarkably strong and directional XB, as observed in similar systems.[14] The O3 of the phosphate anion is also involved in the formation of a dimeric assembly of H-bonded phosphates in the classical hexagonal supramolecular motif, which results in infinite anionic chains developing along the *c* axis. The H-bonded chain features distances of 1.726(3) Å and 1.784(4) Å (H4···O6 and H5···O3, respectively), and angles of 164.87(4)° and 164.22(3)° (O4–H4···O6 and O5–H5···O3, respectively). Further interactions stabilise the crystal lattice of **1**·$H_2PO_4^-$. The DMF solvent molecule interacts both with the oxygen O4 of the phosphate chain, due to weak H-bonds, and with the imidazolium ring by the carbonyl group, which points towards the electropositive carbon C1 of the ring. Feeble CH···π interactions between the imidazolium ring and the methylene groups are also present (see ESI†).

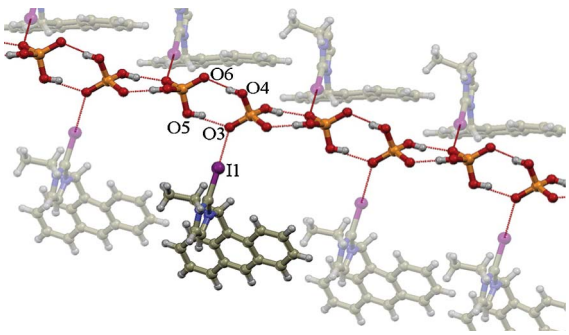


Fig. 2 Single crystal X-ray structure of the salt **1**·$H_2PO_4^-$ shown as ball and stick model. Color code: gray, C; light gray, H; purple, I; blue, N; orange, P; red, O. Short contacts involving anions are shown as dashed red lines.

The anion binding properties of the iodide salts **1**·I^-, **2**·I^-, and **3**·I^- were investigated in DMSO-d6 at 300 K by ^{1}H-NMR titration experiments in which the time averaged signals of the receptor were monitored as a function of increasing concentration of the target anion, added as TBA salt. As an example of a typical experiment, the titration between a 0.010 M solution of the receptor **1**·I^- and (TBA)Cl is shown in Fig. 3a,b (see also ESI†). Some of the receptor protons display small, but discernible upfield shifts upon addition of increasing aliquots of (TBA)Cl. In particular, protons in positions 4 and 5 on the imidazolium ring[15] display the most significant chemical shift variations, but although less pronounced, shifts are also observed for the protons belonging to the anthracenyl moiety. A plot of the observed δ of protons H4 and H5 *versus* the chloride concentration is shown in Fig. 3b. Multiple nonlinear parametric regression of the data using a classical 1 : 1

Table 1 Affinity constants, K (M^{-1}), and maximum δ variations ($\Delta\delta_\infty$, ppm) for the association between the receptors **1**·I^- and **2**·I^- and the salts (TBA)X (X = Cl, Br, I, OAc, H_2PO_4) at 300 K in DMSO-d6

		1	**2**
Cl	K	150 ± 12	9.4 ± 0.5
	$\Delta\delta_\infty$ H4	–0.105	+0.07
	$\Delta\delta_\infty$ H5	–0.150	[a]
	$\Delta\delta_\infty$ H2	—	+0.50
Br	K	67 ± 4	[b]
	$\Delta\delta_\infty$ H4	–0.075	
	$\Delta\delta_\infty$ H5	–0.135	
I[c]	K	34 ± 3 (38 ± 8)	[b]
	$\Delta\delta_\infty$ H4	–0.055	
	$\Delta\delta_\infty$ H5	–0.105	
OAc	K	260 ± 30	23 ± 6
	$\Delta\delta_\infty$ H4	–0.115	–0.02
	$\Delta\delta_\infty$ H5	–0.137	–0.16
	$\Delta\delta_\infty$ H2	—	+1.05
H_2PO_4	K1	1100 ± 300	26 ± 6
	K2	250 ± 100	—
	$\Delta\delta_\infty$ H4	$\Delta\delta_{\infty 1}$ = –0.050 $\Delta\delta_{\infty 2}$ = +0.002	–0.17
	$\Delta\delta_\infty$ H5	$\Delta\delta_{\infty 1}$ = –0.111 $\Delta\delta_{\infty 2}$ = +0.015	–0.69
	$\Delta\delta_\infty$ H2	—	+1.75

[a] Overlap with aromatic protons prevents a precise observation of the signal. [b] No significant shifts were observed (we assumed a negligible affinity). [c] See ref. 21.

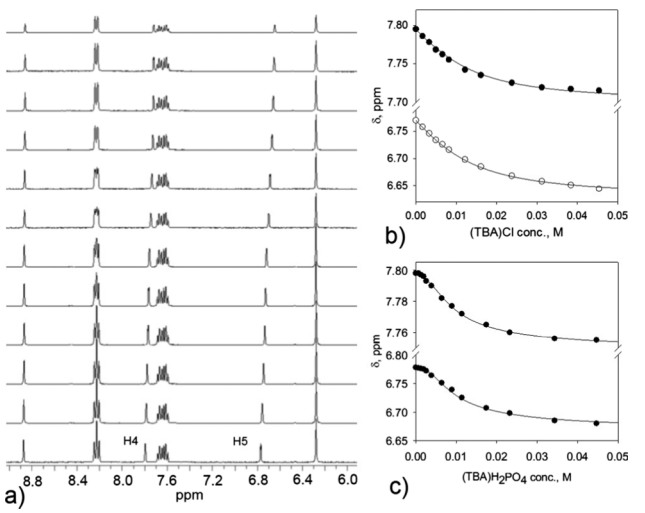


Fig. 3 a) Chemical shift variations of the signals of the receptor **1** upon addition of increasing amounts of (TBA)Cl (from bottom to top). b) Plot of the H4 and H5 chemical shift variations of 1 *vs.* (TBA)Cl concentration. c) Plot of the H4 and H5 chemical shift variations of **1** *vs.* (TBA)H_2PO_4 concentration. Lines represent best fit curves.

binding isotherm allowed calculation of an apparent association constant K (M^{-1}) and maximum δ variations ($\Delta\delta_\infty$, ppm) for the protons H4 and H5. Measurements were run in duplicate and the σ-weighted average[16] of the association constants for each anion are reported in Table 1. In the case of Cl^-, the apparent association constant was calculated to be 150 ± 12 M^{-1}, with $\Delta\delta_\infty$ for the imidazolium protons H4 and H5 of –0.105, and –0.150 ppm, respectively.

In principle, the imidazolium unit **1** is capable of binding the Cl^- anion *via* different modes. XB is one, but also HB may be present, either in a mono- or bi-dentate fashion (Fig. 4). Anion···π interactions[17] may also play a role (Fig. 4, right). Therefore, the

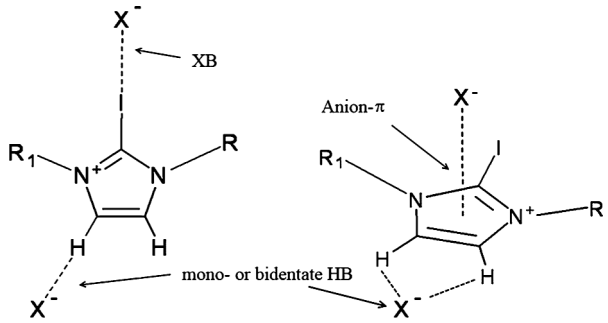


Fig. 4 Possible anion binding modes for the 2-I-imidazolium unit.

chemical shift variations observed could be ascribed to HB of the anion with H4 and/or H5 or to anion···π effects, and not XB alone. Hence, a comparison with a suitable control was conducted.

The 2-H derivative, compound **2**·I^-, was tested for binding with (TBA)Cl under the same experimental conditions. At variance with **1**, the proton signals of **2** were not shifted upfield, but downfield, instead.[18] The 2-H signal is influenced the most by the presence of the Cl^- anion and the plot of its δ *versus* anion concentration is shown in Fig. 4S (ESI†). The data fit a 1 : 1 binding isotherm equation well and the averaged regression parameters obtained are K = 9.4 M^{-1} and $\Delta\delta_\infty$ = +0.50 ppm. The relatively strong acidity of the 2H proton of imidazolium compounds is well known,[19] and HB with the anion is the likely explanation for the observed δ variations. Protons in position 4 and 5 are also downfield shifted, but to a much lesser extent ($\Delta\delta_\infty$ (H4) = +0.07, H5 is overlapping with aromatic protons). HB interactions with H4 and H5 may also be present, but the contribution to the binding of Cl^- is negligible when compared to the contribution of H2, under the present experimental conditions. With these results, a major HB interaction with the 4-H and/or 5-H protons can be ruled out for **1** because that is not supported by the upfield shift variation observed. The nature of such upfield shifts, which may be related to an indirect effect on protons not directly involved in the interaction, can be reasonably imputed to an increase in electron density on the imidazolium ring upon interaction with negatively charged species. Also, given the considerable difference in affinity of **1**·I^- and **2**·I^- for the Cl^- anion and the small electron withdrawing effect of the iodine atom, it is reasonable to exclude the possibility that anion···π interactions are responsible for the observed binding. Comparison between the XB- and the HB-based receptors, **1**·I^- and **2**·I^-, also demonstrates that XB performs more than one order of magnitude better in terms of affinity for chloride in DMSO.

Additionally, the actual occurrence of XB is supported by the comparison of the chloride affinity of **1**·I^- with that of the 2-Br derivative **3**·I^-. Under the same experimental conditions, no significant affinity between chloride and **3** was observed,[20] in line with the generally accepted electrostatic model of XB.[4,5] This finding also supports the argument made above ruling out anion···π interactions as the main driving force for the observed anion binding. Affinity constants between Br^- and I^-[21] anions and the receptor **1** were also measured and the results are reported in Table 1 (all plots can be found in ESI†). Bromide and iodide bind **1** less effectively than chloride, as expected based on general acid–base chemistry considerations. On the other hand, no significant shifts of the relevant protons were observed when increasing

amounts of (TBA)Br and (TBA)I salts were added to a solution of **2**·I^-.

As far as the recognition of oxoanions is concerned, the acetate anion binds to **1** with higher relative affinity than Cl^- and again a significant increase in the association constant (*ca.* 10-fold) is observed when the comparison is made with the HB-based analogue **2**. As for $\Delta\delta_\infty$ values, they are found to be negative for H4 and H5 for both **1** and **2**, while H2 in **2** displays a large positive $\Delta\delta_\infty$ = +1.05 ppm. Interestingly, the H4 and H5 shifts in **2** are highly non-symmetric (*i.e.*, H4 = –0.02 and H5 = –0.17). The fact that the proton H4 is the least upfield shifted indicates the possible occurrence of an additional weaker HB, which however does not significantly influence the XB, which is the main driving force in the association.

From the very short I···O X-bond observed in the structure of **1**·$H_2PO_4^-$, we anticipated the binding ability of **1** for the ion $H_2PO_4^-$ in solution to be extremely interesting. The plot of the chemical shifts of the protons H4 and H5 of the receptor **1** *versus* increasing concentration of the anion is shown in Fig. 1c. The sigmoidal profile of the resulting curve can be explained by the presence of a second associative equilibrium involving the 1 : 1 adduct and a second receptor molecule, with the concomitant formation of a 2 : 1 complex species. Consequently, the data analysis with appropriate equations[22] provides the following fit parameters: K_1 = 1100 ± 300, K_2 = 250 ± 100, $\Delta\delta_{\infty 1}$ (H4) = –0.05, $\Delta\delta_{\infty 1}$(H5) = –0.111 and $\Delta\delta_{\infty 2}$ (H4) = +0.002, $\Delta\delta_{\infty 2}$ (H5) = +0.0015. Although with lower precision, the data obtained can be clearly interpreted. Of the two different equilibria, the 1 : 1 association is favoured, displaying an affinity constant as high as *ca.* 10^3 M^{-1}. Despite the lower effective charge on the phosphate anion when associated to **1**, the 1 : 1 species can still function as an XB-acceptor to form the 2 : 1 species, [(**1**)$_2$·$H_2PO_4^-$]$^+$, with K_2 equal to *ca.* 250 M^{-1}. The second associative step is totally absent with the H-bonding analogue **2**, whose titration profile with $H_2PO_4^-$ is consistent with the presence of a 1 : 1 equilibrium only, and with an association constant K equal to 26 ± 6 M^{-1} (Fig. S6 in ESI†). The comparison between XB and HB, in terms of association constants, is again in favour of the former and, in this case, the increase in affinity is *ca.* 40-fold. The association constant between the $H_2PO_4^-$ ion and the receptor **1** is surprisingly high, especially given the monotopic nature of the receptor.

In summary, we present here a detailed ^{1}H-NMR study on the behaviour of the 2-iodo-imidazolium receptor **1** regarding its ability to bind anions in the competitive DMSO solvent. Detailed inspection of the NMR data proved useful for distinguishing between HB and XB contributions and to provide association models to account for the observed chemical shift variations. Following this, the increased anion affinity encountered in solution with **1**, with respect to its HB analogue **2**, can therefore be unambiguously ascribed to the presence of relatively strong charge-assisted XB. Converse to that previously reported in the literature, oxoanions such as acetate and phosphate display higher affinities than halides when X-bonded to simple receptors. In particular, a relatively strong association (*ca.* 10^3 M^{-1}) is found with $H_2PO_4^-$. Such affinity is especially interesting since a single X-bond is mainly responsible for it. Solid state data obtained by X-ray diffraction on single crystals of halide and phosphate salts of **1** are consistent with solution studies and show the presence of strong X-bonds featuring the iodine atom of **1** and the anionic species.

Given the present knowledge and interest in X-bonded supramolecular systems, detailed studies on structurally simple systems are extremely important and provide the background information on XB-behaviour in solution necessary for the design of more structurally elaborate receptors for oxyanions: an endeavour that is currently receiving considerable attention in our laboratory.

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with respect to the N atom alkylated with the anthracenyl substituent (H4).
16 Final K are weighted average of the values obtained by two independent experiments using the formula $K = (\sum_i^N \frac{K_i}{\sigma^2_i})/(\sum_i^N \frac{1}{\sigma^2_i})$ where σ corresponds to the single measurement fit error.
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20 An example of a titration experiment made with **3**·I^- and (TBA)Cl is given in the ESI†. Fit parameters: K = 2 ± 1 M^{-1}; Δ_∞(H4) = +0.40 ppm; Δ_∞(H5) = –0.1 ppm.
21 The starting solution of the receptor already contains a stoichiometric amount of iodide, present as counteranion. Since the affinity for I^- is low, a semiquantitative comparison remains valid (see Fig. 2S in the ESI†).
22 Derived from the equations reported in Z.-X. Wang, *FEBS Lett.*, 1995, **360**, 111–114.