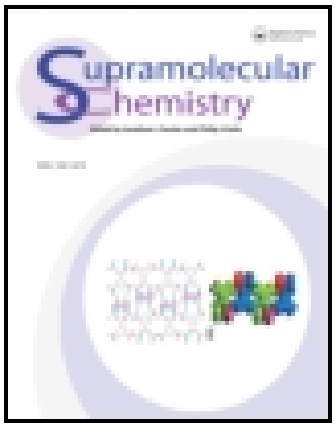

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A new anion receptor utilising aromatic and aliphatic C···H hydrogen bonds

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We have synthesised **2**, which bound weakly basic halide ions only with C—H···anion hydrogen bonds. Compound **2** utilised one aromatic C—H hydrogen bond and one benzylic C—H hydrogen bond to bind weakly halide ions such as chloride, bromide and iodide in solution. *Ab initio* calculations of binding energy values for these anions are in good agreement with experimental data. Although the binding affinities of **2** for these anions were low, **2** could be a unique example of host, which utilised only C—H hydrogen bonds to bind anion.

Keywords: C—H hydrogen bonds; anion receptor; synthesis

Introduction

The development of artificial receptors for the anions has been an important field of supramolecular chemistry and has proven its roles in biological and environmental systems, and in the area of medicine and catalysis (*1–7*). In designing anion receptors, hydrogen bonds are important anion recognition elements due to their directionality. As anions display a wide range of geometries, directionality of hydrogen bonds is frequently utilised to achieve complementarity between anions and receptors. Most hydrogen bonding anion receptors utilise N—H···anion or O—H···anion hydrogen bonds (*8–10*). C—H···anion hydrogen bonds are rarely utilised for anion-binding elements. However, C—H···anion hydrogen bonds play an important role in nature (*11–16*). In addition, increasing evidence has been gathered that C—H groups can participate in bonding and lead to enhanced anion-binding affinity (*7, 17–31*).

In many cases, C—H···anion hydrogen bond interactions usually coexist with other strong hydrogen bonds (*32–37*). However, the receptors involving only C—H···anion hydrogen bonds are still scarce (*38–45*). To investigate the participation of C—H hydrogen bond in the anion-binding event, we have designed compound **1** and expected that this receptor would utilise one N—H hydrogen bond and two benzylic C—H hydrogen bonds to bind anion as shown in Figure 1.

Compound **1** was obtained from the reaction between 2,2-dipyridyl amine and 4-nitro benzyl bromide in acetonitrile in 80% yield. However, characterisation of the product revealed that delocalisation of a lone pair electron from the central amine gave **2** with a resonance structure and only +1 charge (Figure 2). Before titration, the counter anion was exchanged using ammonium hexafluorophosphate.

Experimental

Synthesis and characterisation

Synthesis of **2·Br**$^-$: 2,2-Dipyridyl amine (174.7 mg, 1.01 mmol) and 4-nitro benzyl bromide (521.8 mg, 2.04 mmol) were dissolved in 10 ml acetonitrile. The solution was stirred for a day at 80°C. The precipitate was filtered and washed with MC and ether. The yield was 80.0% (417.9 mg). Anal. Calcd for $C_{24}H_{20}BrN_5O_4$ (279.31), **2·Br**$^-$: C, 55.18; H, 3.86; N, 13.41. Found: C, 55.10; H, 3.85; N, 13.41%. IR (KBr): ν (cm^{-1}) = 1623.9(m), 1555.7(w), 1503.6(s), 1459.6(m), 1402.6(m), 1341.9(m), 1157.6(m), 1112.4(w), 919.6(w), 773.6(m), 734.2(m). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.42 (d, 2H, J = 6.4 Hz), 8.05 (d, 4H, J = 9.6 Hz), 8.00 (t, 2H, J = 6.85, 8.8 Hz), 7.39 (d, 2H, J = 8.8 Hz), 7.16 (d, 4H, J = 9.6 Hz), 7.07 (t, 2H, J = 6.4 Hz), 5.46 (s, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 156.23, 147.54, 143.70, 143.02, 141.89, 127.22, 123.62, 116.45, 114.58, 55.87. FAB MS m/z (M^+): calcd, 279.31, found, 279.25.

Synthesis of **2·PF$_6$**: **2·Br**$^-$ (100 mg) was dissolved in 20 ml water. Then, 10 ml of 1 M NH_4PF_6 in H_2O was added and stirred for 30 min. The precipitate was filtered and washed with diethyl ether. Filtration of precipitate gave **2·PF$_6^-$** (102 mg) in 91% yield.

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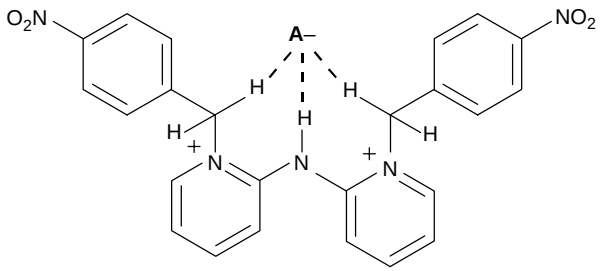

Figure 1. The expected binding mode between compound **1** and anion.

Fluorescence titration

A solution of host 2 (20 μM) in acetonitrile was titrated with a solution of tetrabutylammonium salts (1 M) in acetonitrile. The addition was done stepwise, and after each step, the formation of complex was monitored by fluorescence spectroscopy. The volume change in host solution was about 10% during titration, and dilution effect was ignored.

^{1}H NMR titration

A solution of host 2 (2 mM) in acetonitrile was titrated with a solution of tetrabutylammonium salts (2 M) in acetonitrile. The addition was done stepwise, and after each step, the formation of complex was monitored by ^{1}H NMR spectroscopy. In the NMR titrations, the mole ratio was measured by integration values between host **2** and tetrabutylammonium anion salts.

Results and discussion

Compound **2** displayed strong fluorescence emission in acetonitrile as shown in Figure 3.

The excitation wavelength and emission wavelength were 376 and 432 nm, respectively. The association between **2** and bromide was investigated first by

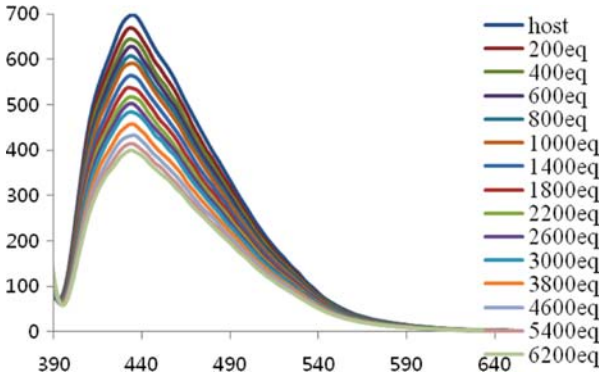

Figure 3. The change in fluorescence spectra in the 20 μM solution of host **2** in acetonitrile when tetrabutylammonium bromide was added (a) and a Benesi–Hildebrand plot by the change in the fluorescence intensity at 432 nm (b).

fluorescence titration. The fluorescence change in **2** was monitored in acetonitrile. The intensity of emission spectrum from 20 μM solution of compound **2** gradually decreased as the concentration of tetrabutylammonium bromide salts increased, which indicates the association between **2** and bromide. However, to reach a saturation point many equivalents of bromide were required, which indicates low affinity of **2** for the bromide. This result suggests that this compound would use only C—H···anion hydrogen bonds. The stoichiometry between **2** and bromide was determined by Job plot using ^{1}H NMR, and it clearly indicated 1:1 stoichiometry (Figure 4) (*46*). A Benesi–Hildebrand plot by the change of the fluorescence intensity at 432 nm gave an association constant (Figure 3(b)) (*47*). From the experiments, host **2** showed association constant of 14.3 (M^{-1}) for bromide.

The complexation ability of **2** to the bromide was also measured by standard ^{1}H NMR titration experiments in CD_3CN using a constant host concentration (2 mM) and increasing concentrations of anions. The addition of tetrabutylammonium anion salts to the solution of compound **2** in CD_3CN resulted in large downfield shifts

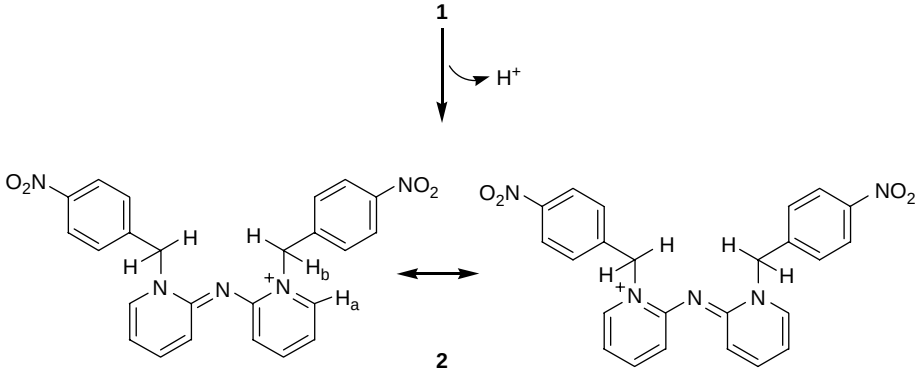

Figure 2. The resonance structure of **2**.

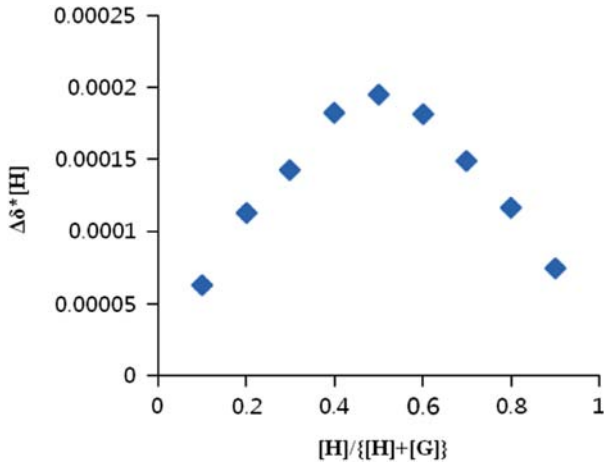

Figure 4. The Job plots of **2** with tetrabutylammonium bromide using ^{1}H NMR.

of one of the aromatic hydrogens (H_a in Figure 2) along with benzylic hydrogen (H_b in Figure 2). For example, addition of tetrabutylammonium bromide moved the aromatic proton (H_a) from 7.99 to 8.46 ppm. In addition, the benzylic proton (H_b) appearing at 5.31 ppm was shifted to 5.54 ppm upon addition of bromide anions (Figure 5).

The large downfield shift of the aromatic proton (H_a) and benzylic proton (H_b) indicated the presence of a hydrogen bond interaction between these C—H hydrogens and bromide ion. However, many equivalents of bromide were also needed, indicating weak affinity of **2** for the bromide. The chemical shift data were analysed by EQNMR (*48*) and the association constant calculated from ^{1}H NMR titration gave 12.7 (M^{-1}) for bromide, which is a similar value to that obtained from the fluorescence titration. Compound **2** showed similarly weak affinity for chloride and iodide. The results are summarised in Table 1. However, in titration with fluoride, acetate, benzoate and dihydrogen phosphate new peaks began to show up upon addition of these anions, which were the evidence of decomposition.

Table 1. The association constants (M^{-1}) of compound **2** with various anions in acetonitrile.

Anion	Fluorescence ($K/\Delta G$, kcal/mol)	NMR ($K/\Delta G$)
Cl^-	31.6/−2.05	15.3[a]/−1.62
Br^-	14.3/−1.58	12.7[a]/−1.51
I^-	14.7/−1.58	10.6[a]/−1.40

[a] The errors are less than 10%.

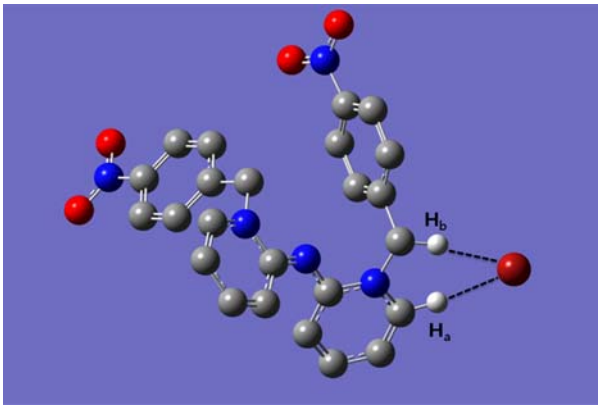

Figure 6. *Ab initio* calculation results of **2** and bromide ion. Hydrogen atoms are omitted for clarity except H_a (aromatic hydrogen) and H_b (benzylic hydrogen). The complexed structures are very similar for all halide ions.

The experimental evidences from fluorescence and ^{1}H NMR titrations supported weak association between host **2** and halides. In order to understand the nature of binding mode of **2** and halides, molecular modelling study was carried out. Quantum mechanical calculations were carried out with the Gaussian 09 suite of programs (*49*) without any

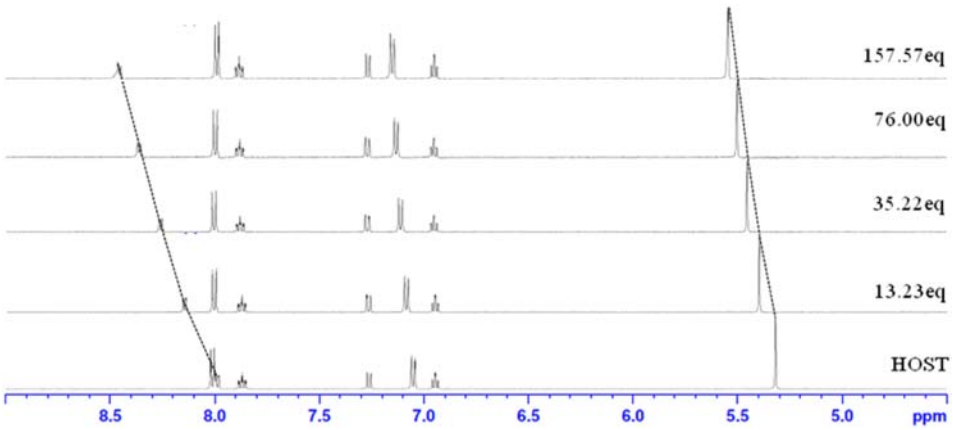

Figure 5. ^{1}H NMR spectra of 2 mM of **2** with an increased amount of tetrabutylammonium bromide in CD_3CN. The shift of aromatic hydrogen (H_a) and benzylic proton (H_b) peaks is designated by dotted lines.

Table 2. The NPA and geometries.

	NPA charge			Distances/bond lengths (Å)			
Species	H_a	H_b	X	H_a—C	H_a—X	H_b—C	H_b—X[a]
Host 2	0.265	0.267		1.084		1.094	
Host 2·F^-	0.353	0.375	−0.820	1.128	1.588	1.128	1.664
Host 2·Cl^-	0.298	0.321	−0.841	1.104	2.164	1.105	2.347
Host 2·Br^-	0.290	0.312	−0.824	1.100	2.319	1.104	2.424
Host 2·I^-	0.289	0.301	−0.873	1.089	3.086	1.097	2.976

Note: X stands for halide ions.

constraint, and geometries were fully optimised with tight convergence criteria at the level of B3LYP/6−31 + G*. For iodine atom, an effective core potential type basis set (LANL2DZ: Los Alamos National Laboratory 2 Double-Zeta) was used (*50*). All the various complex structures were confirmed to be at local minima by frequency calculations. Many possible conformations of **2** with various recognition sites for halide ions were tested. Among them, only one binding mode could explain the NMR data and the binding mode is shown in Figure 6. It is interesting that this binding mode only involves two hydrogen atoms that are attached to host carbons. Here, a bromide chelates **2** through two C—H···Br^- hydrogen bonds. H_a is the aromatic hydrogen, whereas H_b is the benzylic proton. For other halide ions such as F^-, Cl^- and I^-, we obtained very similar structures.

The binding energies through this binding mode are −110.4, −38.9, −45.9 and −21.5 kcal/mol for F^-, Cl^-, Br^- and I^-, respectively (gas phase). This strong binding of F^- would be responsible for the decomposition of host **2**. Since the experiments were carried out in a highly dielectric medium, the calculated binding energies for Cl^-, Br^- and I^- could be crudely interpreted as −2.2, −2.3 and −1.8 kcal/mol using the dielectric constant of acetonitrile, respectively. On the other hand, the binding energies obtained from titration experiments are −1.6 to −2.0 for Cl^- and Br^- and −1.5 kcal/mol for I^-. Therefore, the binding energy values from quantum mechanical calculations are in good agreement with titration experimental data.

To estimate partial charges, natural population analysis (NPA) was carried out (*51*). Partial atomic charges from NPA and geometries concerning hydrogen bonding are listed in Table 2. NPA charge evaluations were carried out at the local minima. The calculated NPA partial charges for H_a and H_b are 0.27 for free host **2**. Upon chloride binding, the NPA charges become 0.30 for H_a and 0.32 for H_b. There is a general tendency that as the halide gets bigger, the charge depletion becomes smaller. The bond lengths for two chelating hydrogens, which are Ha—C and Hb—C for free **2,** are 1.084 and 1.094 Å, respectively. Upon chloride binding, these bond lengths are elongated since the electron densities are depleted upon halide···H bonding. In case of F^-, the bond elongation is much larger with the highest binding energy among halides. This could explain the experimental observation, the decomposition of **2**, upon addition of fluoride ion and possibly other second row element (oxygen) anionic guests such as acetate, benzoate and dihydrogen phosphate. That is, they would have probably acted as bases to decompose **2**, rather than complexed gentle guests.

In conclusion, we have synthesised **2**, which bound weakly basic halide ions only with C—H···anion hydrogen bonds. Compound **2** utilised one aromatic C—H hydrogen bond and one benzylic C—H hydrogen bond to bind weakly basic halide ions such as chloride, bromide and iodide. *Ab initio* calculations of binding energy values for these anions are in good agreement with experimental data. Although the binding affinities of **2** for these anions were low, **2** could be a unique example of host, which utilised only C—H hydrogen bonds to bind anion. However, with strongly basic anions such as fluoride, acetate, benzoate and dihydrogen phosphate, decomposition of **2** was observed.

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