Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article In, Sungjae , Cho, Seung Joo and Kang, Jongmin(2005) 'Anion Receptor with Xylene Bridged Two Imidazolium Rings', Supramolecular Chemistry, 17: 6, 443 — 446
To link to this Article: DOI: 10.1080/10610270500142468
URL: http://dx.doi.org/10.1080/10610270500142468

Supramolecular Chemistry, September 2005 Vol. 17 (6), pp. 443–446

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Anion Receptor with Xylene Bridged Two Imidazolium Rings

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Received (in Austin, USA) 21 January 2005; Accepted 29 March 2005

A m-xylene bridged imidazolium receptor 1 has been designed and synthesized. The receptor 1 utilizes two imidazole (C—H)$^+$—anion hydrogen bonds and one aromatic hydrogen—anion hydrogen bond. The major driving force of complexation between the receptor 1 and anions comes from two imidazole (C—H)$^+$—anion hydrogen bonding. However, some hydrogen bonding energy between aromatic hydrogen and anion exists, although it is expected to be much smaller than that of imidazole (C—H)$^+$—anion hydrogen bonds.

Keywords: Anion receptor; Aromatic hydrogen bond

INTRODUCTION

The design and synthesis of artificial receptors capable of binding anionic guests is of crucial importance due to their importance in bio-medicine, industry and the environment [1–5]. As anions display wide range of geometries, a host–guest complementarity is required for the design of anion receptor. Therefore, hydrogen bonds are frequently used by many researchers as recognition elements due to their directionality. The orientation of hydrogen bonds can differentiate anionic guests with different geometries. While most of hydrogen bonding anion receptors utilize N–H—anion or O–H—anion hydrogen bonds [6–8], 1,3-disubstituted imidazolium groups are recently introduced as new anion binding hydrogen bonding moiety by forming (C—H)$^+$—anion hydrogen bonds between C(2)—H in imidazolium rings and the guest anion. Depending on the spatial arrangement of 1,3-disubstituted imidazolium groups, halide [9,10], dihydrogen phosphate [11,12], dicarboxylate [13] selective receptors have been reported. We have designed m-xylene bridged imidazolium receptor **1**, which utilizes two (C—H)$^+$—anion hydrogen bonds between C(2)-H in imidazolium rings and guest anions. We also expect additional hydrogen bonding interaction between aromatic ring hydrogen and anion although the interaction energy is expected to be much smaller than that of imidazole (C-H)$^+$—anion hydrogen bonds as aromatic hydrogen located near to the anions participates in binding with anions through aromatic C-H—anion hydrogen bonding [14–17]. We report herein the synthesis and binding properties of m-xylene bridged receptor **1** with various anions.

EXPERIMENTAL

Synthesis and Characterization

Compound 2

To a solution of 428 mg 4-nitroimidazole and 545 mg of sodium hydride(3 eq.) in 15 ml DMF was added 500 mg of α,α'-dibromo-m-xylene. The reaction mixture was stirred until no starting material was detected on the TLC. Then the reaction mixture was poured into 200 ml of dichloromethane and the solution was extracted with 50 ml of water three times. Evaporation of the dichloromethane and recrystallization of the residue with 20% methanol in dichlomethane and hexane gave 276 mg (44%) of product. ^{1}H NMR($CDCl_3$) 8.96 (s, 2H) 7.64 (s, 2H) 7.45 (m, 1H) 7.30 (m, 3H) 5.26 (s, 4H) HRMS(FAB) calculated for $C_{14}H_{12}N_6O_4$: 328.0920 found for 328.0918.

Compound 1

To a solution of 200 mg of compound **1** in 4 ml of acetonitrile was added 2.4 ml of diethyl sulfate

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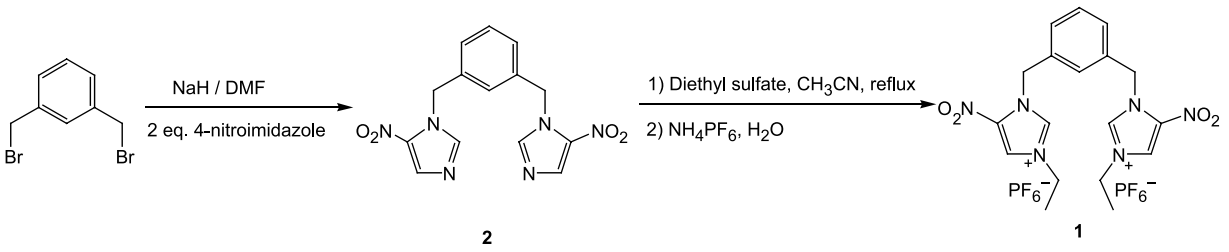
ISSN 1061-0278 print/ISSN 1029-0478 online © 2005 Taylor & Francis
DOI: 10.1080/10610270500142468



SCHEME 1 The synthetic procedure for the anion receptors **1**.

(30 eq.) and refluxed for 20 h. After the solvent was evaporated, the residue was dissolved in 20 ml of water and the undissolved material was removed by filtration. Addition of excess ammonium hexafluorophosphate to the filtered solution formed immediate precipitation. Filtration of the precipitated solid gave 260 mg (64%) of product. ^{1}H NMR(CD_3CN) 8.73 (s, 2H) 8.39 (s, 2H) 7.59 (m, 4H) 4.60 (q, 4H, J = 7.2) 1.57 (t, 6H, J = 7.2) ^{13}C NMR(10% DMSO-d_6 in CD_3CN) δ138.23, 137.61, 133.10, 130.29, 130.22, 129.85, 124.43, 53.71, 46.82, 13.58 HRMS (FAB) M-PF_6 calculated for $C_{18}H_{22}F_6N_6O_4P$: 554.9840 found for 554.9842.

RESULTS AND DISCUSSION

The complexation ability of compound **1** was measured by standard ^{1}H NMR titration experiments in 10% DMSO-d_6 in CD_3CN using a constant host concentration(4 mM) and increasing concentrations of anions(0.1–10 equivalents). The chemical shift data were analyzed by EQNMR [18]. The addition of tetrabutylammonium anion salts to the solution of receptor **1** in 10% DMSO-d_6 in CD_3CN resulted in downfield shifts in C(2) proton of imdazolium moieties along with the inner aromatic proton located between the two imidazolium groups. In case of chloride ions, C(2) proton of imidazolium ring moved from 9.23 to10.64 ppm. In addition, the inner aromatic proton located between the two imidazolium groups originally resonating at δ = 7.54 was shifted to δ = 8.14 upon addition of chloride anions while those of the other aromatic protons remained almost unchanged (Fig. 1). Job plot experiments showed 1:1 binding stoichiometry (Fig. 2). The association constant calculated from the chemical shift change of C(2)—H of imidazolium ring was 1130 ± 97. The downfield shift of C(2)—H of imidazolium ring

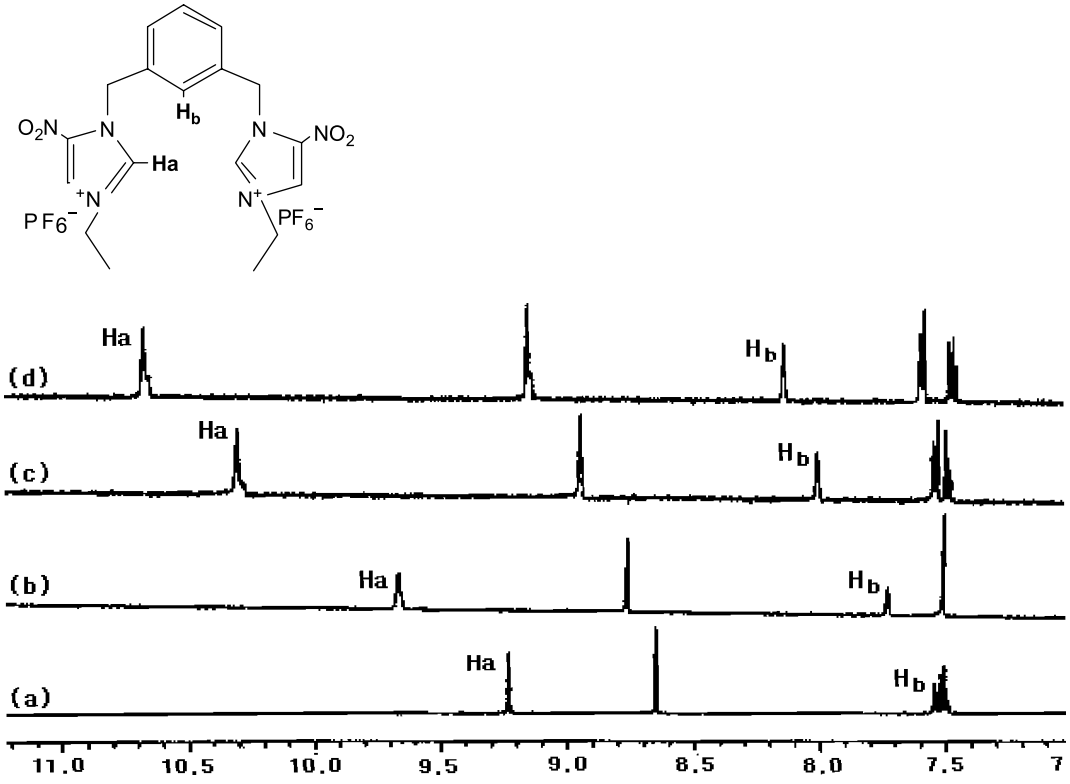


FIGURE 1 Partial ^{1}H NMR (500 MHz) of **1** (4 mM) in 10% DMSO-d_6 in CD_3CN. (a) **1** only (b) **1** + 0.3 equiv of tetrabutylammonium chloride (c) **1** + 1 equiv of tetrabutylammonium chloride (d) **1** + 2 equiv of tetrabutylammonium chloride.

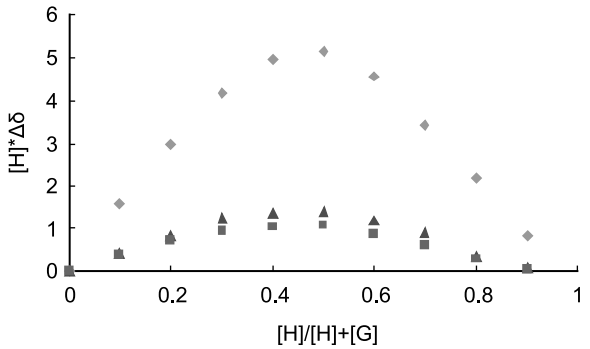


FIGURE 2 The job plot of **1** with tetrabutyammonium chloride (◆). hydrogen sulfate (▲) and nitrate (■).

and 2-H of benzene ring was also observed for other halides. From the ^{1}H NMR titration, the association constants for Br^- and I^- were calculated as 496 ± 40 and 339 ± 39. Unfortunately, we were not able to obtain consistent and reliable association constant for F^- from NMR titration due to severe broadening of NMR spectrum. We also investigated the binding of other anions with receptor **1**. Job plot experiments were performed between **1** and various anions in 10% DMSO-d_6 in CD_3CN. Hydrogen sulfate and nitrate showed 1:1 binding stoichiometry. The downfield shifts of C(2)—H of imidazolium ring and 2-H of benzene ring were observed in these anions too (Fig. 2). The association constants calculated from ^{1}H NMR titration for hydrogen sulfate and nitrate were 1260 ± 44 and 443 ± 48 respectively. Acetate and cyanide gave broad spectrums with the receptor **1**, which prevented reliable calculation of association constants. Perchlorate did not bind to the receptor **1** at all.

Molecular modeling from ab initio calculation shows the nature of complexation between the receptor **1** and guest anion. The free host (Fig. 3a) has two nitro groups near the molecular center. This orientation keeps two charged imidazole moieties apart. The center to center distance of two imidizole rings is 8.6 Å. When guest anions are present, this structure completely reorganizes to accommodate the negatively charged guest, attracting two positively charged imidazole moieties closer. For example, the center to center distance of the two imidazole ring becomes 7.1 Å for Br^- complex (Fig. 3b).

Participation of aromatic hydrogen in hydrogen bonding is well known phenomenon although the contribution to the binding is not large. [14–17]. Involvement of aromatic hydrogen in the hydrogen bonding has been mostly demonstrated by downfield shift of aromatic hydrogen peak while other aromatic peaks remained almost unchanged. The large downfield shift we observed in receptor **1** is consistent with the presence of a hydrogen bonding interaction between the inner aromatic hydrogen and chloride anion in addition to the expected hydrogen bonding

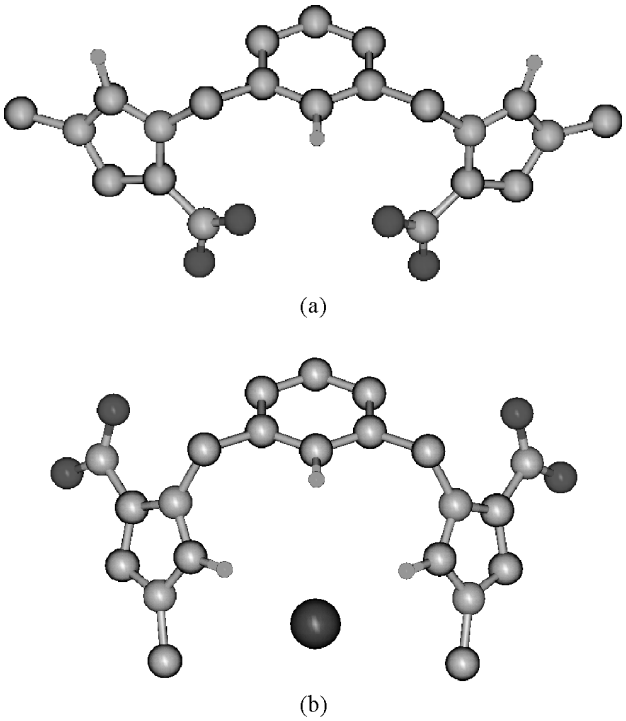


FIGURE 3 Optimized geometry of free host (a) and its Br^- complex (b). (Cs symmetry) Imidazole moieties have rotated upon complexation. All the hydrogens atoms (except 3 shown above) are omitted for clarity. Two ethyl groups were substituted to methyl groups for computational efficiency. All the calculations were performed with the suite of Gaussian03 programs [20]. The geometries were fully optimized without any constraint. The structures were confirmed to be at local minima by Hessian calculations.

interaction between the C(2)—H of imidazolium rings and chloride anions. The two positively charged imidazolium rings would affect the sandwiched aromatic ring to be slightly positively charged, and so the interaction between the aromatic hydrogen and anion can exist. Since two C(2)—H of imidazolium ring and one 2-H of benzene ring are close to the anion guest in the complexed structures (Fig. 3b), we investigated the partial charges of the hydrogen with both Mulliken (**Mull**) and natural population analysis (**NPA**) [19] Although NPA charges are slightly less positive than Mulliken charges, both methods indicate that the charges of hydrogen atoms are positive (more than 0.23, Table I). This implies the possibility of aromatic hydrogen bond in complexation. Therefore, we checked the distances and angles with anion guest. For Br^- complex, the distance between aromatic hydrogen and bromide is 3.249 Å, while the distance between C(2) imidazole hydrogen and bromide is 2.431 Å. The angle of Br^-…H(aromatic ring)—C(aromatic ring) is 131.9°, while Br^- …H(Imidazole ring)—C(Imidazole ring) 149.3°. For Cl^- complex, the distance between aromatic hydrogen and chloride is 3.184 Å, while the distance between aromatic hydrogen and chloride is 2.290 Å. The angle of Cl^-…H(aromatic ring)—C(aromatic ring) is 125.1°, while Cl^-…H(Imidazole ring)—C(Imidazole ring) is 147.2°.

TABLE I Calculated and binding energies and charges of hydrogen atoms

	HSO_4^-	NO_3^-	Cl^-	Br^-
ΔE_{calc}^{gas}	−162.39	−164.78	−164.70	−162.99
ΔE_{rel}^{gas}	2.31	−0.08	0.00	1.71
ΔG_{exp}^{NMR}	−4.22	−3.61	−4.16	−3.67
ΔG_{rel}^{NMR}	−0.06	0.55	0.00	0.49
$Mull_{H(Bz)}$	0.259	0.240	0.248	0.249
$Mull_{H(Im)}$	0.423 (0.413)	0.374	0.369	0.362
$NPA_{H(Bz)}$	0.235	0.233	0.243	0,243
$NPA_{H(Im)}$	0.302 (0.301)	0.294	0.299	0.292

Binding energies were calculated at the Hartree-Fock 6-31G* level of theory. Because the calculations were performed in the gas phase the resultant binding energies are very large. When we compare relative experimental binding energy with respect to Cl^-, the relative binding energy difference between calculation result (ΔE_{rel}^{gas}) and experimental result (ΔG_{rel}^{NMR}) is smaller than 2.4 kcal/mol in every case. Considering the phase difference, this difference seems to be not significant [12]. ΔE_{calc}^{gas} is the calculated binding energy in gas phase. ΔE_{rel}^{gas} is the relative binding energy with respect to the complex of Cl^-. ΔG_{exp}^{NMR} is the NMR binding energy in acetonitrile solution. ΔG_{exp}^{NMR} is the experimental relative binding energy with respect to the complex of Cl^-. $Mull_{H(Bz)}$ is the Mulliken charge of hydrogen atom attached to benzene while $Mull_{H(Im)is}$ the Mulliken charge of two hydrogen atoms attached to imidazole rings (See Fig. 3 for the position). For HSO_4^- the two hydrogens attached to imidazole rings are of slightly different in charge because there is no symmetry. Likewise $NPA_{H(Bz)}$ and $NPA_{H(Im)}$ are charges obtained by natural population analysis.

Considering partial charge, distance and angle, there should be some hydrogen bonding energy between anion and aromatic hydrogen, although it is expected to be much smaller than that of C(2)—H hydrogen in imidazole ring.

In conclusion, we have synthesized an anion receptor **1**, which has two imidazole $(C—H)^+$—anion hydrogen bonds and one aromatic hydrogen—anion hydrogen bond. The major driving force of complexation between the receptor **1** and anions comes from two imidazole $(C—H)^+$—anion hydrogen bonding. However, ^1H NMR titration and ab intio calculation shows that aromatic hydrogen also contribute to the anion complexation although the energy is not large.

Acknowledgements

This study was supported by a grant from the Korea Association of Small Businesses Innovation Research 2004.

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