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Neutral bis(benzimidazole) Λ-shaped anion receptor

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ABSTRACT

A neutral receptor, integrating a series of –N(H) and –C(H) donor groups organized in a Λ-shape motif was designed and prepared. This compound can form stable 1:1 complexes in acetonitrile solution with halides (F^-, Cl^-, Br^-, and I^-) and nitrate (NO_3^-) anions. The main binding site in the receptor is on the cleft and recognition occurs through a series of co-operative hydrogen bonding interactions including intramolecular hydrogen bonds which stabilizes the co-planar conformation of the host–guest complex. For halides, complex stability is determined by anion basicity, but for anions having other geometries, size and shape complementarity play a major role.

Introduction

The detection and removal of certain anions, such as fluoride and nitrate, are issues of relevance in public health and environmental quality. For this purpose, it is important to properly design and synthesize versatile receptors. In synthetic anion receptor chemistry, the molecular design of the host must take into consideration: (i) basicity of the anionic guests, (ii) nature of the non-covalent interactions involved, (iii) solvent, and (iv) host–guest geometric complementarity.[1] According to their electrostatic charge, two different kinds of anion receptors have been developed: cationic and neutral. For the latter, the most common motifs incorporated are: ureas,[2] thioureas,[3] amides,[4] squaramides,[5] pyrroles,[6] indoles,[7] and lately, –C(H) hydrogen bond donors.[8]

Particularly, imidazole- and benzimidazole-based receptors interact with anions predominantly through –N(H)···X^- hydrogen bonding. Baitalik[9] and Ye[10] reported that ruthenium(II) complexes of 4,5-bis(benzimidazol-2-yl)imidazole and 2,2′-biimidazole form hydrogen bonded adducts with a variety of anions in acetonitrile with association constants ranging from 10^4 to 10^6 M^{-1}; especially, the interaction with fluoride and acetate develops intense colors, naked eye visible, due to a stepwise deprotonation of the –N(H) fragments. On the other hand, Gale and co-workers[11] have shown that tautomeric switching in benzimidazole-based receptors in DMSO-aqueous solution can modulate their affinity for certain anionic guests via hydrogen bond interactions, making them selective for a specific anion; however, for the monoatomic anionic guests only weak binding is observed.

As part of our ongoing research on the self-assembly of supramolecular complexes based on benzimidazolium derivatives,[12] we have designed and synthesized a neutral 1,3-bis(benzimidazole)benzene anion receptor, **BBB**. The 1,3-substitution pattern would provide two strong –N(H) hydrogen bonds donors and an aryl –C(H) bond, in a Λ-shaped arrangement, allowing the interaction of this receptor with diverse anions, as it has previously been observed for similar-shaped complexes.[4c,13]

The expected most-stable molecular arrangement of **BBB** would be a non-planar structure, with the central aromatic ring on a different plane respect to the benzimidazole rings. In the presence of anions, a co-planar conformation is anticipated containing three hydrogen bond donors converging into a cleft and two intramolecular hydrogen bonds assisting the complexation (Scheme 1). This host–guest geometrical arrangement, which can establish the maximum number of non-covalent interactions and displays a suitable complementary, is likely to be the most stable.

In this Letter we report the synthesis and characterization of a neutral bis(benzimidazole)benzene receptor with –N(H) and –C(H) donor motifs and its association in acetonitrile with diverse anions such as halides, nitrate, and perchlorate.

Results and discussion

Compound 1,3-bis(1*H*-benzo[*d*]imidazol-2-yl)benzene, **BBB**, was synthesized by a condensation reaction between isophthalic acid and two equivalents of 1,2-diaminobenzene under high temperature and acidic conditions (Scheme 2). This compound was isolated in a 57% yield and is slightly soluble in acetonitrile and soluble in dimethylsulfoxide; it was fully characterized by ^1H and ^{13}C NMR spectroscopy as well as HR-MS (ESI-TOF).

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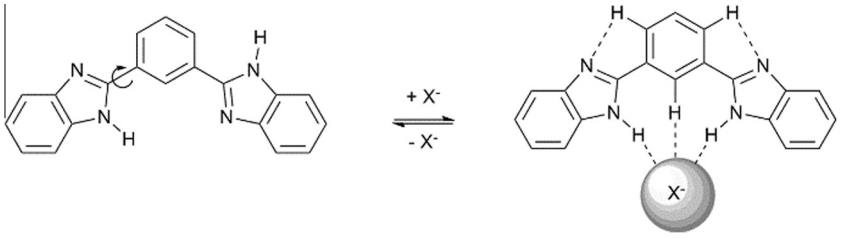
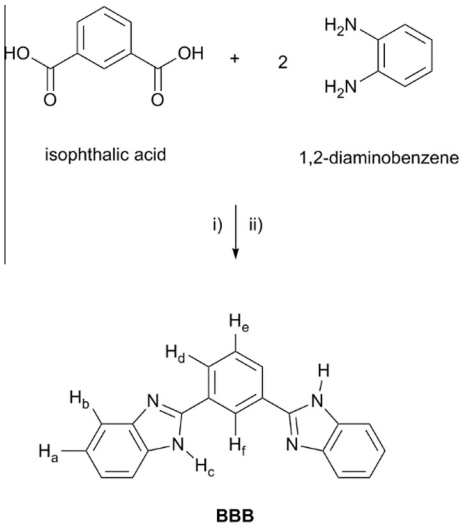


Scheme 1. Binding motif for a hypothetical anion (X^-) in the cleft of a neutral receptor **BBB**.



Scheme 2. Synthetic procedure for the preparation of receptor **BBB** and labeling scheme. Reagents and conditions: (i) polyphosphoric acid, 190 °C, 24 h; (ii) NaOH (aq), pH = 7.

The ^{1}H NMR spectrum of compound **BBB** in DMSO-d_6 showed the expected resonances for the proposed molecular structure: (i) a single high frequency signal (13.1 ppm) attributed to the protons –N(H) of the imidazole rings, (ii) an AB_2C pattern for the aromatic protons of the 1,3-disubstituted benzene, and (iii) an AA′BB′ pattern for the aromatic protons of the benzimidazole rings. In addition, the ^{13}C NMR spectrum displayed the expected eleven signals in the aromatic region. The identity of all signals was confirmed by NMR 2D experiments (see Supplementary data). Experimental high-resolution mass spectra (ESI-TOF) showed a peak at m/z = 311.1294, which corresponds to the expected molecular ion, displaying an isotopic pattern consistent with the proposed formula and with a relative error in the molecular weight of 1 ppm (see Supplementary data).

The neutral **BBB** bis(benzimidazole)benzene compound should act as an anion receptor by combining two strong –N(H) donor groups with a weaker aryl –C(H) donor motif. The orientation of the three hydrogen bonds in a convergent form should optimize the interactions with specific anions. The selected anions have diverse shapes and basicity, and include (i) halides, with a spherical shape, (ii) trigonal planar nitrate, and (iii) perchlorate as a tetrahedral oxoanion.

We performed a series of ^{1}H NMR titrations in acetonitrile between neutral receptor **BBB** with tetrabutylammonium (TBA) salts of several halides (F^-, Cl^-, Br^-, and I^-). Experimental results of the interaction with fluoride will be discussed in the following section due to its particular behavior. The consecutive addition of a concentrated acetonitrile solution, 0.1 M, of TBA halide salts to a 2×10^{-3} M solution of neutral receptor **BBB** in acetonitrile-d_3 led to gradual changes in the chemical shifts and widths of the receptor proton resonances (Fig. 1).

Upon saturation of the corresponding halide (Cl^-, Br^-, and I^-), protons H_f and H_d of receptor as well as the –N(H_c) protons, are shifted toward higher frequencies, characteristic of hydrogen bonding interactions: [**BBB**·Cl^-] (ppm) H_f $\Delta\delta$ = +0.95, H_d $\Delta\delta$ = +0.16; [**BBB**·Br^-] (ppm): H_f $\Delta\delta$ = +0.83, H_d $\Delta\delta$ = +0.17; [**BBB**·I^-] (ppm): H_f $\Delta\delta$ = +0.40, H_d $\Delta\delta$ = +0.16. As a representative example, Figure 2 shows a stacked plot of the titration of **BBB** with TBABr.

There is a direct correlation between the maximum chemical shift of proton H_f and the halide basicity; it is known that halides show a similar trend in their basicity in acetonitrile with respect to their values in aqueous solutions.[14] This behavior is indicative of a direct interaction between this proton and the anion. Furthermore, proton H_d preserves the same chemical shift regardless of the halide used in the titration experiments; this result is probably due to an intramolecular hydrogen bond between proton H_d and the lone pair of the benzimidazole nitrogen atoms. This particular interaction would be a consequence of a co-planar arrangement of the aromatic rings in the receptor, induced by the presence of the anion inside the cleft.

In order to support the proposed host–guest geometrical arrangement, a series of DFT calculations were performed using the Spartan '08 software package[15] (see Supplementary data). Equilibrium geometries for neutral receptor **BBB** and the 1:1 complex with chloride [**BBB**·Cl^-] are shown in Figure 3. Geometrical optimization analysis for **BBB** renders a semi-planar molecular arrangement with both benzimidazole rings in an *anti*-conformation (the four dihedral angles concerning the central aromatic rings and the two benzimidazole substituents span from 4° to 6°), whereas for complex [**BBB**·Cl^-] the anion occupies the cleft formed by two –N(H) (3.26 Å; 178.6°) and one aryl –C(H) (3.49 Å; 178.6°) hydrogen bonds; with the rings in a co-planar conformation

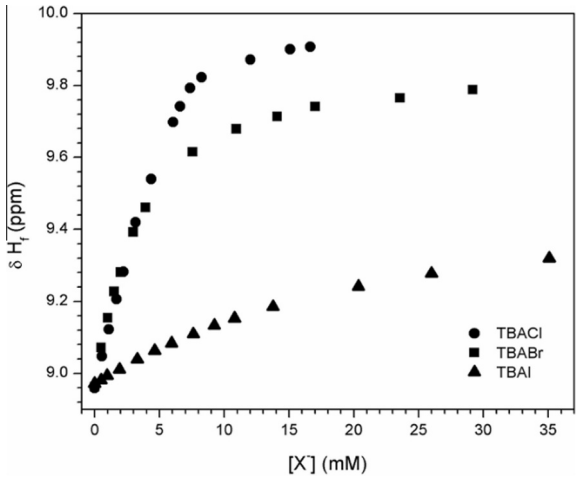


Figure 1. Change in chemical shift of proton H_f for the ^{1}H NMR titration of neutral compound BBB (2×10^{-3} M) with the stepwise addition of tetrabutylammonium salts (0.1 M) of chloride (●), bromide (■) and iodide (▲) in an acetonitrile-d_3 solution.

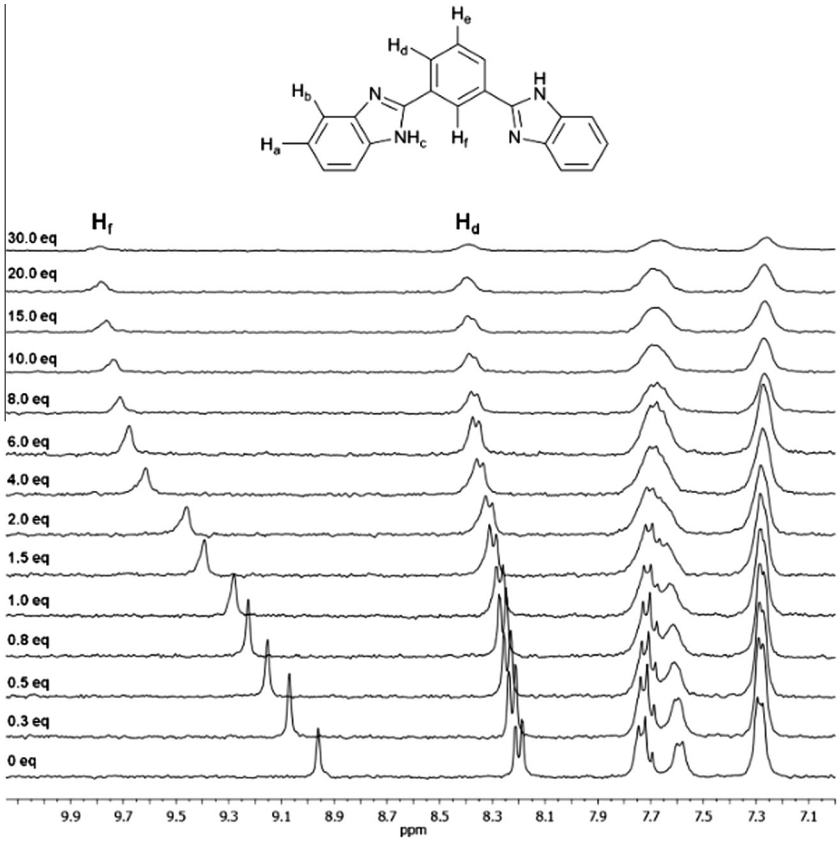


Figure 2. ^{1}H NMR titration stacked plot of receptor **BBB** (2×10^{-3} M) on stepwise addition of TBABr (0.1 M) (300 MHz, acetonitrile-d_3).

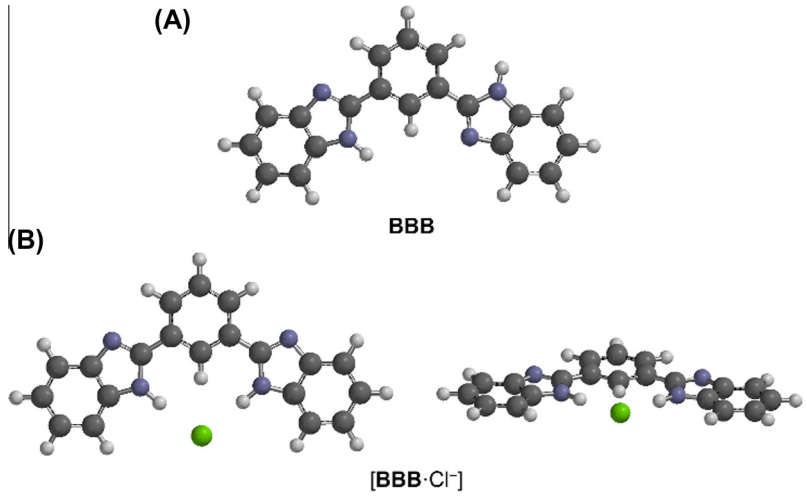


Figure 3. DFT (B3LYP/6-31G*) equilibrium geometry calculated for (A) **BBB** and (B) [**BBB**·Cl^{-}].

(dihedral angles are less than 1°) allowing the formation of hydrogen bond interactions between the lone pair of the benzimidazole nitrogen atoms and the H_d atoms of the central aromatic ring.

A similar calculation was performed for the chloride complex with 1,3-bis(1*H*-benzo[*d*]indole-2-yl)benzene, an isoelectronic compound of **BBB**. This particular indole cannot form the intramolecular hydrogen bonds, as in the case of the imidazole complex; therefore the resulting equilibrium geometry displays a non-planar arrangement (dihedral angles over 13°) (see Supplementary data). These results support the experimental chemical shifts for protons H_f and H_d in ^{1}H NMR titration data as well as the proposed co-planar arrangement for the supramolecular complexes [**BBB**·X] (X = Cl^{-}, Br^{-}, I^{-}) in acetonitrile solution.

Association constants were derived from ^{1}H NMR titration data at 25 °C, in acetonitrile-d_3, by a least-square fitting analysis of the chemical shifts of protons H_f and H_d.[16] Experimental data were fitted by using a 1:1 receptor to anion stoichiometry model; the use of any other model rendered poor correlation (see Supplementary data). There is no significant variation in the magnitude of the association constants regardless the proton used in the analysis, in agreement with the existence of a single binding mode in solution. Association constants values span from 1.1×10^{3} M^{-1},

for the most basic anion chloride, to 4.6×10^1 M^{-1}, for the least basic anion iodide; indicating a lower stability of the complex as the basicity of the halide decreases. A summary of the binding constants is shown in Table 1.

Fluoride ion is the strongest base among the halides, it is well established that compounds containing –N(H) or –O(H) hydrogen bond groups can undergo a deprotonation process upon addition of fluoride.[17] In our case, ^{1}H NMR titration of a 2×10^{-3} M solution of neutral compound **BBB** with a concentrated acetonitrile solution, 0.1 M, of TBA fluoride salt in acetonitrile-d_3 suggests that the interaction of the receptor with fluoride takes place in two steps. Upon addition of the first equivalent of fluoride, a shift toward higher frequency of protons H_f and H_d is observed (H_f $\Delta\delta$ = +0.27, H_d $\Delta\delta$ = +0.19) indicative of hydrogen bonding between receptor **BBB** and the fluoride anion, similar to the other halides. Further addition of fluoride, induces a trend change of the chemical shift to lower frequencies (H_f $\Delta\delta$ = −0.12, H_d $\Delta\delta$ = −0.13) probably due to deprotonation process of benzimidazole –N(H) groups. Figure 4 shows the behavior of proton H_f during titration with TBAF.

We propose that the first added equivalent of fluoride associates with the neutral receptor **BBB** by hydrogen bonding interactions, shifting proton H_f toward higher frequency; it is reasonable to assume that the association constant of the 1:1 complex should be at least ~10^4 M^{-1}, which is the maximum value that can be reliably measured by ^{1}H NMR spectroscopic titration.[18] Subsequent addition of fluoride deprotonates the benzimidazole –N(H) groups with the formation of monoanionic [**BBB**$^-$] and dianionic [**BBB**$^{2-}$] species and the very stable [HF_2^-] self-complex.[19] The observed low frequency shifts for protons H_f and H_d, after one equivalent of fluoride, could be due to an increase in the chemical shielding as a consequence of the presence of formal negative charges in the anionic receptor-based species.

High resolution mass spectrum (negative ESI-TOF) of an acetonitrile solution of neutral receptor **BBB** and two equivalents of TBAF showed two peaks corresponding to: [**BBB**–H^+]$^-$ (calcd, *m*/*z* 309.1145; found, *m*/*z* 309.1146; error = 0.1 ppm) and [**BBB**–2H^+ + TBA]$^-$ (calcd, *m*/*z* 550.3915; found, *m*/*z* 550.3898; error = 3.0 ppm). This result supports the evidence of the formation of the mono- and di-anionic species observed in solution by NMR.

We also undertook ^{1}H NMR titrations of neutral receptor **BBB** with nitrate and perchlorate TBA salts. Stepwise addition of a concentrated acetonitrile solution, 0.1 M, of nitrate TBA salt to a 2×10^{-3} M solution of neutral receptor **BBB** in acetonitrile-d_3, produced progressive changes in the chemical shifts and widths of the receptor proton resonances. Upon saturation with nitrate TBA salt, aromatic protons H_f and H_d of receptor **BBB** were shifted toward higher frequencies in a similar manner to those observed with halide anions: [**BBB**·NO_3] (ppm) H_f $\Delta\delta$ = +0.12, H_d $\Delta\delta$ = +0.14 (see Supplementary data). This behavior is indicative of a phenyl –C(H)···NO_3^- hydrogen bond interaction and the intramolecular hydrogen bonds, suggesting a co-planar arrangement of the host–guest complex, as it would be shown by the crystal structure of a related complex, vide infra. An association constant was derived from the experimental data and is included in Table 1. The measured association constant, under the same experimental conditions, for the nitrate complex is two orders of magnitude weaker than the one determined for the chloride analog. This observation indicates a lower complex stability with nitrate compared to chloride, despite its higher basicity. We attribute this result to a poorer size and shape complementarity between receptor **BBB** with nitrate anion, respect to that observed for halides.

Table 1
Association constants (K_a) and associated free energies ($\Delta G°$) of neutral receptor **BBB** with different anionic guests determined by ^{1}H NMR titration in an acetonitrile-d_3 solution

Anion	K_a[a] (M^{-1})	$\Delta G°$[b] (kJ mol^{-1})
F^-	$>10^4$	<−23
Cl^-	$(1.0 \pm 0.1) \times 10^3$	−17.5 ± 0.2
Br^-	$(4.6 \pm 0.1) \times 10^2$	−15.1 ± 0.2
I^-	$(4.6 \pm 0.1) \times 10^1$	−9.5 ± 0.3
NO_3^-	$(8.1 \pm 0.2) \times 10^1$	−10.9 ± 0.3
ClO_4^-	<1	~0

[a] The data were fitted to a 1:1 receptor to anion stoichiometry model using the least-squares method.
[b] $\Delta G° = -RT\ln K$ (T = 298 K).

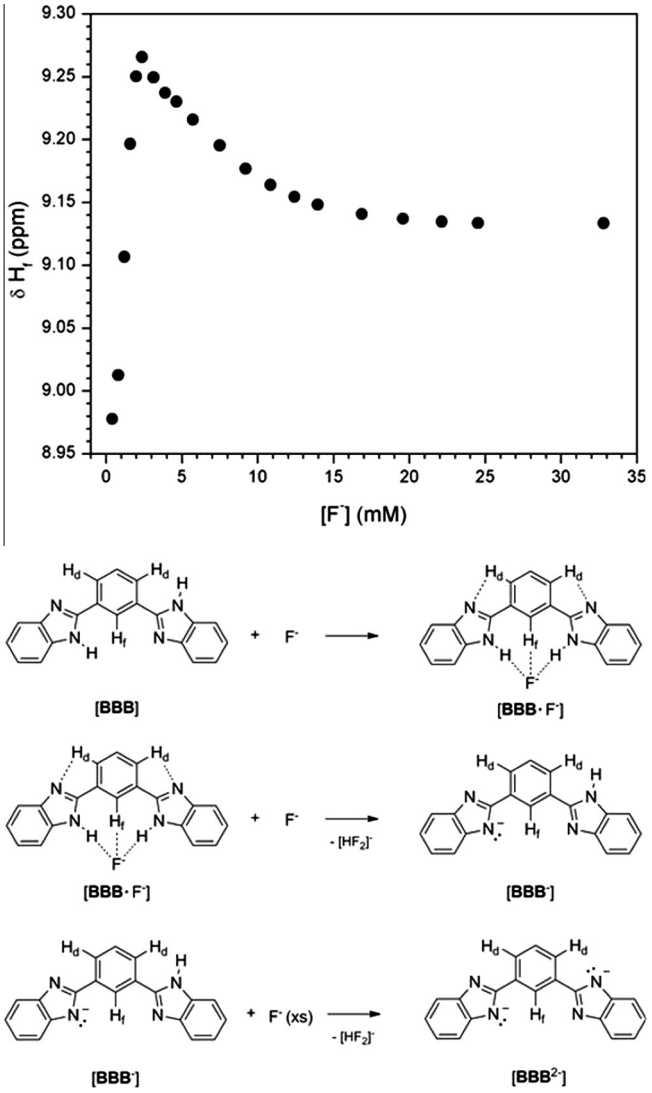


Figure 4. Change in chemical shift of proton H_f during the ^{1}H NMR titration of neutral compound **BBB** (2×10^{-3} M) with the addition of TBA fluoride (0.1 M) in acetonitrile-d_3 solution and the proposed stepwise deprotonation of **BBB**.

Based on these results, no interaction was expected between neutral receptor **BBB** and tetrahedral perchlorate anion in acetonitrile solution. Experimentally, no changes of the chemical shifts of protons H_f and H_d of receptor **BBB** were observed in ^{1}H NMR titration experiments, even in the presence of 80 equivalents of TBA perchlorate salt, indicating an extremely low association or no association at all.

All our efforts to obtain single-crystals of a complex, containing the neutral receptor with any of the different anions employed, were unsuccessful; so we decided to try with the protonated version of the receptor. Addition of nitric acid to an acetonitrile solution of **BBB** led to the isolation of suitable single-crystals of [H_2**BBB**][NO_3]$_2$ for an X-ray diffraction study.[20] Analyzed crystal

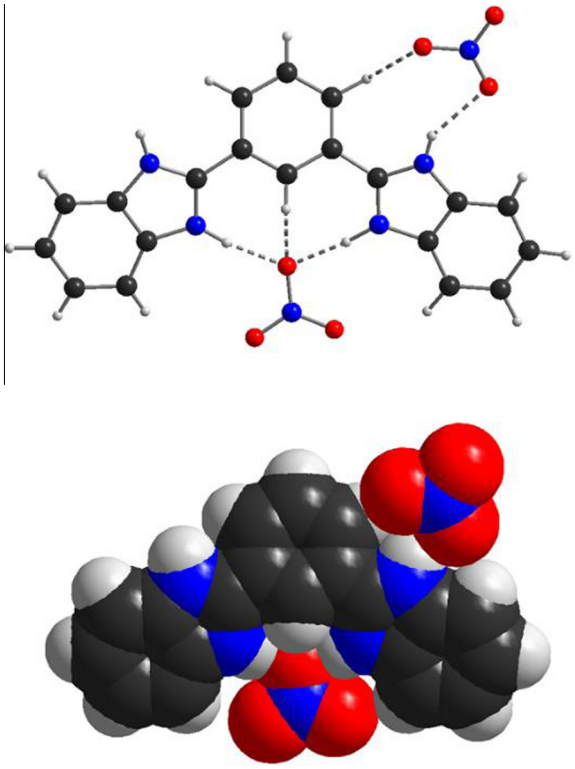


Figure 5. Ball-and-stick and space-filling representations of the molecular structure of $[H_2\mathbf{BBB}][NO_3]_2$ determined by single-crystal X-ray diffraction. N = blue, C = black, O = red, H = white.

belongs to the monoclinic space group $P2_1/n$. The asymmetric unit consists of a complete protonated receptor and two nitrate anions as shown in Figure 5. One anion is situated in the cleft of receptor **BBB** forming two strong hydrogen bonds with the acidic protons of the imidazolium ring (ONO···N(+)(H) 2.83 Å; ONO···H–N(+) 173.1° av) and a weaker one with the hydrogen atom H_f of the central aromatic ring (ONO···C(H_f) 2.93 Å; ONO···H_f–C 126.4°).[21] In order to maximize the three interactions, the receptor converges the hydrogen bonds to one vertex of the nitrate adopting a pseudo-planar geometry with a torsion angle between the central aromatic ring and both benzimidazolium substituents of 22.5° av. The other nitrate anion interacts with one of its edges (two different oxygen atoms) with the external part of the receptor by forming two hydrogen bonds; one with the acidic proton of one benzimidazolium ring (ONO···N(+)(H) 2.82 Å; ONO···H–N(+) 148.2°) and the other with hydrogen atom H_d of the central benzene (ONO3···C(H_d) 3.26 Å; ONO3···H_d–C 131.7°). The 2-D propagation of the crystal structure occurs throughout weak hydrogen bonds between the non-coordinated oxygen atoms of the nitrates and –C(H) or –N(+)(H) donors of different protonated receptors.

The molecular structure of this complex confirms the Λ-shaped binding motif with the anions located inside the cleft of receptor **BBB** in a co-planar conformation stabilized by three hydrogen bonds formed with the two –N(H) and one aryl –C(H) donors. It is worth noticing that ^{1}H NMR titration experiments of the protonated receptor $[H_2\mathbf{BBB}]^{2+}$ with the previously used TBA salts were performed. However, in all cases, the formation of a precipitate in early stages of the titration was observed, thus no reliable association constants could be determined.

Conclusions

A neutral Λ-shaped bis(benzimidazole) receptor incorporating –N(H) and –C(H) donor groups was prepared. This compound forms stable 1:1 complexes in acetonitrile solution with halides (F^-, Cl^-, Br^-, and I^-) and nitrate (NO_3^-) anions with association constants up to 10^4 M^{-1}, these values are slightly lower relative to those observed in analogous receptors. The binding occurs through cooperative hydrogen bonding with the anion inside the cleft including intramolecular hydrogen bonds which stabilizes the co-planar conformation of the host–guest complex. For halides, complex stability is determined by anion basicity, as follows: fluoride > chloride > bromide > iodide; however, in the presence of more than one equivalent of fluoride, the receptor undergoes deprotonation to generate mono- and di-anionic species. For anions having different geometries, a diverse behavior was observed, trigonal planar nitrate (NO_3^-) forms a rather weak complex and no interaction could be determined with tetrahedral perchlorate oxoanion (ClO_4^-).

Acknowledgments

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Supplementary data

Supplementary data (^{1}H and ^{13}C NMR spectra, HR-MS (ESI-TOF), titration experiments with anions as well as details of theoretical calculations) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.09.075.

References and notes

1. (a) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486–516; (b) Alcalde, E.; Dinares, I.; Mesquida, N. In *Anion Recognition in Supramolecular Chemistry*; Gale, P. A., Dehaen, W., Eds.; ; Springer: Berlin, 2010; Vol. 24, pp 267–300.
2. (a) Jia, C.; Wu, B.; Li, S.; Yang, Z.; Zhao, Q.; Liang, J.; Li, Q.-S.; Yang, X.-J. *Chem. Commun.* **2010**, 5376–5378; (b) Custelcean, R.; Remy, P.; Bonnesen, P. V.; Jiang, D.-E.; Moyer, B. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1866–1870; (c) Carroll, C. N.; Coombs, B. A.; McClintock, S. P.; Johnson, C. A., II; Berryman, O. B.; Johnson, D. W.; Haley, M. M. *Chem. Commun.* **2011**, 5539–5541; (d) Kim, M. J.; Lee, H. W.; Moon, D.; Jeong, K. S. *Org. Lett.* **2012**, *14*, 5042–5045; (e) Zhou, Y. P.; Zhang, M.; Li, Y. H.; Guan, Q. R.; Wang, F.; Lin, Z. J.; Lam, C. K.; Feng, X. L.; Chao, H. Y. *Inorg. Chem.* **2012**, *51*, 5099–5109.
3. (a) Pérez-Casas, C.; Höpfl, H.; Yatsimirsky, A. *J. Inclusion Phenom. Macrocyclic Chem.* **2010**, *68*, 387–398; (b) Duke, R. M.; McCabe, T.; Schmitt, W.; Gunnlaugsson, T. *J. Org. Chem.* **2012**, *77*, 3115–3126; (c) Krishnamurthi, J.; Ono, T.; Amemori, S.; Komatsu, H.; Shinkai, S.; Sada, K. *Chem. Commun.* **2011**, 1571–1573.
4. (a) Gross, D. E.; Mikkilineni, V.; Lynch, V. M.; Sessler, J. L. *Supramol. Chem.* **2010**, *22*, 135–141; (b) Ozturk, G.; Colak, M.; Togrul, M. *J. Inclusion Phenom. Macrocyclic Chem.* **2010**, *68*, 49–54; (c) Hossain, M. A.; Kang, S. A.; Kut, J. A.; Day, V. W.; Bowman-James, K. *Inorg. Chem.* **2012**, *51*, 4833–4840; (d) Serpell, C. J.; Cookson, J.; Ozkaya, D.; Beer, P. D. *Nat. Chem.* **2011**, *3*, 478–483; (e) Beeren, S. R.; Sanders, J. K. M. *J. Am. Chem. Soc.* **2011**, *133*, 3804–3807.
5. (a) Amendola, V.; Bergamaschi, G.; Boiocchi, M.; Fabbrizzi, L.; Milani, M. *Chem. Eur. J.* **2010**, *16*, 4368–4380; (b) Rostami, A.; Wei, C. J.; Guerin, G.; Taylor, M. S. *Angew. Chem., Int. Ed.* **2011**, *50*, 2059–2062; (c) Jin, C.; Zhang, M.; Wu, L.; Guan, Y.; Pan, Y.; Jiang, J.; Lin, C.; Wang, L. *Chem. Commun.* **2013**, 2025–2027.
6. (a) Mani, G.; Guchhait, T.; Kumar, R.; Kumar, S. *Org. Lett.* **2010**, *12*, 3910–3913; (b) Yoon, D.-W.; Gross, D. E.; Lynch, V. M.; Sessler, J. L.; Hay, B. P.; Lee, C.-H. *Angew. Chem., Int. Ed.* **2008**, *47*, 5038–5042; (c) Sokkalingam, P.; Kim, D. S.; Hwang, H.; Sessler, J. L.; Lee, C.-H. *Chem. Sci.* **2012**, *3*, 1819–1824.
7. (a) Makuc, D.; Albrecht, M.; Plavec, J. *Supramol. Chem.* **2010**, *22*, 603–611; (b) Suk, J.-M.; Naidu, V. R.; Liu, X.; Lah, M. S.; Jeong, K.-S. *J. Am. Chem. Soc.* **2011**, *133*, 13938–13941; (c) Gale, P. A. *Chem. Commun.* **2008**, 4525–4540.
8. (a) Cao, Q.-Y.; Pradhan, T.; Kim, S.; Kim, J. S. *Org. Lett.* **2011**, *13*, 4386–4389; (b) McDonald, K. P.; Ramabhadran, R. O.; Lee, S.; Raghavachari, K.; Flood, A. H. *Org. Lett.* **2011**, *13*, 6260–6263; (c) Ahmed, N.; Shirinfar, B.; Geronimo, I.; Kim, K. S. *Org. Lett.* **2011**, *13*, 5476–5479; (d) McDonald, K. P.; Hua, Y.; Lee, S.; Flood, A. H. *Chem. Commun.* **2012**, 5065–5075.
9. Saha, D.; Das, S.; Bhaumik, C.; Dutta, S.; Baitalik, S. *Inorg. Chem.* **2010**, *49*, 2334–2348.
10. Cui, Y.; Mo, H.-J.; Chen, J.-C.; Niu, Y.-L.; Zhong, Y.-R.; Zheng, K.-C.; Ye, B.-H. *Inorg. Chem.* **2007**, *46*, 6427–6436.
11. (a) Gale, P. A.; Hiscock, J. R.; Lalaoui, N.; Light, M. E.; Wells, N. J.; Wenzel, M. *Org. Biomol. Chem.* **2012**, *10*, 5909–5915; (b) Hiscock, J. R.; Gale, P. A.; Lalaoui, N.; Light, M. E.; Wells, N. J. *Org. Biomol. Chem.* **2012**, *10*, 7780–7788.

12. (a) Castillo, D.; Astudillo, P.; Mares, J.; González, F. J.; Vela, A.; Tiburcio, J. *Org. Biomol. Chem.* **2007**, *5*, 2252–2256; (b) Moreno-Olivares, S. I.; Cervantes, R.; Tiburcio, J. *J. Org. Chem.* **2013**, *78*, 10724–10731; (c) Castillo, D.; Cervantes, R.; Frontana, C.; González, F. J.; Tiburcio, J. *J. Phys. Org. Chem.* **2014**, *27*, 701–706.
13. (a) Yoon, D. W.; Gross, D. E.; Lynch, V. M.; Sessler, J. L.; Hay, B. P.; Lee, C.-H. *Angew. Chem., Int. Ed.* **2008**, *47*, 5038–5042; (b) Wisner, J. A.; Beer, P. D.; Drew, M. G. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3606–3609.
14. (a) Kütt, A.; Rodima, T.; Saame, J.; Raamat, E.; Mäemets, V.; Kaljurand, I.; Koppel, I. A.; Garlyauskayte, R. Y.; Yagupolskii, Y. L.; Yagupolskii, L. M.; Bernhardt, E.; Willner, H.; Leito, I. *J. Org. Chem.* **2011**, *76*, 391–395; (b) Raamat, E.; Kaupmees, K.; Ovsjannikov, G.; Trummal, A.; Kütt, A.; Saame, J.; Koppel, I.; Kaljurand, I.; Lipping, L.; Rodima, T.; Pihl, V.; Koppel, I. A.; Leito, I. *J. Phys. Org. Chem.* **2013**, *26*, 162–170.
15. Spartan Software, Wavefunction Inc., Irvine, California, USA, Version 08.
16. Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311–312.
17. (a) Shenderovich, I. G.; Tolstoy, P. M.; Golubev, N. S.; Denisov, G. S.; Limbach, H.-H. *J. Am. Chem. Soc.* **2003**, *125*, 11710–11720; (b) Camiolo, S.; Gale, P. A.; Hursthouse, M. B.; Light, M. E.; Shi, A. J. *Chem. Commun.* **2002**, 758–759.
18. Sessler, J. L.; Gross, D. E.; Cho, W.-S.; Lynch, V. M.; Schmidtchen, F. P.; Bates, G. W.; Light, M. E.; Gale, P. A. *J. Am. Chem. Soc.* **2006**, *128*, 12281–12288.
19. Esteban-Gómez, D.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *Org. Biomol. Chem.* **2005**, *3*, 1495–1500.
20. CCDC 1024679 contains the supplementary crystallographic data for this Letter. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif.
21. (a) Desiraju, G. R. *Acc. Chem. Res.* **2002**, *35*, 565–573; (b) Desiraju, G. R. *Chem. Commun.* **2005**, 2995–3001; Sheldrick, G. M. *SHELXTL 6.14 Program Library*; Brüker Analytical Instrument Division: Madison, Wisconsin, USA, 2003.