Computational and Theoretical Chemistry 980 (2012) 138–143

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Recognition of anions through the combination of halogen and hydrogen bonding: A theoretical study

Yunxiang Lu [a,*], Haiying Li [a], Xiang Zhu [a], Honglai Liu [a], Weiliang Zhu [b]

[a] Key Laboratory for Advanced Material and Department of Chemistry, East China University of Science and Technology, Shanghai 200237, China
[b] Drug Discovery and Design Center, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 201203, China

ARTICLE INFO

Article history:
Received 14 September 2011
Received in revised form 30 October 2011
Accepted 25 November 2011
Available online 6 December 2011

Keywords:
Anion recognition
Halogen bonding
Hydrogen bonding
Interaction energy

ABSTRACT

Anion recognition by the combination of different kinds of intermolecular forces has been evidenced in recent years. In this work, the binding behaviors of three urea-based receptors **1**–**3** towards several anions (Cl^-, Br^-, I^-, NO_3^-) have been investigated using density functional theory calculations. Distinct noncovalent interactions, involving halogen bonding, hydrogen bonding, and anion–π interactions, in the host–guest complexes under study are characterized. For the iodide receptor **1** composed of halogen- and hydrogen-bond donor groups (C—I and N—H), the anions are held by bidentate halogen and hydrogen bonds, while N—H···anion and anion–π interactions are presented in the complexes of the perfluorinated receptor **2**. On the other hand, multiple hydrogen bonding interactions (N—H/C—H···anion) occur between the host benzoate ester **3** and anionic guests. The introduction of iodine atoms into the phenyl groups of the receptor also leads to highly improved binding affinity of anions. The results presented here would provide a basis for the design and synthesis of new and functional host molecules exhibiting specific anion recognition.

1. Introduction

The development of molecular receptors capable of selective anion recognition through noncovalent interactions is an active area of current research, due to the essential roles that anions play in biology, medicine, catalysis, and environmental sciences [1–3]. One successful approach for preparing anion hosts has been to synthesize molecules that offer an array of hydrogen bonding sites to the guests [4–6]. Complementary electrostatic, Lewis acid–base, and more recently, anion–π interactions have also been exploited in the construction of host molecules that bind anions with high affinity and selectivity [7–9].

Halogen bonding, a specific nonbonding interaction between halogen atoms that act as electrophilic centers (Lewis acids) and neutral or anionic Lewis bases, has gained widespread applications in crystal engineering, supramolecular architecture, and biological design [10–12]. This attractive interaction arises from the terminal positive electrostatic potential, known as sigma-hole, of covalently bonded halogen atoms along the direction of the R—X bonds [13–15]. To data, the major investigations of halogen bonding were conducted in the solid state, while evidence of this interaction in the solution phase is rare and only a few studies in solution have been reported [16–21]. However, the increasing number of thermodynamic data suggests that certain halogen bonds are sufficiently strong to drive molecular recognition processes in solution, and recently developed anions receptors and interlocked host systems have demonstrated that the recognition of anions in solution by halogen bonding is indeed achievable [22–25].

Previous X-ray crystallography studies evidenced the concurrent formation of noncovalent interactions, including hydrogen bonding, anion–π and lone pair–π interactions, in specific host–guest complexes [26]. Moreover, the mutual influence of these nonbonding interactions in the π-electron deficient cavities of tetraoxacalix[2]arene[2]triazine was rationalized by using first principle calculations [27]. Very recently, Taylor and co-workers have developed a series of urea-based anion receptors to probe the potential anion recognition by the combination of halogen and hydrogen bonding [28]. Nonetheless, accurate structures and properties of nonbonding interactions in these systems still remain unclear. The knowledge of preferred binding motifs or evidence of concurrent different kinds of interactions should provide a basis for the development of new and functional host molecules exhibiting specific anion recognition.

In this work, the binding behaviors of three urea-based receptors **1**–**3** (see Fig. S1 in Supplementary material) towards several anions (Cl^-, Br^-, I^-, NO_3^-) have been investigated by quantum chemical calculations at density functional theory (DFT) level. The binding affinities of these anions were determined experimentally for the iodide receptor **1** and the perfluorinated receptor **2** [28]. The host benzoate ester **3** was built from **2** by replacing the F atoms on the phenyl groups with the H atom, to compare the binding properties of halogen and hydrogen bonding receptors. The major purpose of this

---

* Corresponding author. Tel./fax: +86 21 64252767.
E-mail address: yxlu@ecust.edu.cn (Y. Lu).

2210-271X/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.comptc.2011.11.045

work is to analyze different kinds of noncovalent interactions that contribute to the global stability of the anion complexes, and in particular, to elucidate the effects of concurrent nonbonding interactions, including halogen bonding, hydrogen bonding, and anion–π interactions, on receptor selectivity.

2. Computational methods

In order to investigate the binding behaviors of the urea-based receptors, DFT calculations were carried out with the Gaussian 03 program [29] using Becke's three parameter exchange functional combined with the gradient corrected correlation functional of Lee, Yang and Parr (B3LYP) [30,31]. The B3LYP method has recently been demonstrated reliable in the description of charged strong halogen bonds [32]. The geometries of all the free receptors and anion complexes were preliminarily optimized with the cc-pVDZ basis set (cc-pVDZ-PP was used for iodine). Then, the geometries obtained were further optimized using a hybrid basis set: aug-cc-pVDZ (aVDZ) for Cl, Br, I and 6-311++G(d,p) for the rest atoms. Frequency calculations were performed at the same theoretical levels to confirm that the structures found are real minima on the potential energy surface. The interaction energy (ΔE_{int}) was estimated as the difference between the total energy of the complex and the sum of total energies of the minimum geometry of the receptor and guest anion. Basis set superposition error (BSSE) was corrected by the standard counterpoise (CP) method [33].

3. Results and discussion

3.1. Optimized structures of the urea-based receptors ***1–3***

Ureas have been recognized as good hydrogen-bond donors for the construction of anion receptors that bind anions by two hydrogen bonds (N—H···anion). Over the past several years, a number of receptors containing a urea subunit were developed and applied for anion complexation and sensing [34–36]. By performing B3LYP/6-311++(d,p)-aVDZ calculations, two representative conformations (*anti* and *syn*) of the iodide receptor **1** are located and graphically depicted in Fig. S1. In the *anti* structure, the two iodo-perfluorobenzene groups adopt almost orthogonal geometry with the I···I distance equal to 3.98 Å, while the distance amounts to 9.01 Å in the *syn* structure with a small angle (40°) between the two phenyl planes. Clearly, the N—H and C—I moieties in the *anti* structure preorganize into a cavity that can hold guest anions by concurrent halogen and hydrogen bonds. On the other hand, the two structures are calculated to be almost the same energy (the energy difference of the two structures is only 0.06 kcal/mol). Thus, in the following discussion only the *anti* structure of the receptor **1** will be considered. Striking differences are observed for the structures of the receptors **2** and **3**: the two pentafluorobenzene rings in the structure of **2** adopt a chair-like shape, while in the structure of **3** the two phenyl groups adopt an open calix-like shape with much larger separation between them. It is worth mentioning that intramolecular hydrogen bonds (N—H···F) occur in the structure of **2** (see Fig. S1), which may prevent the two pentafluorobenzene rings moving freely. Overall, the structures of the urea subunit in the receptors are quite similar to each other, while the two aromatic groups have remarkably different orientations.

3.2. Binding geometries of the anion complexes

The optimized geometries of the anion complexes under investigation are displayed in Figs. 1–3. The key structural parameters of these examined complexes are collected in Tables 1 and 2. As anticipated, for the iodide receptor **1** composed of hydrogen- and halogen-bond donor groups, halide anions are held by two hydrogen bonds (N—H···X$^-$) and two halogen bonds (C—I···X$^-$). Notably, asymmetrical N—H···X$^-$ interactions are found in these systems; the largest difference of H···X$^-$ bond lengths amounts to 0.42 Å. As a consequence, the concurrent formation of halogen bonds affects the properties of N—H···X$^-$ interactions to a large degree. From Table 1, it is seen that the calculated intermolecular I···X$^-$ distances in the complexes range from 3.06 Å to 3.45 Å, significantly smaller than the sums of vdW radii of the atoms involved (3.45–3.96 Å) [37]. Moreover, all the C—I···X$^-$ interactions are essentially linear with the C—I···X$^-$ angles larger than 170°, coincide with the general characteristics of conventional strong halogen bonds [32]. Not surprisingly, C—I···X$^-$ interactions are more linear than N—H···X$^-$ hydrogen bonds and exhibit longer intermolecular I···X$^-$ distances. It is well documented that halogen bonding shows strength comparable to hydrogen bonding but has a more strictly linear geometry and different steric requirements. Nevertheless, the H···X$^-$ and I···X$^-$ bond lengths in these complexes tend to decrease in the same order I$^-$ > Br$^-$ > Cl$^-$, which has been widely established in numerous macrocyclic receptor systems with halide ions, such as triazolophanes, tetramine hexaether, and triurea [38–40]. In the complex

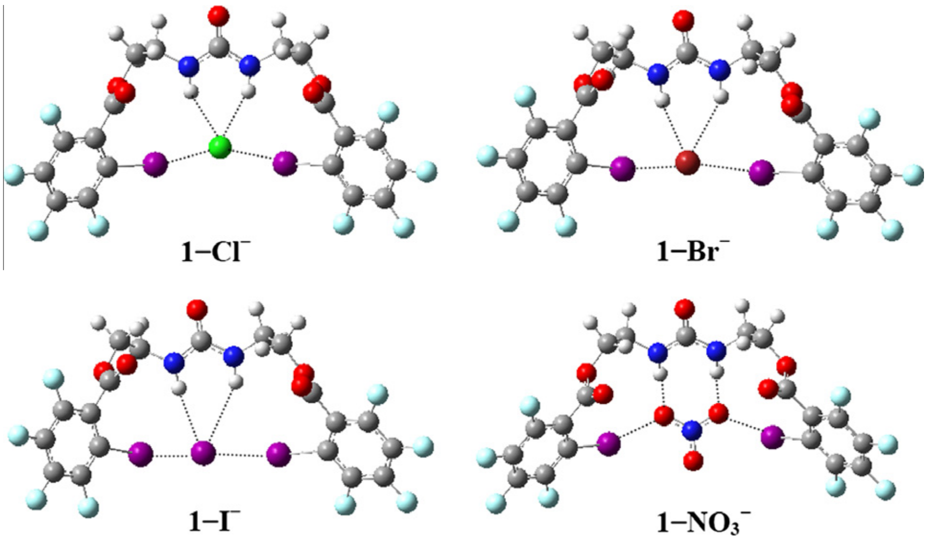
1–Cl$^-$ **1–Br$^-$**
1–I$^-$ **1–NO$_3^-$**

Fig. 1. Optimized structures of the complexes of the receptor **1**.

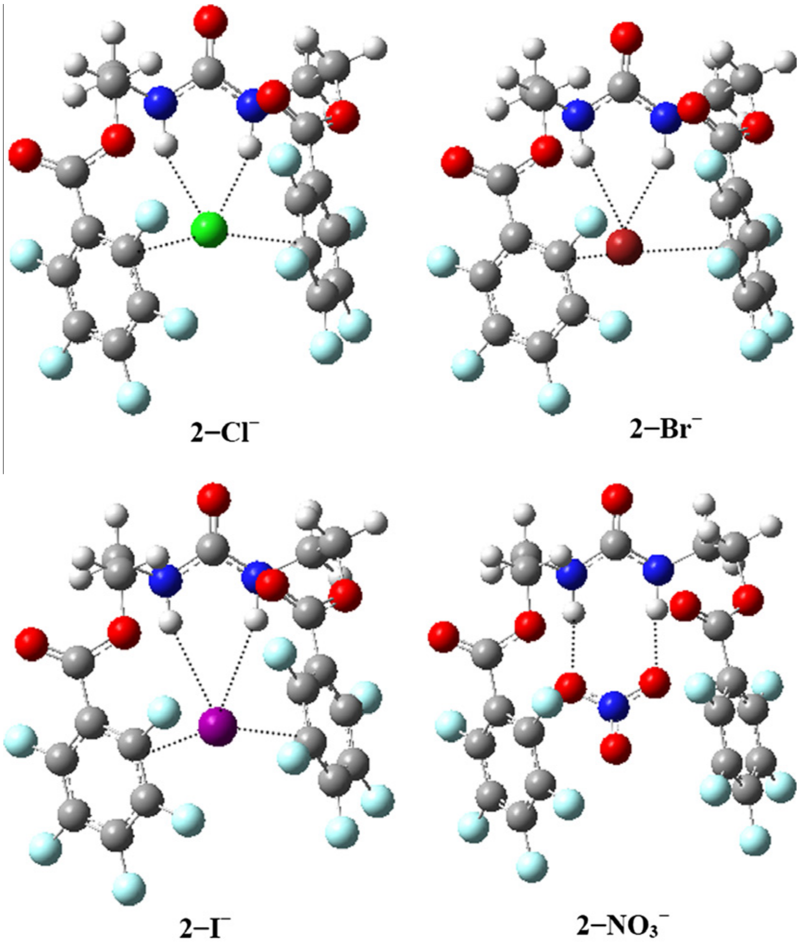

Fig. 2. Optimized structures of the complexes of the receptor **2**.

of the oxoanion NO_3^- ($1-NO_3^-$), the N—H groups form two linear H···O hydrogen bonds with two different O atoms on NO_3^-, while the C—I moieties on the benzene are involved in two I···O interactions with the same O atoms (see Fig. 1).

From Fig. 2, it is clear that for the perfluorinated receptor **2**, halide anions are held by bidentate N—H···X^- hydrogen bonds. Moreover, hydrogen bonds in the systems of **2** are highly symmetrical with the largest difference of the two H···X^- distances less than 0.02 Å. In $2-NO_3^-$ system, the N—H groups are involved in two H···O hydrogen bonds with different O atoms on NO_3^-, as shown in Fig. 2. Here it should be pointed out that in addition to H···anion hydrogen bonds, there might exist anion–π interactions between the anions and the perfluoroaryl rings in these complexes. The shortest distances between the C atoms on the benzene and the anions vary from 2.96 Å to 3.92 Å (see Table 2), almost equal to or slightly larger than the vdW radii of the atoms involved (3.17–3.68 Å) [37]. In recent years, anion–arene interactions involving perfluoroaryl groups have been extensively studied from both theoretical and experimental viewpoints [8,9,41]. To further understand the characteristics of anion–π interactions in the complexes of **2**, B3LYP/6-311++G(d,p)-aVDZ calculations were also performed on the simple complexes of pentafluoro-benzoate ester with the anions. The optimized geometries and interaction energies for these systems are shown in Fig. S2 in Supplementary material. Clearly, halide ions are located above the benzene ring with relatively smaller centroid···X^- distances (see Fig. S2). The interaction energies are predicted to be within a range from −7.16 kcal/mol to −10.36 kcal/mol for these model dimers. Therefore, anion-arene interactions become comparable in strength to traditional halogen or hydrogen bonding, in good agreement with previous calculation results [41]. For example, at the B3LYP/6-31++G** level of theory, the interaction energies for the anion–π complexes of C_6F_6 with Cl^- and Br^- are evaluated to be −10.97 kcal/mol and −9.42 kcal/mol, respectively [41]. These weak noncovalent interactions thus may play a role in the binding of anions for the perfluorinated receptor **2**.

Inspection of Fig. 3 reveals that four hydrogen bonding interactions (two urea N—H···anion and two benzene C—H···anion hydrogen bonds) are presented in the complexes of the receptor **3**. The C—H···anion interactions have long been recognized and explored, because of their important role in anion-receptor binding [42–44]. Predictions and insights of the C—H···anion bonds were also provided by gas-phase calculations on substituted aryls and strapped calix[4]pyrroles [45–47]. Apparently, the urea N—H···X^- interactions appear much stronger in strength in relation to the benzene C—H···X^- hydrogen bonds, as indicated by the much shorter H(N)···X^- distances. Thus, the major driving force of complexation between the receptor **3** and halide ions should come from the urea N—H···X^- hydrogen bonds, while the benzene C—H···X^- interactions also contribute to the stability of the complexes. In $3-NO_3^-$ system, two O atoms on NO_3^- form bidentate hydrogen bonds with the urea N—H and benzene C—H groups (see Fig. 3). As such, N—H···O interactions are stronger than C—H···O hydrogen bonds in this complex. In general, the intermolecular H(N)···anion distances in the systems of the three receptors increase in the order **2** < **3** < **1**, which indicates that as compared to

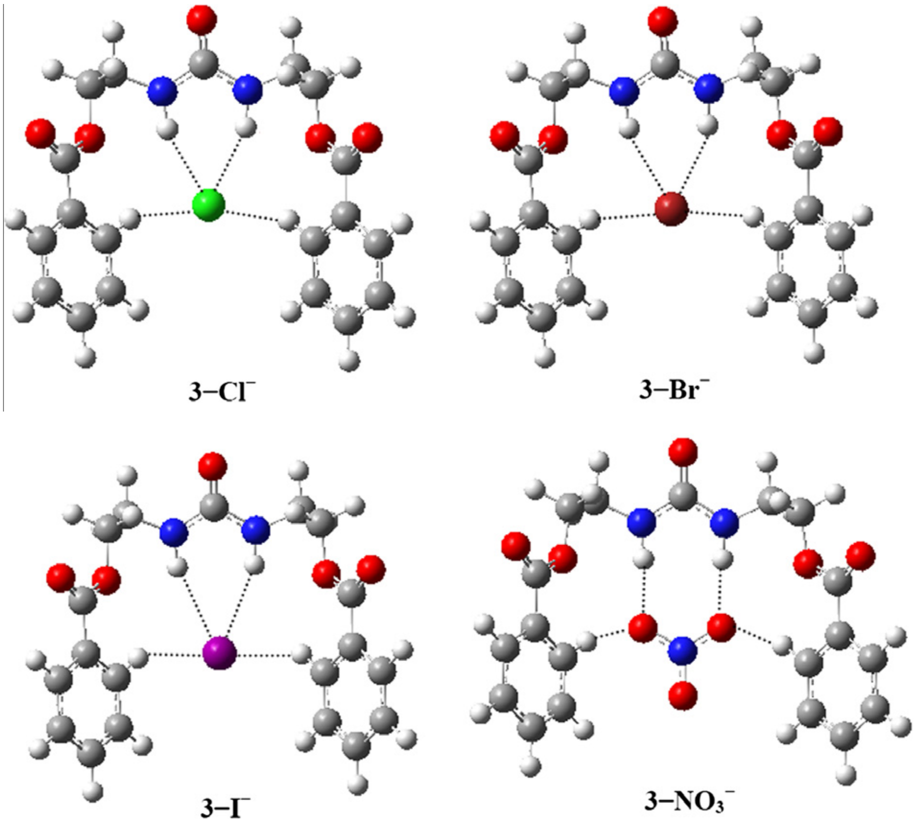

Fig. 3. Optimized structures of the complexes of the receptor **3**.

Table 1
Selected structural parameters of the complexes of **1**.[a]

Parameters	$1-Cl^-$	$1-Br^-$	$1-I^-$	$1-NO_3^-$
d(H(2)···X$^-$)	2.518	2.583	2.802	2.010
∠(N(1)-H(2)···X$^-$)	158.4	167.7	170.5	178.6
d(H(6)···X$^-$)	2.535	2.934	3.225	2.020
∠(N(5)-H(6)···X$^-$)	157.6	151.6	151.0	178.1
d(I(8)···X$^-$)	3.062	3.232	3.447	2.829
∠(C(7)-I(8)···X$^-$)	170.1	169.6	170.5	159.5
d(I(10)···X$^-$)	3.060	3.194	3.407	2.810
∠(C(9)-I(10)···X$^-$)	170.0	172.3	174.2	160.6
Δ*d*(N(1)-H(2))	0.007	0.008	0.007	0.009
Δ*d*(N(5)-H(6))	0.008	0.005	0.004	0.010
Δ*d*(C(7)-I(8))	0.034	0.035	0.041	0.010
Δ*d*(C(9)-I(10))	0.033	0.041	0.048	0.009

[a] Distances are given in angstroms and angles in degrees. The atomic numbers are given in Fig. 1.

secondary C—H···O interactions, the concurrent formation of halogen bonds attenuates N—H···anion hydrogen bonds to a larger degree.

Upon complexation, the C—I distances in the iodide receptor **1** tend to increase by about 9–48 mÅ, consistent with the weakening of the C—I bond by electron donation from anions into the C—I antibonding orbital. Particularly, the strength of H···anion hydrogen bonds in the complexes of **3** can be inferred from the increase in the N—H and C—H bond distances. Owing to the much greater elongations of the N—H distances relative to the C—H bond lengths (see Table 2), N—H···anion hydrogen bonds should be stronger in strength than C—H···anion interactions. Generally, larger increments of the N—H distances are discovered for the complexes of **2**, thus implying stronger N—H···anion hydrogen bonds in the these systems.

Table 2
Selected structural parameters of the complexes of **2** and **3**.[a]

Parameters	$2-Cl^-$	$2-Br^-$	$2-I^-$	$2-NO_3^-$
d(H(N)···X$^-$)	2.330	2.524	2.786	1.946
∠(N—H···X$^-$)	160.2	161.7	162.3	169.1
d(centroid···X$^-$)	3.706	3.870	4.055	3.236
d(C···X$^-$)[b]	3.471	3.724	3.913	2.955
Δ*d*(N—H)	0.016	0.014	0.012	0.013
	$3-Cl^-$	$3-Br^-$	$3-I^-$	$3-NO_3^-$
d(H(N)···X$^-$)	2.331	2.526	2.800	1.928
∠(N—H···X$^-$)	159.1	160.3	161.2	176.3
d(H(C)···X$^-$)	2.722	2.935	3.213	2.244
∠(C—H···X$^-$)	156.9	154.8	151.9	166.1
Δ*d*(N—H)	0.014	0.012	0.009	0.012
Δ*d*(C—H)	0.004	0.003	0.002	0.002

[a] Distances are given in angstroms and angles in degrees. The mean values of the distances and angles are given due to the symmetrical structures of the anion complexes.

[b] The shortest distances between the C atom on the benzenes and the guest anions.

To accommodate the negatively charged guest anions, the two iodo-perfluorobenzene groups in the iodide receptor **1** completely reorganize into a calix-like shape, giving rise to the two positively charged iodine atoms more separately, as shown in Fig. 1. When guest anions are presented in the receptor **2**, the two perfluorobenzene moieties also fully reorganize to form a cavity with the two N—H groups, destroying intramolecular N—H···F hydrogen bonds. Upon complexation, the two benzene rings in the receptor **3** to some extent reorganize to form a cage-like shape with the two N—H groups, in which the anions are held by multiple hydrogen bonding interactions. A comparison of Figs. 1–3 reveals striking differences for the structures of the anion complexes. Firstly, the two perfluorobenzene groups in the systems of **2** adopt "close"

Table 3
Calculated energetic data and the amount of charge transfer for the complexes under study.[a]

Complexes	ΔE_{int}	ΔH^{gas}	ΔG^{gas}
$1 - Cl^-$	−47.23 (−49.68)	−47.94	−38.11
$1 - Br^-$	−42.06 (−45.40)	−42.87	−33.36
$1 - I^-$	−36.32 (−38.64)	−37.08	−28.29
$1 - NO_3^-$	−36.98 (−37.77)	−37.53	−24.77
$2 - Cl^-$	−33.05 (−32.74)	−33.63	−24.13
$2 - Br^-$	−28.89 (−28.91)	−29.51	−20.23
$2 - I^-$	−24.17 (−23.95)	−24.65	−15.05
$2 - NO_3^-$	−31.43 (−27.98)	−32.95	−20.31
$3 - Cl^-$	−33.71 (−35.41)	−34.14	−25.43
$3 - Br^-$	−29.58 (−31.50)	−30.02	−21.16
$3 - I^-$	−24.92 (−26.23)	−25.27	−17.11
$3 - NO_3^-$	−32.08 (−29.17)	−32.14	−19.85

[a] Energies are given in kcal/mol, and the values in parentheses are the interaction energies obtained with B3LYP/cc-pVDZ.

orientations to facilitate the anions located over the rings, while in the complexes of **1** and **3** the two benzene rings undergo "open" fashions to form bidentate halogen and hydrogen bonds with the anions. Secondly, relative to the complexes of **3**, remarkably larger separations between the two phenyl groups are observed for the systems of **1**, which can be ascribed to the much longer intermolecular I···anion distances in the latter cases. Additionally, the two C=O moieties in the systems of **2** seem to be in the *syn* position, resulting in the two benzene rings close to each other. In contrast, the two C=O groups in the complexes of **1** and **3** are in the *anti* position that prevents the two rings approaching closely.

3.3. Interaction energies of the anion complexes

Calculated energetic data for the anion complexes under study are collected in Table 3. At the B3LYP/6-311++G(d,p)-aVDZ level, the interaction energies are predicted within a range of −36.32 to −47.23 kcal/mol for the complexes of **1**, −24.17 to −33.05 kcal/mol for the complexes of **2**, and −24.92 to −33.71 kcal/mol for the complexes of **3**. Apparently, the absolute values of the computed interaction energies follow the order **1** > **3** ≈ **2**, and the absolute values of free energies also show the same trend. Therefore, the binding affinity of anions in gas phase becomes much stronger with the addition of the iodine atoms into the phenyl groups of the urea-based receptor, which agrees well with the improved affinity of anions for the iodide receptor **1** determined in solution [25]. From Table 3, it is also seen that the binding affinity of halide ions for the receptors **1–3** increases in the same order $I^- < Br^- < Cl^-$, consistent with the decreasing tendency ($I^- > Br^- > Cl^-$) of the intermolecular distances in the complexes (see above). This strength order has been widely established in many macrocyilc receptor systems with halide anions [38–40]. Notably, the differences of the interaction energies between the two methods used in this work are quite limited (cf. Table 3); moreover, the B3LYP/cc-pVDZ interaction energies correlate well with those of B3LYP/6-311++G(d,p)-aVDZ ($R^2 = 0.95$). Thus, the B3LYP/cc-pVDZ method is recommended to study larger and more complex host–guest systems containing halogen bonding.

4. Conclusions

In this work, B3LYP/6-311++G(d,p)-aVDZ calculations have been carried out on the complexes of the urea-based receptors **1–3** with four anions (Cl^-, Br^-, I^-, NO_3^-). For the iodide receptor **1** composed of hydrogen- and halogen-bond donor groups, the anions are held by bidentate hydrogen and halogen bonds. Notably, asymmetrical N—H···X⁻ interactions are found in these systems; the largest difference of H···X⁻ bond lengths amounts to 0.42 Å. As a consequence, the concurrent formation of halogen bonds affects the properties of N—H···X⁻ interactions to a large degree. For the perfluorinated receptor **2**, the anions are held by two N—H···anion hydrogen bonds. In addition, there might exist weak anion-π interactions between the perfluoroaryl moieties and the anions in the complexes of **2**. On the other hand, multiple hydrogen bonding interactions (N—H/C—H···anion) are presented in the systems of the receptor **3**. The urea N—H···anion interactions appear stronger in strength in relation to the benzene C—H···anion hydrogen bonds, as indicated by the much shorter H(N)···anion distances. Thus, the major driving force of complexation between the receptor **3** and the anions should come from the urea N—H···anion hydrogen bonds, while the benzene C—H···anion interactions also play a role in the stability of these complexes. In general, the intermolecular H(N)···anion distances in the complexes of the three receptors increases in the order **2** < **3** < **1**, indicating that the concurrent formation of halogen bonds attenuates the N—H···anion hydrogen bonds to a larger degree.

To accommodate the negatively charged guest anions, the two iodo-perfluorobenzene groups in the receptor **1** completely reorganize into a calix-like shape, giving rise to the two positively charged iodine atoms more separately. When guest anions are presented in the host molecule **2**, the two perfluorobenzene moieties also fully reorganize to form a cavity with the two N—H groups, destroying intramolecular N—H···F hydrogen bonds. Upon complexation, the two phenyl moieties in the receptor **3** to some extent reorganize to form a cage-like shape with the two N—H groups, in which the anions are held by multiple hydrogen bonding interactions.

At the B3LYP/6-311++G(d,p)-aVDZ level, the interaction energies are predicted within a range of −24.17 to −47.23 kcal/mol for the anions complexes under study. The computed interaction energies show a decrease in absolute value in the order **1** > **3** ≈ **2**, and therefore, the binding affinity of anions in gas phase becomes stronger with the addition of iodine atoms into the phenyl groups of the urea-based receptor.

In summary, the incorporation of halogen atoms into urea-based framework results in disparate conformations of the receptor to accommodate guest anions and also entirely different binding behaviors towards the anions, hence enabling anion recognition to take place by the combination of halogen and hydrogen bonding. Moreover, the binding affinity of anions is shown to be enhanced with the introduction of iodine atoms into the phenyl groups of the urea-based receptor. The results presented here would be of vital importance in the design and synthesis of anion receptors with high affinity and selectivity.

Acknowledgments

This work was supported by the Natural Science Foundation of Shanghai (11ZR1408700), the National Natural Science Foundation of China (20736002 and 21103047), the Program for Changjiang Scholars and Innovative Research Team in the University of China (IRT0721), and the 111 Project of China (B08021).

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.comptc.2011.11.045.

References

[1] J.L. Sessler, P.A. Gale, W.-S. Cho, Anion Receptor Chemistry, Royal Society of Chemistry, Cambridge, 2006.
[2] C. Caltagirone, P.A. Gale, Anion receptor chemistry: highlights from 2007, Chem. Soc. Rev. 38 (2009) 520–563.
[3] S. Kubik, Amino acid containing anion receptors, Chem. Soc. Rev. 38 (2009) 585–605.

[4] S.O. Kang, R.A. Begum, K. Bowman-James, Amide-based ligands for anion coordination, Angew. Chem., Int. Ed. 45 (2006) 7882–7894.

[5] D. Pal, J. Suhnel, M.S. Weiss, New principle of protein structures: nests, eggs and what next?, Angew Chem., Int. Ed. 41 (2002) 4663–4665.

[6] S. Kubik, R. Kirchner, D. Nolting, J. Seidel, A molecular oyster – a neutral anion receptor containing two cyclopeptide subunits with a remarkable sulfate affinity in aqueous solution, J. Am. Chem. Soc. 124 (2002) 12752–12760.

[7] T.W. Hudnall, C.-W. Chiu, F.P. Gabbai, Fluoride ion recognition by chelating and cationic boranes, Acc. Chem. Soc. 42 (2009) 388–397.

[8] P. Gamez, T.L. Mooibroek, S.J. Teat, J. Reedijk, Anion binding involving π-acidic heteroaromatic rings, Acc. Chem. Res. 40 (2007) 435–444.

[9] B.L. Schottel, H.T. Chifotides, K.R. Dunbar, Anion–π interactions: a tutorial review, Chem. Soc. Rev. 37 (2008) 68–83.

[10] P. Metrangolo, H. Neukirch, T. Pilati, G. Resnati, Halogen bonding based recognition process: a world parallel to hydrogen bonding, Acc. Chem. Res. 38 (2005) 386–395.

[11] P. Auffinger, F.A. Hays, E. Westhof, P.S. Ho, Halogen bonds in biological systems, Proc. Natl. Acad. Sci. USA 101 (2004) 16789–16794.

[12] Y.X. Lu, T. Shi, Y. Wang, H.Y. Yang, Y.H. Yan, X.M. Luo, H.L. Jiang, W.L. Zhu, Halogen bonding – a novel interaction for rational drug design, J. Med. Chem. 52 (2009) 2854–2862.

[13] P. Politzer, P. Lane, M.C. Concha, Y. Ma, J.S. Murray, An overview of halogen bonding, J. Mol. Model. 13 (2007) 305–311.

[14] P. Politzer, J.S. Murray, T. Clark, Halogen bonding: an electrostatically-driven highly directional noncovalent interaction, Phys. Chem. Chem. Phys. 12 (2010) 7748–7757.

[15] J.S. Murray, K.E. Riley, P. Politer, T. Clark, Directional weak intermolecular interactions: σ-hole bonding, Aust. J. Chem. 63 (2010) 1598–1607.

[16] M.-C. Bernard-Houplain, C. Bourderon, J.J. Peron, C. Sandorfy, On the effect of bromine atoms on the opening and formation of hydrogen bonds, Chem. Phys. Lett. 11 (1971) 149–151.

[17] T.D. Paolo, C. Sandorfy, On the biological importance of the hydrogen bond breaking potency of fluorocarbons, Chem. Phys. Lett. 26 (1974) 466–469.

[18] J. Favrot, J.-M. Leclercq, R. Roberge, C. Sandorfy, D. Vocelle, The photochemical step of vision: the hydrogen bond and other associations, Chem. Phys. Lett. 53 (1978) 433–435.

[19] S. Libri, N.A. Jasim, R.N. Perutz, L. Brammer, Metal fluorides form strong hydrogen bonds and halogen bonds: measuring interaction enthalpies and entropies in solution, J. Am. Chem. Soc. 130 (2008) 7842–7844.

[20] E. Dimitrijevic, O. Kvak, M.S. Tayor, Measurements of weak halogen bond donor abilities with tridentate anion receptors, Chem. Commun. (2010) 9025–9028.

[21] M.G. Sarwar, B. Dragisic, L.J. Salsberg, C. Gouliaras, M.S. Tayor, Thermodynamics of halogen bonding in solution: substituent, structural, and solvent effects, J. Am. Chem. Soc. 132 (2010) 1646–1653.

[22] M.G. Sarwar, B. Dragisic, S. Sagoo, M.S. Taylor, A tridentate halogen-bonding receptor for tight binding of halide anions, Angew. Chem., Int. Ed. 49 (2010) 1674–1677.

[23] A. Caballero, N.G. White, P.D. Beer, A bidentate halogen-bonding bromoimidazoliophane receptor for bromide ion recognition in aqueous media, Angew. Chem., Int. Ed. 50 (2011) 1845–1848.

[24] C.J. Serpell, N.L. Kilah, P.J. Costa, V. Felix, P.D. Beer, Halogen bond anion templated assembly of an imidazolium pseudorotaxane, Angew. Chem., Int. Ed. 49 (2010) 5322–5326.

[25] N.L. Kilah, M.D. Wise, C.J. Serpell, A.L. Thompson, N.G. White, K.E. Christensen, P.D. Beer, Enhancement of anion recognition exhibited by a halogen-bonding rotaxane host system, J. Am. Chem. Soc. 132 (2010) 11893–11895.

[26] D.X. Wang, Q.Y. Zheng, Q.Q. Wang, M.X. Wang, Halide recognition by tetraoxacalix[2]arene[2]triazine receptors: concurrent noncovalent halide-π and lone-pair-π interactions in host-halide-water ternary complexes, Angew. Chem., Int. Ed. 47 (2008) 7485–7488.

[27] M.E. Alberto, G. Mazzone, N. Russo, E. Siciia, The mutural influence of non-covalent interactions in π-electron deficient cavities: the case of anion recognition by tetraoxacalix[2]arene[2]triazine, Chem. Commun. (2010) 5894–5896.

[28] M.G. Chudzinski, C.A. McClary, M.S. Taylor, Anion receptors composed of hydrogen- and halogen-bond donor groups: modulating selectivity with combinations of district noncovalent interactions, J. Am. Chem. Soc. 133 (2011) 10559–10568.

[29] M.J. Frisch et al., Gaussian 03 (Revision D. 01), Gaussian, Inc., Wallingford, CT, 2004.

[30] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, Phys. Rev. A 38 (1988) 3098–3100.

[31] C. Lee, W. Yang, R.G. Parr, Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 785–789.

[32] Y. Lu, H. Li, X. Zhu, W. Zhu, H. Liu, How does halogen bonding behave in solution: a theoretical study using implicit solvation model, J. Phys. Chem. A 115 (2011) 4467–4475.

[33] S.F. Boys, F. Bernardi, The calculation of small molecular interactions by the difference of separate total energies. Some procedures with reduced errors, Mol. Phys. 19 (1970) 553–566.

[34] Z. Zhang, P.R. Schreiner, (Thio)urea organocatalysis – what can be learn from anion recognition?, Chem Soc. Rev. 38 (2009) 1187–1198.

[35] V. Amendola, L. Fabbrizzi, L. Mosca, Anion recognition by hydrogen bonding: urea-based receptors, Chem. Soc. Rev. 39 (2010) 3889–3915.

[36] A.F. Li, J.H. Wang, F. Wang, Y.B. Jiang, Anion complexation and sensing using modified urea and thiourea-based receptors, Chem. Soc. Rev. 39 (2010) 3729–3745.

[37] A. Bondi, van der Waals volumes and radii, J. Phys. Chem. 68 (1964) 441–451.

[38] Y. Chen, X. Pan, H. Yan, N. Tan, Multiple hydrogen-bonding interactions between macrocyclic triurea and F$^-$, Cl$^-$, Br$^-$, I$^-$ and NO$_3^-$: a theoretical investigation, Phys. Chem. Chem. Phys. 13 (2011) 7384–7395.

[39] I. Bandyopadhyay, K. Raghavachari, A.H. Flood, Strong CH$\cdots$ halide hydrogen bonds from 1,2,3-triazoles quantified using pre-organized and shape-persistent trizolophanes, ChemPhysChem. 10 (2009) 2535–2540.

[40] C. Bazzicalupi, A. Bencini, A. Bianchi, A. Danesi, C. Giorgi, M.A.M. Lorente, B. Valtancoli, Inclusive coordination of F$^-$, Cl$^-$ and Br$^-$ anions into macrocyclic polyammonium receptors, New. J. Chem. 30 (2006) 959–965.

[41] I. Alkorta, I. Rozas, J. Elgueo, Interactions of anions with perfluoro aromatic compounds, J. Am. Chem. Soc. 124 (2002) 8593–8598.

[42] S. Zhu, H. Staats, K. Brandhorst, J. Grunenberg, F. Gruppi, E. Dalcanale, A. Luetzen, K. Rissanen, C.A. Schalley, Anion binding to resorcinarene-based cavitands: the importance of C—H$\cdots$anion interactions, Angew. Chem., Int. Ed. 47 (2008) 788–792.

[43] W. Yoon, D.E. Gross, V.M. Lynch, J.L. Sessler, B.P. Hay, C.H. Lee, Phenyl-, pyrrole-, and furan-containing diametrically strapped calix[4]pyrroles: an experimental and theoretical study of hydrogen bonding effects in chloride anion recognition, Angew. Chem., Int. Ed. 47 (2008) 5038–5042.

[44] O.B. Berryman, D.W. Johnson, Experimental evidence for interactions between anions and electron-deficient rings, Chem. Commun. (2009) 3143–3153.

[45] S. Zuo, J.M. Quan, Y. Wu, Oxa-bicyclocalixarenes: a new cage for anion via C—H$\cdots$anion hydrogen bonds and anion$\cdots\pi$ interactions, Org. Lett. 9 (2007) 4219–4222.

[46] L. Pedzisa, B.P. Hay, Aliphatic C—H$\cdots$anion hydrogen bonds: weak contacts or strong interactions?, J Org. Chem. 74 (2009) 2554–2560.

[47] V.S. Bryantsev, B.P. Hay, Are C—H groups significant hydrogen bonding sites in anion receptors? Benzene complexes with Cl$^-$, NO$_3^-$ and ClO$_4^-$, J. Am. Chem. Soc. 127 (2005) 8282–8283.