A new class of halogen bonds that avoids the σ-hole

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ABSTRACT

A new class of halogen bonds of the type X = Hal···Y has been investigated by using the density functional theory calculations. The strength of this new class of halogen bonds is in the range of 90–120 kcal/mol, which is greatly larger than that of the conventional halogen bond of the type X-Hal···Y. The geometry of this new class of halogen bonds is not determined by the halogen's positive σ-hole. Natural bond orbital analysis shows it is the $n \to \pi^*$ interaction that determines the geometry of this new class of halogen bonds. Experimental results are in good agreement with the theoretical predictions.

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1. Introduction

Halogen bond is the Hal···Y interaction wherein Hal is an electrophilic halogen and Y is an electron density donor. The study of the halogen bond can be dated back to 1863 when Frederick Guthrie gave the first report on the halogen-bonded complex formed between iodine and ammonia [1]. However, the important role of the halogen bond in crystal engineering, molecular recognition, functional materials, biomolecular systems, and biomedical applications has been uncovered only in recent years [2–13]. As a group, the halogens are among the most electronegative elements and they are always assigned a formal oxidation number of −1. So the attractive interaction between a covalently-bound halogen and an electron density donor is a little unexpected. This issue can be explained by the misshaped electron cloud of the covalently-bound halogen which often gives rise to a significant positive electrostatic potential at the extreme end of the halogen along the bond axis, through which it can interact attractively with negative site of the electron density donor [14–18]. Politzer and coworkers subsequently termed this electropositive crown 'σ-hole' and called the halogen bonding 'σ-hole bonding' [19,20].

In fact, the concept of σ-hole bonding indicates that the halogen bond is an electrostatically-driven highly directional noncovalent interaction [7]. Now, we know that, either for the hydrogen bond or for the halogen bond, the consideration of only the electrostatic interaction may not be sufficient in describing their ground-state structure and stabilization, and the charge-transfer, polarization, and dispersion contributions also play an important role [21]. Note that the halogen-bonded complexes were originally classified as the charge-transfer complexes in which the charge-transfer is thought to be the dominant factor

to determine the supramolecular structure [22]. In a recent study, Hobza and Riley investigated the nature of halogen bonding employing symmetry adapted perturbation theory (SAPT) analyses and found that the largest SAPT interaction energy component for unfluorinated systems containing chlorine and bromine is dispersion [23]. Hobza and Riley also pointed out that, even in cases where the electrostatic effects are not the dominant ones, the halogen's positive σ-hole still tends to line up with the negative site of the electron density donor and determines the geometries of halogen-bonded complexes [23].

Are there any halogen bonds in which their geometries are not determined by the σ-hole? To answer this question, we must go back to the interaction energy components other than electrostatics. In the halogen bond of the type X-Hal···Y (X is any atom), the direction of charge transfer is from the lone pair(s) on Y to the σ^* antibonding orbital of X-Hal single bond in most cases, which coincides with the direction of σ-hole bonding; so it is difficult to distinguish whether the geometry of a halogen bond is determined by the charge transfer or by the σ-hole. In order to avoid the ambiguity, we can consider the halogen bond of the type X = Hal···Y because the direction of charge transfer from the lone pair(s) on Y to the π^* antibonding orbital of an X = Hal double bond is different from the direction of σ-hole bonding. An X = Hal double bond will be formed if the X-Hal single bond becomes shorter and shorter. There are two ways to make the X-Hal single bond shorter and shorter. First, a strong electron-withdrawing group can make the X-Hal single bond shorter. For example, the exceptionally short C–Cl bond (1.694(1) Å) has been reported in the crystal structure of chlorotrinitromethane [24]. The second way to shorten the X-Hal single bond is to use the blue-shifting halogen bond [25–27]. In the present study, we selected the halogen-bonded complexes $CH_3OCZCl^+\cdots Y$ (Z = H, F or Cl; Y = F^-, Cl^- or Br^-) as models to study theoretically the role of $n \to \pi^*$ interactions in determining the geometry of the halogen bond.

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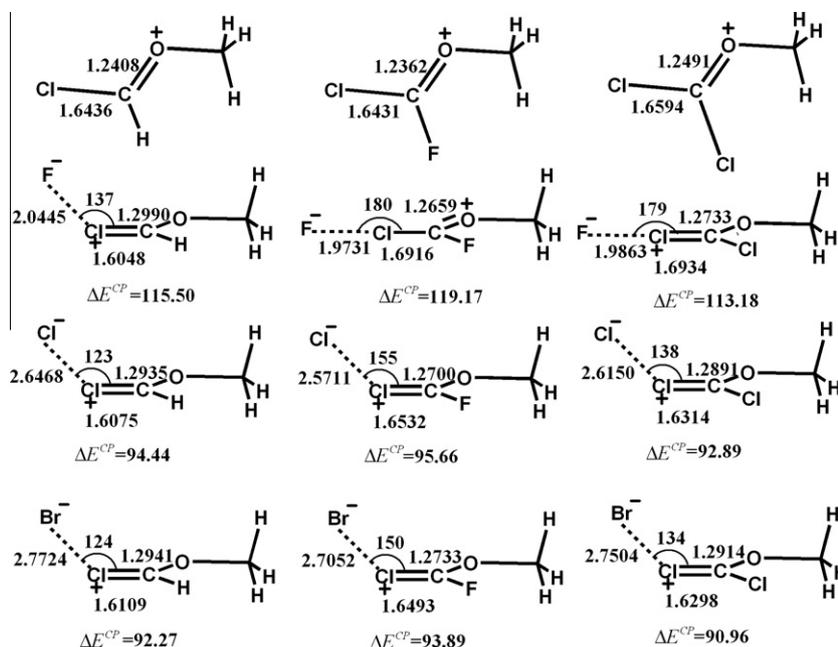
Figure 1. Geometries and binding energies of the complexes $CH_3OCHCl^+\cdots F^-$, $CH_3OCHCl^+\cdots Cl^-$, $CH_3OCHCl^+\cdots Br^-$, $CH_3O^+CFCl\cdots F^-$, $CH_3OCFCl^+\cdots Cl^-$, $CH_3OCFCl^+\cdots Br^-$, $CH_3OCClCl^+\cdots F^-$, $CH_3OCClCl^+\cdots Cl^-$, and $CH_3OCClCl^+\cdots Br^-$. Geometries of the monomers CH_3O^+CHCl, CH_3O^+CFCl, and CH_3O^+CClCl are also shown for comparisons. Bond length is in Å, bond angle is in degree, and binding energy is in kcal/mol. The bonding type (single bond or double bond) is determined by the NBO analysis.
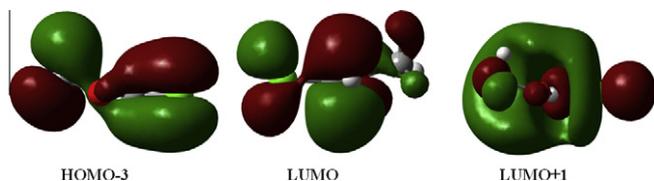
Figure 2. Selected molecular orbitals of CH_3OCHCl^+. CH_3OCHCl^+ taken from $CH_3OCHCl^+\cdots F^-$.

Finally, it is worth pointing out that the halogen bonds studied here are very similar to the cation–anion hydrogen bonds reported by D'Oria and Novoa et al. in a very recent paper [28], which confirms once again that the properties of the halogen bond are pretty similar to the properties of the hydrogen bond [2].

2. Computational details

Geometries were all fully optimized with tight convergence criteria and characterized by frequency computations and wave function stability checks at the M05-2X/6-311++G(d,p) theory level [29,30]. In our previous paper [31], we have examined the reliability of the M05-2X/6-311++G(d,p) calculation for the study of the halogen-bonded complexes. It was found that M05-2X provides more accurate results on average for a series of halogen-bonded complexes when compared to B3LYP, M05, M06, M06-L, M06-HF or M06-2X [31]. All the structures reported in this Letter were confirmed as true minima on the potential energy surface by the presence of only real frequencies after the corresponding harmonic vibrational analysis. The binding energies of the complexes were calculated using the supermolecule method. All binding energies are corrected for basis set superposition error using the counterpoise method of Boys and Bernardi [32]. It is well-known that the accuracy of density functional theory (DFT) calculations also depends on the number of points used in the numerical integration. In the present study, an 'ultrafine' integration grid (99 radial,

590 angular points) was used for all the DFT calculations to avoid the possible integration grid errors.

All the calculations were performed using the GAUSSIAN 09 suite of electronic structure programs [33]. Natural bond orbital (NBO) analyses [34] were carried out at the M05-2X/6-311++G(d,p) level of theory on each optimized structure with the built-in subroutines of the GAUSSIAN 09 program. The NBO method transforms a calculated wavefunction into a localized form, which corresponds to a lone pair or a localized bond of the Lewis structure. The interaction between filled orbitals in one subsystem and unfilled orbitals of the other represents a deviation of the complex from its Lewis structure and can be used as a measure of the intermolecular delocalization. The stabilization from the donor → acceptor interaction can be estimated by using second-order perturbation theory. The bonding type (single bond or double bond) is also determined by the NBO analysis.

3. Results and discussion

Geometries and binding energies of the complexes $CH_3OCHCl^+\cdots F^-$, $CH_3OCHCl^+\cdots Cl^-$, $CH_3OCHCl^+\cdots Br^-$, $CH_3O^+CFCl\cdots F^-$, $CH_3OCFCl^+\cdots Cl^-$, $CH_3OCFCl^+\cdots Br^-$, $CH_3OCClCl^+\cdots F^-$, $CH_3OCClCl^+\cdots Cl^-$, and $CH_3OCClCl^+\cdots Br^-$ are shown in Figure 1. Geometries of the monomers CH_3O^+CHCl, CH_3O^+CFCl, and CH_3O^+CClCl are also shown in Figure 1 for comparisons. The bonding type (single bond or double bond) is determined by the NBO analysis. The existence of the C=Cl double bond is further confirmed by the diagram of the fourth highest occupied molecular orbital (HOMO−3) of CH_3OCHCl^+ (Figure 2). The HOMO−3, which is lower in energy than the HOMO, features a large contribution from the C–Cl π bond. As shown in Figure 1, the lengths of C–Cl or C=Cl bonds are all less than 1.70 Å. Let us add here that the normal bond length of C–Cl single bond is about 1.767(2) Å [35]. The shortest C=Cl bond of 1.6048 Å is found in $CH_3OCHCl^+\cdots F^-$, which is much less than the mean C=S bond length of about 1.71(1) Å [35]. A comparison of the C=Cl bond length in $CH_3OCHCl^+\cdots F^-$ and the C–Cl bond length in CH_3O^+CHCl shows that the formation of the C=Cl$\cdots$F$^-$

halogen bond makes the C–Cl bond much more shorter. In Figure 1, the C=Cl···Y angles are all less than 180°. Obviously, the C=Cl···Y angles in CH_3OCHCl^+···Y are much smaller than those in other complexes. The binding energy of this new class of halogen bonds is in the range of 90–120 kcal/mol, which attains the strength of covalent bonds and is greatly beyond the so-called covalent limit (50 kcal/mol). To the best of our knowledge, such strong halogen bonds have not been reported before.

The electrostatic potential map of CH_3OCHCl^+ is shown in Figure 3. The existence of a σ-hole on Cl is very clear. The interaction between the positive σ-hole and the negative site on Y should be highly directional, along the extension of the C=Cl double bond. That is to say, the C=Cl···Y angle should tend to linearity as the C=Cl···Y halogen bond is formed. However, as shown in Figure 1, the C=Cl···Y angles are all less than 180° in the halogen-bonded complexes CH_3OCZCl^+···Y. The largest deviation angle of 57° is found in CH_3OCHCl^+···Cl^-. Evidently, the geometry of the C=Cl···Y halogen bond is not determined by the Cl's positive σ-hole. The diagrams of the lowest unoccupied molecular orbital (LUMO) and the second lowest unoccupied molecular orbital (LUMO+1) of CH_3OCHCl^+ are also shown in Figure 2. The LUMO+1, which is higher in energy than the LUMO, features a large contribution from the σ* antibonding orbital of C=Cl double bond; the LUMO itself features the π* antibonding orbital of C=Cl double bond. From a molecular orbital point of view, the charge transfer from the lone pair(s) on Y to the π* antibonding orbital of C=Cl double bond should be favorable. When combining with the preferred spatial orientations of the σ* antibonding orbital and the π* antibonding orbital, it is reasonable to assume that the $n \to \pi^*$ interactions determine the geometry of the halogen bond.

To quantitatively evaluate the $n \to \sigma^*$ and $n \to \pi^*$ interactions involved in the formation of the halogen bond, NBO analysis has been carried out at the M05-2X/6-311++G(d,p) level of theory. Some significant donor–acceptor orbital interactions and their second-order perturbation stabilization energies are collected in Table 1. Since Y has four nonbonded lone electron pairs and each of these electron pairs has different direction, it is not difficult to understand that both $n \to \sigma^*$ and $n \to \pi^*$ interactions can coexist in the halogen-bonded complexes considered in this Letter. As clearly shown in Table 1, the only exception is for $CH_3O^+CFCl^+$···F^- in which there is no $n \to \pi^*$ interaction upon the complex formation. Correspondingly, Figure 1 shows that the C–Cl···F^- angle is 180° in $CH_3O^+CFCl^+$···F^-. Here, it is the σ-hole that determines the geometry of the C–Cl···F^- halogen bond in $CH_3O^+CFCl^+$···F^-. For the complexes CH_3OCHCl^+···Cl^-, CH_3OCHCl^+···Br^-, CH_3OCFCl^+···Cl^-, CH_3OCFCl^+···Br^-, $CH_3OCClCl^+$···F^-, $CH_3OCClCl^+$···Cl^-, and

Table 1
Some significant donor–acceptor orbital interactions and their second-order perturbation stabilization energies (ΔE^2, kcal/mol) of the nine halogen-bonded complexes.[a]

Complex	Donor	Acceptor	Interaction	ΔE^2
CH_3OCHCl^+···F^-	LP(4) F^-	BD*(1) C=Cl	$n \to \pi^*$	5.17
	LP(4) F^-	BD*(2) C=Cl	$n \to \sigma^*$	38.64
CH_3OCHCl^+···Cl^-	LP(4) Cl^-	BD*(1) C=Cl	$n \to \pi^*$	16.77
	LP(4) Cl^-	BD*(2) C=Cl	$n \to \sigma^*$	10.75
CH_3OCHCl^+···Br^-	LP(4) Br^-	BD*(1) C=Cl	$n \to \pi^*$	18.95
	LP(4) Br^-	BD*(2) C=Cl	$n \to \sigma^*$	9.79
$CH_3O^+CFCl^+$···F^-	LP(4) F^-	BD*(1) C–Cl	$n \to \sigma^*$	53.99
CH_3OCFCl^+···Cl^-	LP(4) Cl^-	BD*(1) C=Cl	$n \to \pi^*$	7.17
	LP(4) Cl^-	BD*(2) C=Cl	$n \to \sigma^*$	25.95
CH_3OCFCl^+···Br^-	LP(4) Br^-	BD*(1) C=Cl	$n \to \pi^*$	10.45
	LP(4) Br^-	BD*(2) C=Cl	$n \to \sigma^*$	23.33
$CH_3OCClCl^+$···F^-	LP(3) F^-	BD*(1) C=Cl	$n \to \pi^*$	5.36
	LP(4) F^-	BD*(2) C=Cl	$n \to \sigma^*$	49.14
$CH_3OCClCl^+$···Cl^-	LP(4) Cl^-	BD*(1) C=Cl	$n \to \pi^*$	12.22
	LP(4) Cl^-	BD*(2) C=Cl	$n \to \sigma^*$	18.09
$CH_3OCClCl^+$···Br^-	LP(4) Br^-	BD*(1) C=Cl	$n \to \pi^*$	15.47
	LP(4) Br^-	BD*(2) C=Cl	$n \to \sigma^*$	15.42

[a] BD* denotes the formally empty antibonding orbital and LP denotes the occupied lone pair.

$CH_3OCClCl^+$···Br^-, Figure 4 shows the correlation of their second-order perturbation stabilization energies for $n \to \pi^*$ interactions with the deviation angles of $\angle C = Cl$···Y. Plot of ΔE^2 versus the deviation angle gives a straight line and the coefficient of determination of the linear fit (R^2) is 0.90123, which shows that the correlation between ΔE^2 and the deviation angle is good in these halogen-bonded complexes. These results indicate it is the $n \to \pi^*$ interaction not the σ-hole that determines the geometry of the C=Cl···Y halogen bond. It must be pointed out that the case for CH_3OCHCl^+···F^- is very special: the small ΔE^2 value (5.17 kcal/mol) for $n \to \pi^*$ interaction is accompanied by a large deviation angle of 43°. The distance between F^- and its adjacent H is only 3.9383 Å. The strong electrostatic attraction between F^- and H makes $\angle C$=Cl···F^- much smaller and the deviation angle much larger. Such case does not exist in the other complexes.

The Cambridge Structure Database (CSD version 5.22+30 updates) [36,37] search gives some information for the existence of this new class of halogen bonds. Although there are no crystal structures of the complexes considered in this study, the crystal structure of the complex $CH_3OCHCl^+SbF_6^-$ was found in CSD [38]. The geometry of the C=Cl···F halogen bond contained in this


Figure 3. Electrostatic potentials of CH_3OCHCl^+ with a scale of 62.8 (red) to 113.0 (blue) kcal/mol. CH_3OCHCl^+ is taken from CH_3OCHCl^+···F^-. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
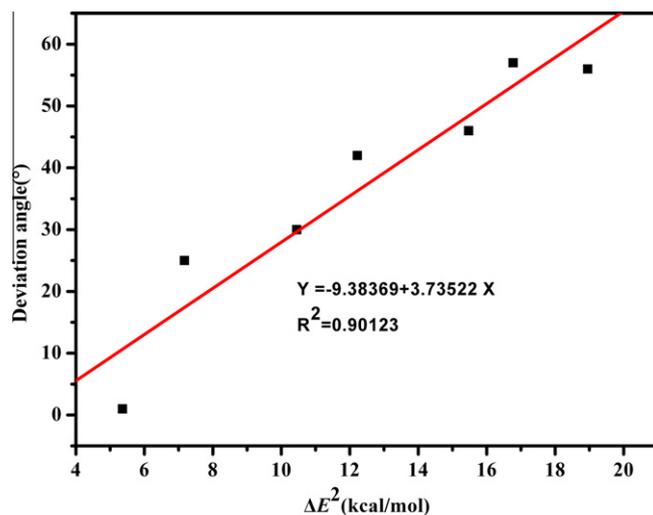
Figure 4. Correlation of ΔE^2 for $n \to \pi^*$ interaction with the deviation angle of $\angle C$=Cl···Y.
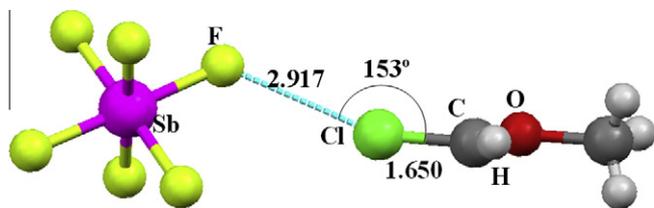
Figure 5. C=Cl···F halogen bond from the crystal structure of $CH_3OCHCl^+SbF_6^-$.

crystal structure is shown in Figure 5. Here, the negative charge is not only on one F atom, but over six F atoms and one Sb atom. So the C=Cl···F halogen bond is not as strong as those studied above, which is indicated by the larger distance (2.917 Å) between Cl and F. More important is that the C=Cl···F angle is only 153° and not 180° as those in the conventional halogen bond with the type of X-Hal···Y always are. The experimental observation agrees very well with our theoretical prediction.

4. Conclusions

A series of strong halogen-bonded complexes CH_3OCZCl^+···Y have been investigated by the density functional theory calculations at the M05-2X/6-311++G(d,p) level of theory. In these complexes, the strong electron-withdrawing group CH_3O^+= results in the C–Cl bond contraction and the formation of the C=Cl double bond and further the formation of a new class of halogen bonds with the type of C=Cl···Y. The existence of the C=Cl double bond is confirmed by both the molecular orbital analysis and the NBO analysis. The strength of this new class of halogen bonds is in the range of 90–120 kcal/mol, which is greatly beyond the so-called covalent limit. It is found that, unlike the conventional halogen bond with the type of X-Hal···Y, the geometry of this new class of halogen bonds is not determined by the halogen's positive σ-hole. NBO analyses show that there is a competition between the $n \rightarrow \sigma^*$ interaction and the $n \rightarrow \pi^*$ interaction and the correlation of the second-order perturbation stabilization energy for $n \rightarrow \pi^*$ interaction with the deviation angle of ∠C=Cl···Y is pretty good. These results indicate it is the $n \rightarrow \pi^*$ interaction that determines the geometry of this new class of halogen bonds. Crystal structure analyses provide further support for our theoretical prediction.

International Union of Pure and Applied Chemistry (IUPAC) recently initiated one project to examine the definition of the halogen bond (IUPAC project 2009-032-1-200, see www.halogenbond-ing.eu). The new definition of the halogen bond is still in discussion [8,39]. We hope the results presented in this study will be helpful for the definition and development of the halogen bond.

References

[1] F. Guthrie, J. Chem. Soc. 16 (1863) 239.
[2] P. Metrangolo, H. Neukirch, T. Pilati, G. Resnati, Acc. Chem. Res. 38 (2005) 386.
[3] P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, G. Terraneo, Angew. Chem. Int. Ed. 47 (2008) 6114.
[4] P. Metrangolo, G. Resnati (Eds.), Halogen Bonding: Fundamentals and Applications, Springer, Berlin, 2008.
[5] G. Cavallo, P. Metrangolo, T. Pilati, G. Resnati, M. Sansotera, G. Terraneo, Chem. Soc. Rev. 39 (2010) 3772.
[6] R. Bertani et al., Coord. Chem. Rev. 254 (2010) 677.
[7] P. Politzer, J.S. Murray, T. Clark, Phys. Chem. Chem. Phys. 12 (2010) 7748.
[8] A.C. Legon, Phys. Chem. Chem. Phys. 12 (2010) 7736.
[9] Y.X. Lu, Y. Wang, W.L. Zhu, Phys. Chem. Chem. Phys. 12 (2010) 4543.
[10] E. Parisini, P. Metrangolo, T. Pilati, G. Resnati, G. Terraneo, Chem. Soc. Rev. 40 (2011) 2267.
[11] G.R. Desiraju, R. Parthasarathy, J. Am. Chem. Soc. 111 (1989) 8725.
[12] F.F. Awwadi, R.D. Willett, K.A. Peterson, B. Twamley, Chem. Eur. J. 12 (2006) 8952.
[13] B.K. Saha, A. Nangia, J.-F. Nicoud, Cryst. Growth Des. 6 (2006) 1278.
[14] T. Brinck, J.S. Murray, P. Politzer, J. Quantum Chem. Quantum Biol. Symp. 19 (1992) 57.
[15] J.S. Murray, K. Paulsen, P. Politzer, Proc. Indiana Acad. Sci. 106 (1994) 267.
[16] E. Bosch, C.L. Barnes, Cryst. Growth Des. 2 (2002) 299.
[17] P. Auffinger, F.A. Hays, E. Westhof, P.S. Ho, Proc. Natl. Acad. Sci. U S A 101 (2004) 16789.
[18] W. Wang, A. Tian, N.B. Wong, J. Phys. Chem. A 109 (2005) 8035.
[19] T. Clark, M. Hennemann, J.S. Murray, P. Politzer, J. Mol. Model. 13 (2007) 291.
[20] P. Politzer, P. Lane, M.C. Concha, Y.G. Ma, J.S. Murray, J. Mol. Model. 13 (2007) 305.
[21] J.P.M. Lommerse, A.J. Stone, R. Taylor, F.H. Allen, J. Am. Chem. Soc. 118 (1996) 3108.
[22] R.S. Mulliken, J. Am. Chem. Soc. 72 (1950) 600.
[23] K.E. Riley, P. Hobza, J. Chem. Theory Comput. 4 (2008) 232.
[24] M. Göbel1, B.H. Tchitchanov, J.S. Murray, P. Politzer, T.M. Klapötke1, Nat. Chem. 1 (2009) 229.
[25] W. Wang, N.B. Wong, W. Zheng, A. Tian, J. Phys. Chem. A 108 (2004) 1799.
[26] W. Wang, P. Hobza, J. Phys. Chem. A 112 (2008) 4114.
[27] W. Wang, Y. Zhang, B. Ji, J. Phys. Chem. A 114 (2010) 7257.
[28] E. D'Oria, J.J. Novoa, J. Phys. Chem. A 115 (2011) 13114.
[29] Y. Zhao, D.G. Truhlar, Acc. Chem. Res. 41 (2008) 157.
[30] Y. Zhao, D.G. Truhlar, J. Chem. Theory Comput. 2 (2006) 1009.
[31] W. Wang, Y. Zhang, B. Ji, A. Tian, J. Chem. Phys. 134 (2011) 224303.
[32] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553.
[33] M.J. Frisch et al., GAUSSIAN 09, Revision B.01, GAUSSIAN, Inc., Wallingford CT, 2009.
[34] A.E. Reed, L.A. Curitss, F. Weinhold, Chem. Rev. 88 (1988) 899.
[35] J.A. Dean (Ed.), Lange's Handbook of Chemistry (ebook), 15th Edn., McGraw-Hill, New York, 1999.
[36] F.H. Allen, Acta Crystallogr., Sect. B 58 (2002) 380.
[37] F.H. Allen, W.D.S. Motherwell, Acta Crystallogr., Sect. B 58 (2002) 407.
[38] R. Minkwitz, S. Reinemann, O. Blecher, H. Hartl, I. Brüdgam, Inorg. Chem. 38 (1999) 844.
[39] W. Wang, J. Phys. Chem. A 115 (2011) 9294.