Computational and Theoretical Chemistry 998 (2012) 164–172

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

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

On the strength of the halogen bonds: Mutual penetration, atomic quadrupole moment and Laplacian distribution of the charge density analyses

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ARTICLE INFO

Article history:
Received 23 May 2012
Received in revised form 13 July 2012
Accepted 16 July 2012
Available online 9 August 2012

Keywords:
Charge density
Laplacian
VSCC
Halogen bonds
Atomic quadrupole moment

ABSTRACT

Analyses of the atomic quadrupole moment and Laplacian distribution of the charge density were employed in the description of the strength of halogen bonds between ammonia as Lewis base and Lewis acids, D—X (with X = F, Cl, Br, I and D = —H, —CN, —F as halogen donor group). The geometries of all the complexes were fully optimized using the Møller–Plesset second-order perturbation theory with the 6-311++G(2d, 2p) basis set. For iodine atoms, an effective core potential (ECP) was used. Mutual penetration of electron charge densities, charge transference between Lewis base and Lewis acid, atomic dipole moment on nitrogen atom and change of atomic quadrupole moment on the halogen atom, were considered in this study. A significant charge density transference from the Lewis base to the Lewis acid is observed and the relation between the strength of the halogen bond and the amount of charge density transferred is explored. In addition, the analysis of the dipole moment at nitrogen atom in these complexes reflects the electronic rearrangement produced by the formation of the halogen bond and its strength. Moreover, we studied where the transferred electron charge is. We found that the Laplacian distribution and the atomic quadrupole moment on the halogen atom show that the electron density is not increased in the direction of the X···N bond, but it increases in the orthogonal direction to the bond forming (X···N). Finally, this work shows the important answers that the AIM analysis provides on the characteristics of the halogen bonds.

1. Introduction

Halogen bonds (XBs) are primarily stabilizing electrostatic interactions between a polarizable halogen and an electron-rich Lewis base such as oxygen, nitrogen or sulfur atoms. In the XBs a halogen atom is shared between an atom, a group or a molecule that "donates" the halogen and another one that "accepts" it. In other words, a halogen atom X is shared among a donor D and an acceptor A. In halogen bonding, (like hydrogen bonding) the donor tends to be electron-withdrawing with high electronegativity [1]. It is not surprising that hydrogen (with partial positive charges) interacts attractively with electronegative atoms (such as N, O, S, F and Cl) but why halogen atoms (with partial negative charges) show a behavior similar to hydrogen atoms and can be attracted by other atoms with available lone pair. The explanation is simple: the halogen atoms are electron rich and the electron withdrawing group, bonded to them (D—X), produces an asymmetrical distribution of the halogen electrons and creates an electropositive region at the crown of the atom, sometimes referred to as a "σ-hole" [2–5a,b] and more recently as "positive σ-hole" [6]. This positive σ-hole acts as a Lewis acid to interact electrostatically with a Lewis base. These interactions, which are shorter than the sum of the atoms' van der Waals radii but longer than covalent bonds, are now known as XBs to emphasize their similarity to the more well-known hydrogen bonds (HBs). Moreover, the electronic structure of the halogen atom is quite different from that of the hydrogen atom. There must be some difference in the properties between the HBs and XBs. For example, the greater directionality of the XBs relative to the HBs can be understood by the analysis of the electron distribution using the quantum theory of atoms in molecules (QTAIMs) theory [7a–c]. From the topological analysis of the Laplacian distribution, ours previous results show that the halogen-bonded complexes result from the interaction between the charge density provided by the lone pair of the donor atom of Lewis base (N, O, and S atoms or π-electron in aromatic halogen bonds (aXBs)) and the charge density depletion localized at the outermost portion of the X halogen atom centered on the D—X axis bonds (similar to the σ-hole in electrostatic potential) [8,9]. Such charge depletion on the X atom is due to electron density extraction produced on it by the D group. This generates a decrease of the charge density in the front part of the X atom, and this asymmetrical electron distribution increases with the capacity of deformation of the electron charge density on the X atom. In other

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http://dx.doi.org/10.1016/j.comptc.2012.07.019

words it increases with their polarizability. Also, from the theoretical and experimental electron charge density distribution, several studies point out the similarity between XBs and HBs as a lump-hole interaction [10].

The QTAIM and Natural Bond Orbital (NBO) analyses have been successfully applied in characterizing hydrogen bonds, halogen bonds [11–13] and chalcogen bonds [14] of different strengths in a wide variety of molecular complexes. Halogen···anion interactions [13] and halogen···cation interactions have not received as much attention as neutral halogen bonds. Such interactions, termed as charge-assisted halogen bonds, are indeed of vital importance in crystal engineering. The great potential of XBs interaction involving halogens as electron acceptors, in the design of new and high-value functional materials is now emerging clearly [15].

It is generally well accepted that the strength and effectiveness of halogen atoms (chlorine and also fluorine) in XBs formation depend on the nature of the halogen and of the halogen donor. As it is well known the halogen electronegativities increase and their polarizabilities decrease when going from iodine to fluorine. Then, if the halogen is bonded to an electronegative moiety, it is more likely to form stronger halogen bonds. Many works [2,16–20] have reported that the XBs are stronger than HBs; for example, we found that the XBs formed with ammonia and sulfide base are stronger than the HBs formed with these bases [9].

In addition, Grabowski [21] has studied different types of non-covalent interactions such as, halogen bond, hydrogen bond, and dihalogen bond in complexes of F_3CCl wherein the Cl—C bond can act as Lewis acid and as Lewis base. It was found that the change of s-character of the C hybrid orbital is connected with the strength of interaction, (the increase if C—Cl acts as the Lewis acid and the decrease if it acts as the Lewis base). Recently, similar dependencies between the s-parameter and the strength of interaction have also been found for hydrogen bond systems [22].

Between the halogen bonded complexes the case of fluorine is particularly interesting. It has been long pointed out that, the fluorine atom (the most compact and least polarizable atom) has no or little possibility to form XBs. Moreover, a recent work based on the Laplacian of the electron density and the topology of the valence shell charge concentration (VSCC) of the halogen atom was carried out by Eskandari and Zariny [10]. These authors reported that the fluorine atom, unlike the chlorine and bromine ones, is not able to form a XB because the "hole" is missing in its valence shell charge concentration. However, as it has been strongly established by Politzer et al. [6] and taking in consideration two very recent works of Metrangolo et al. (wherein computational and crystallographic evidence of XBs formed by fluorine atom was shown) the fluorine atom can certainly function as a XB donor and form complexes with lone-pair-containing neutral atoms and anions [23,24]. According to this information provided through molecular electrostatic potential and in disagreement with the requirement of the existence of the "hole" on the VSCC of halogen atom as a necessary condition in the formation of XBs, we believe that the inspection of the Laplacian topology can provide a good description of the XBs in halogen bonded complexes.

With this in mind, we have chosen ammonia as Lewis base and different Lewis acids, to examine firstly, how the electronegativity difference ($\Delta\chi_{D-X}$) (between the halogen donor group and the halogen atom) affects the capacity of D—X Lewis acid to form halogen bonded complexes and subsequently how this affects the strength of the halogen bonds. Secondly, we would like to know if a relationship between the Laplacian topology in the VSCC at halogen atom and the strength of the XBs can be established; and thirdly, where the electron charge transferred from Lewis base is going to.

2. Methods and calculation details

For this study, halogen bonds formed between ammonia as Lewis base and D—X as Lewis acids, (with X = F, Cl, Br, I; and with D = —H, —CN, —F as halogen donor group) were selected. The geometries of all complexes were fully optimized using the Møller–Plesset second-order perturbation theory [25] with the 6-311++G(2d, 2p) basis set. For iodine atoms, an effective core potential (ECP) was used [26]. Geometrical variables were optimized using the Berny's analytical gradient method [27]. All stationary points were characterized as minimal energetic by calculating the Hessian matrix. The basis set superposition error (BSSE) was taken into account using the counterpoise method proposed by Boys and Bernardi [28]. The Natural Bond Orbital analysis was performed with the NBO 3.1 program [29], as implemented in the Gaussian 03. All these calculations were carried out using the Gaussian 03 suite of programs [30]. The calculations of local topological properties of the electron charge density at the critical points and the integrated atomic properties on the atomic basin, as well as the display of the molecular graphs were performed with the AIM2000 [31] and AIMAll [32] software, with the electron density obtained at B3LYP level [33,34] with the 6-311G(d, p) basis set.

3. Results

3.1. Geometrical and energetic parameters

In this work, all the optimized complexes have shown a C_{3v} symmetry wherein the D—X···N bond angle is near to 180°. Table 1 reports the selected structural and topological parameters in the halogen bonding complexes. The first properties reported in this table are: d(X···N) halogen bond distance and the (r(X) + r(N)) van der Waals radii sum; and the second ones are the local topological properties calculated at D—X···NH_3 bond critical points (BCPs), these are the electron density $\rho(\mathbf{r}_b)$, the Laplacian of the electron density $\nabla^2\rho(\mathbf{r}_b)$, and the total electronic energy density $H(\mathbf{r}_b)$. The binding energy corrected ($-\Delta E_{BSSE}$) by basis set superposition error (BSSE) is also given in Table 1.

As it can be seen in Table 1 through the binding energy analysis, the studied complexes display a significant range of strength from −0.65 (in H—Cl···NH_3 complex) to −15.78 kcal/mol, (in F—I···NH_3 complex) indicating that the halogen bonding interactions studied here are comparable in strength to the well-documented hydrogen bonding interactions [35]. These can be considered: weak, moderate and strong depending on the bridged halogen atom and more significantly on all the rest of the halogen donor molecule. In other words, fluorine is always weakly bonded to ammonia but the XB strength forming with Cl, Br, and I halogen atoms show a broad variation depending on the environment in which the halogen is covalently bonded. For example, the H—X···NH_3 (with X = Cl, Br, I) complexes are weak halogen bonds, $\Delta E_{BSSE} < \sim 4$ kcal/mol; NC—X···NH_3 are moderate halogen bonds, and $\sim 4 < \Delta E_{BSSE} < 10$ kcal/mol and F—X···NH_3 can be considered strong halogen bonds with $\Delta E_{BSSE} > 10$ kcal/mol. The results from Table 1 show that the intermolecular distances are lower than the van der Waals radii sum, with the exception of the H—Cl···NH_3 complex, wherein the d(Cl···N) is slightly larger (by 0.01 Å). It is observed, in all the rest of the complexes, that the interpenetration between the electron cloud of the halogen atom and that of the nitrogen atom is significant. Likewise, the results reported by Amezaga et al. have demonstrated that the distance of penetration electronic densities reaches the highest values in complexes formed with ammonia [9]. The results from Table 1 show that the interaction energy of F—Cl···NH_3 is 2.66 times greater than in NC—Cl···NH_3 complex, while the interaction energy of this one, is 2.32 times greater than