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Halogen bond, hydrogen bond and N···C interaction – On interrelation among these three noncovalent interactions

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ABSTRACT

The analysis of interrelation among halogen bond, hydrogen bond and weak N···C interaction in the $(CH_3X)(HNC)(HCN)$ complexes (X = Cl, Br) was performed on the basis of MP2 calculations. The model system was chosen for the complexes in such a way that all three interactions stabilize the complexes consisting of three molecular fragments. Both two-body additive contributions and three-body nonadditive contributions to the total interaction energy are discussed. Additionally, interaction energy decomposition was performed with the use of SAPT, such that both two- and three-body contributions were also estimated. QTAIM was used for topological analysis of electron density. In the case of investigated complexes both hydrogen bond and N···C interaction predominate over halogen bond. The SAPT results indicate that the electrostatic contribution to interaction energy dominates for the hydrogen bond and the N···C interaction, while the dispersion component is mostly responsible for the halogen bonding, which is weakest of all. The QTAIM analysis reveals that the noticeable transfer of electron charge occurs only between the molecular fragments forming the hydrogen bond. Finally, we establish the influence of CP-corrected optimization and MP2 variant on the geometries and interaction energies of the complexes.

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1. Introduction

Since last a few years the halogen bond (X-bond) became one of the most thoroughly investigated noncovalent interaction [1,2]. This is due to the fact that this interaction is responsible for several physical and chemical properties exhibited by various molecular species [3–14]. Although the mechanism of formation of X-bond seems to be well recognized, still some discrepancies regarding its origin can be noticed in the literature. In general it has been thoroughly accepted that the anisotropy of charge distribution of halogen atom is the property being responsible for X-bond formation [1,15–24]. In the consequence of that anisotropy the partial positive charge occurs at the extension of the bond between the halogen and the adjacent atom. Since this positive charge can interact with a center possessing local negative charge concentration (lone pairs, π-electrons, etc.), it has been postulated that the X-bond is an electrostatically driven interaction [1]. There are, however, studies which show that purely electrostatic nature of this interaction can be questionable and that partially covalent character resulting from e.g. charge transfer, orbital overlapping, induction, etc. can be at least equally important in the case of X-bonding [15,25–28]. Therefore, X-bond is often considered as Lewis acid–Lewis base interaction in which molecular fragment with the halogen atom acts as Lewis acid, that is, the electron acceptor. Although the final agreement about the X-bond nature has not been reached yet, undoubtedly the anisotropy of charge distribution is always considered as this basic property of the halogen atom, which lays directly in the foundation of the mechanism of X-bond formation. The term "sigma-hole" is also used in the context of X-bond [29], since the region of partial positive charge (the "hole") is placed at the extension of the sigma bond between halogen atom and the other atom (usually carbon) bonded to it. The classic X-bond is characteristic of these species in which halogen atom is bonded to carbon atom, preferably of sp^3 type [1]. However, this is not any particular restriction and X-bonds with contribution of halogen atom linked to e.g. aromatic carbon were also observed [30]. It is also important to mention that X-bond usually can be observed for heavier halogen atoms, with the strength increasing with the size of the halogen. X-bonds with contribution of fluorine atom acting as Lewis acid are rather uncommon, if they exist at all [28].

The halogen atom possesses lone pairs, and as such it may also act as a Lewis base. Recently one of us had shown that halogen atom may act not only as Lewis acid, but may reflect the dual character, being Lewis acid in the direction opposite to the R–X bond and simultaneously the Lewis base in direction perpendicular to that bond, and that these properties of halogen atom can be explained with the spatial distribution of HOMO and LUMO orbitals [26]. More recently Grabowski [31] explained the nature of

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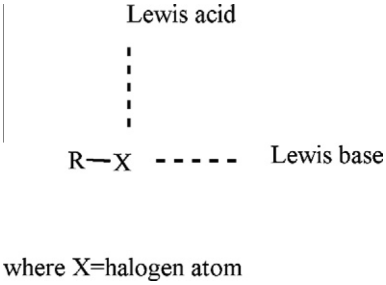

Scheme 1. Spatial arrangement of interacting fragments in Lewis acid/base complexes of halogen atom.

interactions between the halogen atom and several different molecules acting as Lewis bases or Lewis acids using the 'Bent's rule'. The obvious consequence of mentioned studies is the analysis of a system in which the halogen atom plays the role of both Lewis acid and Lewis base simultaneously. The interaction between the halogen atom and the Lewis acid would be the hydrogen bond (H-bond), whereas the X-bond would correspond to halogen atom–Lewis base interaction. One would expect that in such situation the Lewis base and the Lewis acid additionally reinforce anisotropy of the charge distribution on halogen atom. Therefore, the cooperativity between H-bond and X-bond can be expected in systems shown in Scheme 1.

Recently Zhou et al. [32] and earlier McDowell [33] performed analysis of related systems in which the halogen atom in halogen molecule acts as Lewis acid and Lewis base simultaneously. However, the halogen atom in halogen molecule is not the interacting center being typical for classical X-bond. As it was mentioned, the X-bond is considered classical rather when the halogen atom is covalently bonded to the carbon atom, preferably of sp^3 type, since for this type "organic" halogens the sigma hole most effectively interacts with Lewis base center (or in other words the anisotropy of halogen atoms is most significant) [1]. Therefore, in the present work we decided to take a closer look on the ternary molecular complexes from Scheme 1, performing quantum-chemical calculations for a representative model. In the first part of our paper we focus our attention on interrelation among different types of interactions present in our model systems. We build discussion on results obtained by the use of supermolecular (SM) approach [34] and by calculations performed within the framework of Symmetry-Adapted Perturbation Theory (SAPT). The latter approach allows us to decompose the interaction energies of the investigated complexes into a few physically meaningful components. In the second part of our manuscript we discuss some technical issues associated with the computational approaches and methods applied in the first part.

2. Computational details

2.1. The choice of the model

Our aim was to find a model system in which the halogen atom attached to sp^3 carbon atom may play the role of Lewis base and Lewis acid simultaneously. Thus, it was necessary to find additional molecules which would be able to interact with CH_3X (**1**), where X is halogen, through the H-bond and the X-bond, respectively. We wanted to make a choice such that the possibility of formation of any other interactions within our system would be minimized. For this reason we immediately excluded ammonium, water, and HF molecules since we knew from earlier related studies that these systems have large possibilities of formation of additional contacts [32]. Therefore, we chose hydrogen isocyanide HNC (**2**) and isoelectronic hydrogen cyanide HCN (**3**). In this way we considered a complex as this shown in Fig. 1 as our best choice, which allowed us to expect the presence of classic X-bond of N···X type, and classic H-bond of N–H···X type. However, after the preliminary studies it turned out that an extra interaction between **2** and **3** also appears (see Fig. 1). Since we found this additional interaction as important and interesting as H- and X-bonding, we decided to keep this choice of model system in our further analysis. Calculations were performed for the $(CH_3X)(HNC)(HCN)$ complexes (further denoted by **1**···**2**···**3**) with X = Cl, Br such that the influence of halogen atom on complexation was also taken into account. It is common to refer to such complexes as trimers, even though their individual elements (i.e., monomers) do not have to be the same. For clarity, the trimers with X = Cl and X = Br will be called Cl-complex and Br-complex, respectively. The spatial arrangement of monomers in the trimers is shown in Fig. 1.

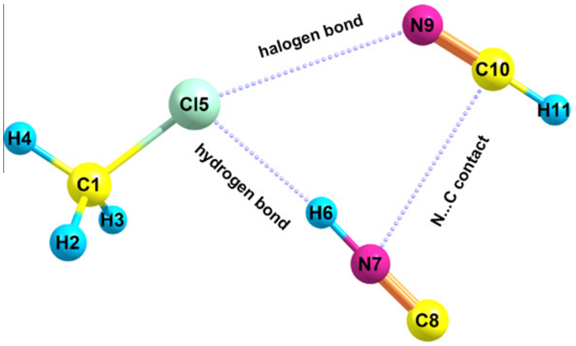

Fig. 1. Spatial arrangement of interacting fragments (monomers) in complexes (trimers). The Cl-complex is shown as an example. In the case of the Br-complex the spatial arrangement was practically the same.

2.2. Geometry optimizations

Geometry optimizations were performed using the MP2 method [35] in the resolution of identity (RI) [36,37] and conventional [38] variants. RI-MP2 was combined with the frozen core (FC) approximation, whereas the conventional MP2 used both the FC approximation and the (full) inclusion of core orbitals in the correlation treatment. The resulting three MP2-based methods differ in computational cost (which increases in the order RI-MP2(FC) < MP2(FC) < MP2(full)) and our motivation for the application of these methods to the complexes with three different noncovalent interactions was to check whether the growing computational cost was accompanied by any significant changes in the predicted geometries and interaction energies. In addition, for each MP2 variant we carried out the optimizations without and with counterpoise (CP) corrections of the basis-set superposition error (BSSE). In the CP-corrected optimizations (further named as CP optimizations for short) the investigated complexes were partitioned into three fragments that corresponded to the monomers **1**, **2**, and **3**. No symmetry constraints were imposed on the geometries of the complexes in the course of optimizations. All optimizations fulfilled tight convergence criteria (the appropriate thresholds $\sim 10^{-5}$). The optimized geometries were confirmed to be true local minima with the aid of vibrational frequency analysis. The aug-cc-pVTZ basis set [39,40] was ascribed to all atoms in the complexes. Gaussian 09 [41] and TURBOMOLE [42,43] were applied for the conventional MP2 and RI-MP2 calculations, respectively. RMS values of the residual distances between corresponding atoms in the complexes were computed using HyperChem [44].

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