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The halogen···oxygen interaction in 3-halogenopropenal revisited – The *dimer model* vs. QTAIM indications

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ABSTRACT

Even though a bond path and the corresponding bond critical point were found for the intramolecular X···O (X = Cl, Br) interaction in 3-halogenopropenal, thus according to QTAIM suggesting the stabilizing nature of this interaction, it was shown that this contact is repulsive. In order to utilize the well-defined energy of the intermolecular interaction, a dimer model was used. The C–X···O=C fragment from the ZZ conformer of 3-halogenopropenal was preserved with its original geometrical arrangement. Such approach leads to the conclusion according to which the presence of a bond path and the corresponding bond critical point do not necessarily indicate a stabilizing interaction between a pair of atoms, but rather is a direct consequence of a large accumulation of the electron density between atoms. Values of QTAIM parameters characterizing both BCP of X···O and RCP remain rather unchanged if the C–X···O=C fragment with its preserved geometry is embedded in a dimer. It was also shown that atoms X and O are interacting by negative surfaces of the molecular electrostatic potential. Also the charge transfer between interacting fragments is opposite to expected.

1. Introduction

According to the Quantum Theory of Atoms in Molecules (QTAIM) of Bader [1,2] the existence of a bond path (BP) and a corresponding bond critical point (BCP) between any two atoms is a necessary and sufficient condition for the existence of the attractive interaction linking these atoms [3]. Thus the detailed analysis of the electron density distribution provides a rigorous tool for uncovering predominant interactions between atoms in molecular systems. In a decisive majority of instances this pair of topological features indeed accompany connections between atoms which are comprehended as chemical bonds by a wide community of chemists. Nevertheless, a rich collection of theoretical data [4-15] shows that such a pair of a bond path and the corresponding bond critical point can also be found between atoms that normally would not be considered to form a chemical bond in a specific molecular arrangement. The most basic example may be the H···H contact. For instance, in the case of kekulene, the unique arrangement of six hydrogen atoms inside the inner molecular cavity yields highly curved H···H bond paths forming a hexagonal ring [4]. The other elementary instances may be the flattened biphenyl [5,6], phenanthrene, and other planar benzenoid hydrocarbons possessing the phenanthrene moiety where BPs and BCPs corresponding to H···H contacts between hydrogen atoms in positions 4 and 5 are observed [6].

By no means is such an unexpected presence of a bond path limited to H···H contacts only. It has also been found for such pairs of atoms as Ng···C [8–12], O···O [4,13], N···N [4], X···X (X = halogen) [7,14,15], and X···O [14]. In the case of $C(NO_2)_3^-$ three pairs of BPs and corresponding BCPs were found [4] between oxygen atoms of the adjacent nitro groups. Calculation based on QTAIM also revealed bond paths between oxygen atoms in open conformers of enol forms of *cis*-β-diketones [13]. The intramolecular F···F bond path was found in 1,8-difluoronaphtalene and then profoundly studied by Matta et al. [15]. Bond paths indicating X···X interactions can also be found, for example, in perhalogenated cyclohexanes, dodecahedranes and fullerenes [7]. The repulsive nature of X···X interaction within all these systems was marked by computing the energy of the transhalogenation reaction and by the significant expansion of the C–C bond while hydrogens in $C_{60}H_{60}$ are replaced by fluorines and then by chlorines [7]. Similar expansion of a cage has been found in the case of He@adamantane [8] where the antibonding nature of the He···^{t}C interaction has been judged based on the negative value of the dissociation energy [8,9]. Negative value of the dissociation energy has also been announced for the He@cubane endohedral complex [11]. Atomic interaction line of the He···C type has also been found in the case of much smaller He···CH_4 system even that positive, i.e. nonbonding, interaction

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energies have been obtained for a wide range of He···C distances [8].

According to Cioslowski et al. [4–7], the presence of BP (or the so-called interaction line [1]) delineate major interactions in a molecular system which, however, do not have to be bonding. Instead, it may indicate a significant *nonbonding*, i.e. *repulsive* interaction [5–7]. Then the bond critical point corresponding to such an unexpected bond path (or interaction line) is characterized by low values of the electron density and its Laplacian. The corresponding bond paths (or attractor interaction lines) are usually considerably curved [5,6]. The repulsive nature of the H···H interaction between *ortho*-hydrogen atoms in planar biphenyl has also been shown by Poater, Solà and Bickelhaupt [16]. These Authors concluded that BP and BCP are not indicators of a stabilizing interaction [17]. Haaland et al. [8,9] have shown that the interaction between a helium atom and the adamantane cage is antibonding in spite of bond paths that link this helium atom with carbon atoms of the cage. Similar result has also been obtained for other endohedral complexes [10,11]. Based on the energy decomposition analysis [18], Cerpa et al. [12] have found that the overall interaction between the He_2 fragment and the dodecahedrane ($C_{20}H_{20}$) cage is repulsive and results from the Pauli repulsion term. They have also shown that the large value of the electron density in BCP may result from the close proximity of atoms which, however, can be forced and does not necessarily indicate a bonding interaction between them, thus a short distance between a pair of atoms does not necessarily imply the existence of a chemical bond – conclusion that is similar to that previously found by Cioslowski et al. [4–7]. Moreover, in this case, the He–He bond order is close to zero [12] as indicated by means of Wiberg Bond Index [19]. A multitude of BPs and BCPs can also be present as a consequence of a large symmetry of a system [11]. In this case, as Cerpa et al. [11] stress "it is risky to make the one-to-one analogy between a bond path and a chemical bond in the usual chemical sense of the word".

Nevertheless, it should be pointed out that the concept of BP and related BCP as a tight criterion for the existence of the bonding between the linked atoms was defended in a very convincing way by Bader and his co-workers [20–26]. Thus, a dichotomy in understanding and interpretation of the electron density topology attributed to the atomic interaction exists in minds of chemists and the consensus in the discussion probably had not been reached yet. This paper contributes to this discussion. The earlier-investigated contact between Cl and O in 3-chloropropenal is revisited. Recently the 3-chloropropenal molecule was supposed to be a system with the intramolecular halogen bond of the Cl···O type [27]. Here the nature of the Cl···O contact in 3-chloropropenal is studied by means of a dimer model – a model which allows to estimate the interaction energy directly from the supermolecular approach.

The intramolecular interaction of the Cl···O type in 3-chloropropenal and its fluoro-derivatives was studied [27] by means of a theoretical approach. Based on total energies and geometrical parameters of open and closed forms of 3-chloropropenal it was concluded that the closure of the five-membered pseudo-ring through the Cl···O contact does *not* lead to the electron density redistribution and that it has a meaningless influence on both the geometrical parameters and the energetic characteristics. Thus, if the Cl···O contact stabilizes the considered structure of 3-chloropropenal and its derivatives, this stabilization is only weak. Interestingly, the Cl···O contact was indicated by the bond path and its corresponding bond critical point. Based on this finding as well as on the value of ca. 0.01 au of the electron density in the BCP of this interaction it was then concluded that the Cl···O contact in 3-chloropropenal is a stabilizing interaction. However, it was also shown [27] that the closed form of 3-chloropropenal is *less* stable than the open form. It leads to the conclusion that the Cl···O interaction in this system is in fact repulsive if the open form is treated as a reference system [28]. This conclusion was then supported [28] by positive (thus *repulsive*) estimates of the interaction energy of the Cl···O contact obtained by means of several methods.

Because of the indefiniteness of the interaction energy of an intramolecular interaction, many different methods can be proposed. As a consequence they may, in general, lead to a wide range of estimated values [29–34]. Thus it seems advisable to obtain an estimate of the intramolecular interaction energy based on few methods. To estimate the interaction energy of the X···O (X = F, Cl, Br, I) contact in 3-halogenopropenal (**5X**) one of us had recently used [28] the open-closed method [35,36], its recently modified version termed as Method A [33,37], and the so-called isodesmic reactions [38–40]. In this article we use another one method that is aimed for the estimation of the interaction energy of the X···O (X = F, Cl, Br) contact in 3-halogenopropenal (**5X**). This method is, however, based on referring to a properly built dimer. From this reason, this method will be henceforth termed as the dimer model. Details regarding the usage of this method and the comprehensive discussion of its reliability can be found in the Results and discussion section.

It should be underlined that due to the almost parallel rather than coaxial arrangement of C–X and C=O bonds, the X···O interaction studied here will not be termed as an intramolecular halogen bond, but rather as the X···O interaction or contact. Moreover, in our opinion the intramolecular halogen bond should clearly be stabilizing and, as such, should be characterized by negative estimate of the interaction energy (by definition its negative value means the attractive, i.e. bonding character of this interaction).

2. Methodology

All calculations have been performed by means of Gaussian 03 set of codes [41] at the level of the second-order Møller–Plesset perturbation theory (MP2) [42] with aug-cc-pVTZ basis set [43,44]. For the geometry fully optimized 3-halogenopropenal (**5X**) molecules (X = F, Cl, Br) the frequency analysis has been used to verify that the optimized structures correspond to the ground state stationary points. No imaginary frequencies were found in these cases. The QTAIM based analysis of the electron density topology has been obtained by means of the AIMAll program [45]. To support our final conclusions we have also computed the molecular electrostatic potential (MEP) which was mapped on the electron density isosurface of 0.01 au. Plots have been obtained by means of Molekel 4.3 program [46,47]. Cube files generated by Gaussian 03 [41] were used for electron potential mapping.

3. Results and discussion

3.1. Structure of 3-halogenopropenal

All four conformers of 3-halogenopropenal (X = F, Cl, Br) are shown in Fig. 1. The cis-s-cis (ZZ) conformer possesses the intramolecular X···O interaction whose energy is to be estimated based on the dimer model. The influence of the presence of this interaction to the geometry of the ZZ form can be studied by means of other conformers which are treated as references. Although in the case of 3-halogenopropenal (**5X**) its EZ conformer seems to be the most reasonable reference [28], all conformers are used as references to investigate changes of geometrical parameters while the X···O contact is formed. The most important geometrical parameters are listed in Tables 1 and 2.

The formation of the X···O contact leads to the elongation of the C=C bond, while C–C and C–X bonds are shortened. The length of the C=O bond is almost unchanged upon the formation of the