



**PRESENTS A DETAILED BONDING ANALYSIS OF HALOGEN
BONDING IN VARIOUS ORIENTATIONS**

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ABSTRACT

Halogen bonding (XB), as a directional interaction between covalently bound halogen atoms (XB donor) and Lewis bases (A, XB acceptor), has been recently intensively investigated as a powerful tool in crystal engineering. After a short review on the origin and general features of halogen bonding, current developments towards (i) the elaboration of three-dimensional networks, (ii) the interaction with anionic XB acceptors, (iii) its identification in biological systems and (iv) the formation of liquid crystal phases will be described. Theoretical analyses, statistical studies and experimental electron density determinations converge to describe halogen bonding as a relatively weak structure directing tool, when compared with hydrogen bonding. However, when the halogen atom is strongly activated as in iodoperfluorinated molecules or cationic aromatic systems can halogen bonding act as an efficient and reliable structure directing tool.

Keywords: - Bonding, Halogen, Donor, Atoms, CCSD

I. INTRODUCTION

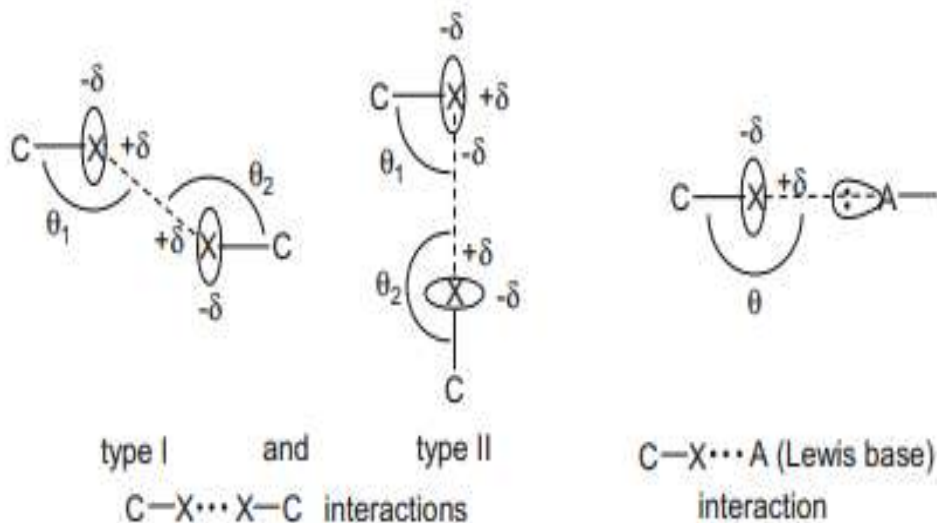
Halogen bonding describes a directional interaction between covalently bound halogen atoms (X) and Lewis bases (A). The halogen atom is typically bonded to a carbon or another halogen. Halogen atoms themselves can act as Lewis bases in halogen interactions. The strong observed preference for linear DAXA interaction parallels that known for DAHA hydrogen bonds (HB) and preferences for the geometries at the acceptor (Lewis base) are also consistent with those observed in hydrogen bonding. This analogy has led to define the halogen atom as XB donor, the Lewis base as XB acceptor even if the latter is the electron density donor in these interactions. While Hassel was one of the very first to realize that halogen atoms could form attractive interactions with Lewis bases, the following studies concentrated on adducts of dialoged molecules with Lewis bases. The role of choro–choro interactions reported by Schmidt in crystal engineering the preference for two distinct geometries, identified as type I and type II by Parthasarathy and Jeffrey

, further discussions on the geometry and nature of XB by DesiRaju are important landmarks in this domain, soon followed in the last 10 years by the extensive contributions of Resnati and Metrangolo who highlighted the potential of aliphatic and aromatic iodoperfluorocarbons such as $C_nF_{2n+1}AI$ or F_5C_6AI to act as strong XB donor molecules.

II. ORIGIN AND GENERAL FEATURES OF HALOGEN BONDING

If we restrict ourselves to carbon-bound halogen atoms, halogen bonding can be separated into two groups which were often investigated separately (i) the halogen halogen CAXX0 AC interactions in the one hand and (ii) the CAXA where A is a Lewis base in the other hand. In these systems, halogen bonds are characterized by XX0 or XA distances significantly shorter than the sum of van der Waals radii. Furthermore, for the XX interactions, two preferred geometries were identified, noted type I and type II in Scheme 1, while the CAXA interaction with Lewis bases is characterized by its strong linearity (Scheme 1). Despite some earlier controversies, there is now a general agreement to consider that halogen bonding is essentially controlled by electrostatic factors, even if dispersion forces and charge-transfer might also contribute to the observed structural motifs.

Statistical analysis of XX contacts in crystal structures have shown that an halogen atom can actually be described with two different radii rather than a single van der Waals radius, a shorter one along the CAX axis, a longer one perpendicular to it, a behavior known as “polar flattening”. Theoretical calculations and experimental high resolution X-ray determinations have shown that indeed the electron density around a bonded halogen atom is not spherical but anisotropic ally distributed, with a charge concentration in the equatorial area, and charge depletion along the polar CAX axis, the so-called r-hole (Fig. 1).



Scheme 1. Geometrical preferences (i) for the halogen interactions: type I: h1

h2; type II: h1

90 involving the XB acceptor, h2

180 involving the XB donor; (ii) for the CAXA interaction where A is a Lewis base and h

180.

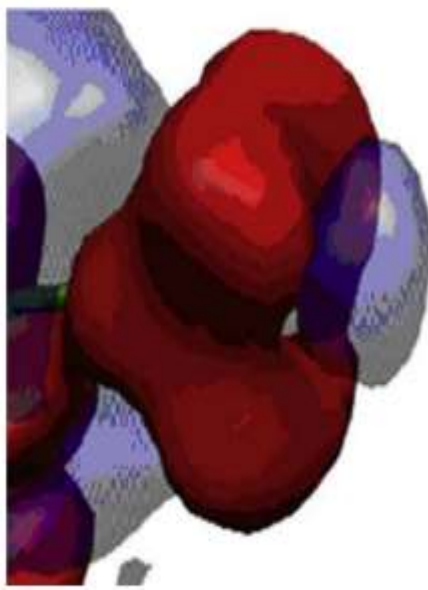


Fig. 1. Electron-deficient (+d, blue) and rich (d, red) regions observed around Clatoms in chloranil C6O2Cl4, as deduced from an experimental high resolution X-ray crystallography investigation [18] (Courtesy of Pr. E. Espinosa, Nancy, France.). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

III. MATERIALSANDMETHODS

The starting geometries of the weakly bonded complexes were built by using the AmsterdamModelling Suite–Graphical User Interface (AMS-GUI). The aromatic molecule (furan/thiophene/selenophene) was complexed with a small molecule with sp², and sp³ hybridization (C₂F₃X or CF₃X, with X = Cl, Br, I), which were placed in a parallel and perpendicular orientation, Figure 1. This procedure rendered 36 different geometries..

Geometry optimizations were performed with the PBE0 functional (following the work of), together with density-dependent dispersion corrections (dDsC) [88], and using thuds, TZ2P, and QZ4P basis sets. Scalar relativistic effects were taken into consideration by using the ZORA formalism. Frequency calculations were performed at the same level of theory for all basis sets to confirm that all stationary points are minima on the PES (see SI for a list of all frequencies for all molecules obtained with the QZ4P basis set). At the optimized geometries, the interaction energies were further analyzed by using the energy decomposition analysis (EDA). These calculations were performed with the AMS-2022 suite. Single-point energy calculations were also performed with the CCSD(T) DLPNO method, with the ORCA-5.070 package, with extrapolation to the complete basis set limit by using the def2-TZVP and def2-QZVP basis sets on the PBE0-dDsC/QZ4P optimized geometries. The aromaticity of the weakly bonded complexes was studied by using the magnetic criterion, and the magnetically induced current density was calculated by using Games-UK and SYSMO by using the PBE0 functional, def2-TZVP basis set, and CTOCD-DZ method. Time-dependent DFT calculations were performed with AMS (PBE0-dDsC/QZ4P) to explore the excited state properties. Spin-orbit coupling was taken into account by using the perturbational approach.

IV. RESULT AND DISCUSSION

Interaction Energies at Different Levels of Theory

The interaction energies obtained with different basis sets, for the complexes in the parallel orientation, are shown in Figure 2. The interaction energies (without zero-point vibrational energy correction) change significantly with the increase of the basis set size, with differences ranging between 0.1 to 13.6 kJ/mol (Figure 2). It shows, as expected, the importance of the use of a large basis set for weakly bonded complexes. Note that for $\text{C}_2\text{F}_3\text{Cl} \cdot \cdot \text{selenophene}$ in parallel orientation, hardly any interaction is found with all three basis sets. However, the differences in the interaction energies obtained by using the TZ2P and QZ4P basis sets are considerably smaller and range only from 0 to 3.9 kJ/mol; this indicates that the interaction energy is close to convergence with a TZ2P basis set, showing that the QZ4P basis therefore is certainly sufficiently large enough.

For the perpendicular oriented complexes, the same trend is observed (Figure 3). The interaction energies calculated with the DZP basis set differ at most 10.2 kJ/mol and at least 6.5 kJ/mol. The differences between the interaction energies evaluated by using the TZ2P and QZ4P basis sets decrease again. Here, the largest difference is 2.1 kJ/mol and the minimum difference calculated is 0 kJ/mol (supplementary information). Taking into account the small differences between the interaction energies with a TZ2P and QZ4P basis set, we can conclude that the QZ4P basis set is of sufficient quality. Hence, this basis set will be used for the EDA calculations.

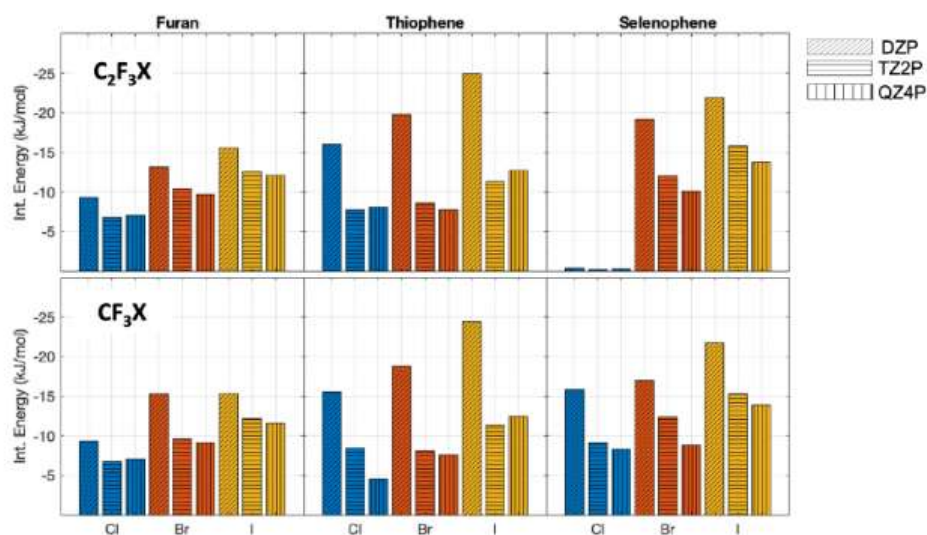


Figure 2. PBE0-dDsC We changed it interaction energies (without zero-point vibrational energy correction) with different basis sets for the complexes oriented in parallel. The different halogens are depicted with the following colormap: chlorine blue, bromine red, and iodine yellow. The DZP basis set is represented with slanted lines, the TZ2P with horizontal lines, and QZ4P with vertical lines

Although the DFT results are robust with basis set size, an important question remains to be answered: “Does the PBE0 functional with dispersion corrections give a reasonable description of these weak interacting complexes?” Thus, we have calculated the interaction energies also by using the CCSD(T)-DLPNO/CBS approach. For both the parallel oriented complexes (Table 1) and the perpendicular oriented complexes (Table 2), the differences between the CCSD(T) interaction energies and the DFT ones are largest for the iodine halogen bonds but do not vary more than 5 kJ/mol. Hence, PBE0-dDsC/QZ4P is suitable to describe the weak bonding interactions in these complexes and captures most of the relevant physics.

V. CONCLUSION

The halogen bond complexes $CF_3X \cdots Y$ and $C_2F_3X \cdots Y$, with $Y = \text{furan, thiophene, selenophene}$ and $X = \text{Cl, Br, I}$, have been studied by using DFT and CCSD (T). It turns out that the PBE0-dDsC/QZ4P gives an adequate description of the interaction energies in these complexes, compared to CCSD (T) and experimental results. The energy decomposition analysis shows that all complexes are significantly stabilized by electrostatic, orbital, and dispersion interactions: not one factor dominates the interaction energy. In general, the interaction between the halogen atom and the π -bonds is stronger than with the lone pairs: the interaction is larger in the perpendicular orientation. The strength of the interaction follows the trend $\text{Cl} < \text{Br} < \text{I}$; the chalcogenide in the aromatic ring nor the hybridization plays a decisive role. Upon halogen bond formation, the aromaticity of the five-membered ring is unaffected: the π -ring current remains

equally strong and diatropic in the complex as it is for the free aromatic ring. However, the photophysical properties of the complex are affected.

Table 1. Interaction energies (kJ/mol) for the parallel oriented complexes calculated with PBE0-dDsC/QZ4P and CCSD(T)-DLPNO/CBS.

		Furan		Thiophene		Selenophene	
		CCSD(T) CBS	DFT QZ4P	CCSD(T) CBS	DFT QZ4P	CCSD(T) CBS	DFT QZ4P
C ₂ F ₃ X	Cl	-7.2	-7.0	-9.1	-8.1	-0.5	-0.3
	Br	-9.4	-9.7	-8.5	-7.7	-10.8	-10.1
	I	-13.9	-12.1	-16.2	-12.7	-17.2	-13.8
CF ₃ X	Cl	-7.0	-7.1	-5.1	-4.6	-9.6	-8.3
	Br	-9.1	-9.1	-8.0	-7.6	-8.7	-8.8
	I	-13.3	-11.5	-15.7	-12.4	-16.2	-13.9

Table 2. Interaction energies (kJ/mol) for the perpendicular oriented complexes calculated with PBE0-dDsC/QZ4P and CCSD(T)-DLPNO/CBS.

		Furan		Thiophene		Selenophene	
		CCSD(T) CBS	DFT QZ4P	CCSD(T) CBS	DFT QZ4P	CCSD(T) CBS	DFT QZ4P
C ₂ F ₃ X	Cl	-7.7	-7.2	-10.1	-8.9	-10.0	-8.7
	Br	-10.4	-10.1	-10.8	-9.9	-12.3	-11.5
	I	-15.0	-13.6	-17.7	-14.4	-17.8	-15.1
CF ₃ X	Cl	-7.8	-7.7	-10.0	-9.0	-9.7	-8.8
	Br	-11.0	-10.9	-11.8	-10.9	-11.3	-10.9
	I	-14.5	-13.4	-16.6	-14.2	-17.5	-14.7

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