

The Importance of Halogen Bonding: A Tutorial

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Abstract

Halogen atoms in a molecule are traditionally considered as electron donors, since they have unshared electrons. Normally when they are bonded, there are three lone pair electrons. These lone pairs can function as Lewis bases. However, when they are bound to electron withdrawing groups, they can act as Lewis acids. Since the situation is similar hydrogen bonding (HB), this type of interaction is named as halogen bonding (XB). This mainly comes from the uneven distribution of electron density around the halogen atoms. Since the electron density around halogen atom opposite to σ -bond is depleted, its electropositive region is called σ -hole. This σ -hole can attract halogen bond acceptors, requiring more stringent directionality compared to HB. Since this interaction mainly comes from electrostatic origin, the geometry tends to be linear. Since the XB energy is comparable to corresponding HB. Still in its infancy, XB shows a broad range of applicability, with potentially more useful properties, compared to corresponding HB.

Key words : Hydrogen Bonding, Halogen Bonding, σ -Hole, Electronegativity, Polarizability

1. Introduction

“There is nothing new under the sun but there are lots of old things we don't know.” This old saying can describe the current status of halogen bonding. Its existence was first proved by the existence of bonding between bromine and 1,4-dioxane molecule. Here, Br-Br bond line joins the oxygen atoms of two dioxane ring^[1]. A decade later, ammonia and iodine adducts were reported^[2]. With the help of new supersonic jet technology, a little striking structure as shown in Fig. 1 was reported^[3]. Stewart et al found that the equilibrium structure of HF --- ClF was not hydrogen bonded. Since there was no terminology such as halogen bonding, they speculated this interaction arising from van der Waals force.^[4-8] One thing that can be concluded is the striking similarity between hydrogen bonding. Here, more electropositive chlorine atom as like proton as in hydrogen bonding. Now it is termed as halogen bonding, in an analogy of hydrogen bonding. In this type of bonding, halogen atom acts as a Lewis acid toward halogen bonding acceptors.

2. Result and Discussion

2.1. σ -Hole Concept

In Fig. 2, the most widely accepted theory on halogen bonding is described. The central concept of halogen bonding is actually σ -hole on terminal halogen. Here, in R—X, R represents any functional group, and X denotes any halogen atom. This is actually a simplified version of dotted structure to describe octet rule. When you look at this dotted structure, since there are many electrons are available around X, it is difficult to conceive why the two halogen atoms behave as Lewis acids as shown in Fig. 1. This puzzle can be resolved when we closely look at the orbital structures. By convention, the σ -bond which connects R and X is assigned as z-axis. For a halogen atom, there are two s electrons, four p_x and p_y electrons which are perpendicular to the σ -bond, and one p_z electron which lies along the extension of σ -bond. Since p_x and p_y orbitals are equivalent in this scheme, they form a ring like hybrid orbital. But how

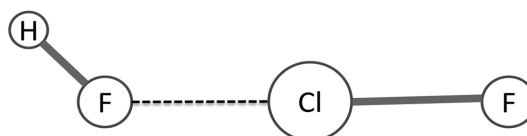


Fig. 1. Equilibrium geometry of HF --- ClF complex.

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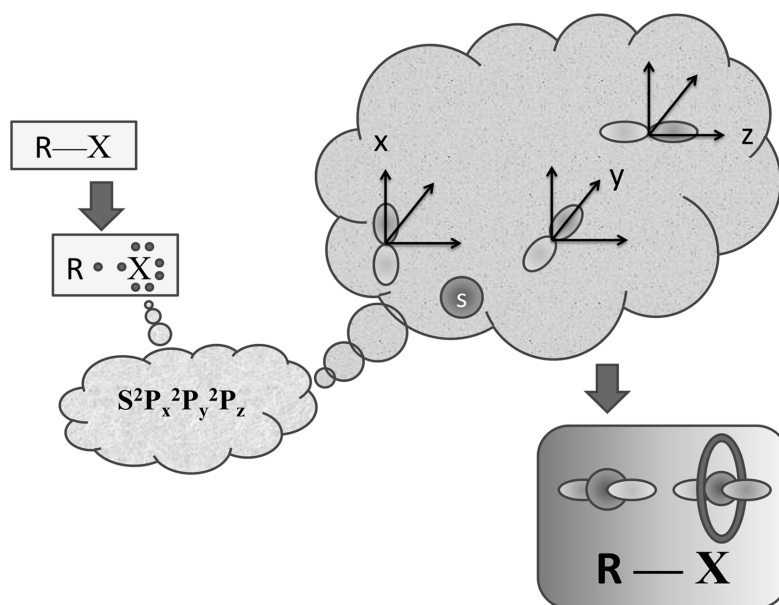


Fig. 2. Current view of σ -hole which is responsible for halogen bonding.

a halogen atom acts as a Lewis acid as shown in Fig. 1? The answer lies in the nature of R. When R group is electron withdrawing, it will attract the electrons of halogen atom mainly through p_z orbital. Since the electrons are attracted toward R group, the electron density of (the p_z orbital) at the opposite site of σ -bond, could be depleted. This electro-positive spot (σ -hole) is responsible for halogen bonding as shown in Fig. 1. This electropositive character of σ -hole is mainly governed by two factors. The electron withdrawing power of R and the electronegativity and polarizability of X (halogen). Therefore, the order of halogen bonding strength is $I > Br > Cl > F$.

2.2. Structure of Halogen Bonding Compared with Hydrogen Bonding

By the same argument, hydrogen in hydrogen bond-

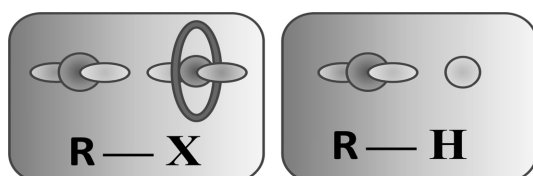


Fig. 3. Orbital interaction difference of halogen bonding (left) and hydrogen bonding(right).

ing, the electron density depletion can occur by electron withdrawing groups (R) in Fig. 3. But there is a difference. This time, the electron depletion occurs on 1s orbital of hydrogen atom. Unlike p_z orbital of halogen (X) atom, since s orbital is spherical, the electron depletion occurs more isotropically around the hydrogen atom. This results in difference in angular dependence. Since hydrogen bond lacks the electro-negative ring which exists in halogen bonding, it shows much reduced propensity for linearity^[9].

2.3. Halogen Bonding with Bromobenzene

Like the halogen bonding, the major force of hydrogen bonding comes from electrostatic effect. However van der Waals interaction, polarization, charge transfer also participate. It seems more natural to occur red shift rather than blue shift in R-H bond when hydrogen bonding occurs. Actually for the majority of cases, red shift happens^[10]. However, bond lengthening, red shift, or and more intensive IR are all reversed in blue-shifting hydrogen bonds, while energetically favorable. It is now generally accepted that this blue-shifting occurs in both hydrogen and halogen bonding, however, the rationalization is still somehow controversial. Hobza et al. suggested that in Cl_3CH -p systems, the CH blue shift mainly originates from the dispersion interaction^[11,12].

3. Conclusion

Halogen bonding shows an enormous possibility because its strong binding and its directionality. The application area includes crystal engineering^[13], supramolecular chemistry^[14], ionic liquid^[15], etc.

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