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LETTERS

Halogen Bonding in Fluoroalkylhalides: A Quantum Chemical Study of Increasing Fluorine Substitution

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We describe the results of quantum chemical calculations (DFT and MP2) on the intermolecular interactions involving ammonia and halofluoromethanes. The equilibrium C−X···N geometries are linear and the X···N distances are shorter than the sum of the van der Waals radii. The binding energies of $CF_3X\cdots NH_3$ increase from 2 to 6 kcal/mol on following the sequence X = Cl, Br, I. Also, progressive introduction of F atoms in methyliodides raises the interaction energy from 2 kcal/mol for CH_3I to 6 kcal/mol for CF_3I. Therefore, halogen bonding involving perfluorinated alkylhalides and appropriate donors can be comparable in strength to strong hydrogen bonding. This agrees with recent experimental observations, that also the former can drive the construction of supramolecular edifices overcoming the low affinity between perfluorocarbons and hydrocarbons. Calculation of the atomic charges by the Atoms in Molecules method indicates that the charge-transfer contribution to the interaction energy is much less important for the present systems than for dihalogen−ammonia complexes.

Introduction

The understanding of specific intermolecular interactions is required for a rational approach to molecular recognition and self-organization in fields as diverse as materials engineering and biomolecular sciences.[1,2] Halogen bonding involving dihalogen systems has been extensively studied experimentally[3−5] and also theoretically.[6−14] Lommerse et al.[15] demonstrated the crucial importance of the chlorine environment for the quality of the C−Cl···D (D = O, N) interaction. It has been recently shown[16−21] that halogens (specifically iodine and bromine), also when bound to aliphatic or aromatic perfluorocarbon residues, interact with appropriate electron-donating molecules giving stable bindings whose strength and specificity appear to compare favorably with hydrogen bonding. Such interactions have allowed, for example, the first resolution of a racemic perfluorocarbon dihalide by cocrystal formation with an optically active ammonium salt.[17]

In this letter we present the results of quantum chemical calculations, carried out in order to evaluate the strength and the geometry of the nitrogen−halogen intermolecular interaction of appropriate electron donors and fluoroalkylhalides. We used ammonia as a simple but representative donor, while six molecules ($CH_{3-n}F_nI$ with $n = 0-3$, CF_3Br, and CF_3Cl) were considered to investigate the effect of the electron-withdrawing fluorine atoms on the C−X···N interaction (X = I, Br, Cl). In this perspective the same linear arrangement was used for all the studied complexes (Figure 1). Accordingly we did not examine alternative approaches of NH_3, leading to nucleophilic substitution reactions typical of nonfluorinated alkyl halides.

Most of the results reported here were obtained at the density fuctional theory (DFT) level. A few second-order Møller-Plesset (MP2) calculations were carried out for comparative purposes.

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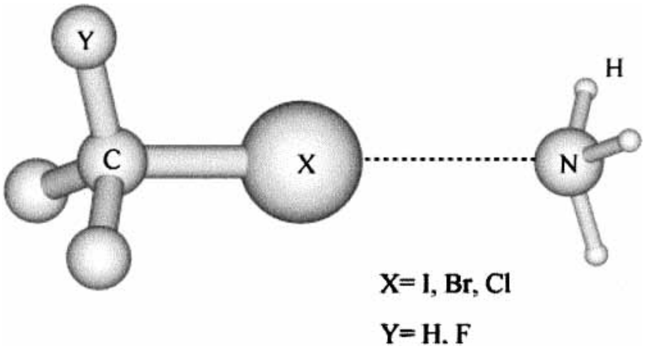

Figure 1. Schematic representation of the halogen-bonded complexes studied in this work.

Indeed, because of the lack of experimental gas-phase measurements it is important to verify the agreement between different methods in order to assess their reliability. The DFT calculations have been performed with the program deMon-KS,[22] within the linear combination of Gaussian type orbitals formalism (LCGTO) and the generalized gradient approximation (GGA). The Becke functional[23] for the exchange (*B*) and the Perdew functional[24] for correlation (*P*) have been employed. All-electron basis sets of double-ζ with polarization (DZVP) quality have been used for all atoms.[25] A grid of 64 radial and 26 angular points has been used for the evaluation of the exchange-correlation potential. The MP2 calculations have been performed with the GAMESS-US program,[26] with the internally stored Stevens-Bash-Krauss valence-only basis set[27] (equivalent to −31G) augmented with a set of polarization functions on all atoms.

Results and Discussion

The geometries of monomers and adducts have been fully optimized at both DFT (BP) and MP2 levels. Starting points were as shown in Figure 1 with deviations from collinearity up to 30°. The equilibrium C−X···N contacts are closely linear, consistent with experimental data on halogen-bonded perfluorohalides,[16−19] on ammonia···dihalogen complexes[4,5] and with the general results of searches on the Cambridge Structural Database (CSD) for C−Cl···D systems with Cl···D distances shorter than the sum of the van der Waals radii.[15] Our equilibrium geometries always correspond to a staggered conformation. We expect the rotational barriers about the C−I···N axis to be very low, of the order of 0.1 kcal/mol. This is confirmed by test calculations on the eclipsed conformation of $CF_3I{\cdots}NH_3$. An accurate evaluation of such small quantities is beyond the scope of the present paper and would indeed require removal of the basis set superposition error (BSSE: see below) not only from the interaction energies, but also from the optimized equilibrium geometries.[28]

The calculated interaction energies and equilibrium X···N and C−X distances are given in Table 1. We indicate with ΔE the interaction energy calculated as the difference between the energy of the complex (AB) and the sum of the energies of the monomers (A and B):

$$\Delta E = E_{\mathrm{CG}}^{\alpha\cup\beta}(\mathrm{AB}) - [E_{\mathrm{MG}}^{\alpha}(\mathrm{A}) + E_{\mathrm{MG}}^{\beta}(\mathrm{B})]$$

where CG and MG stand, respectively, for the complex and the monomer geometry, and α and β are the basis sets of the monomers A and B. To correct the interaction energy for the BSSE, the Boys-Bernardi counterpoise technique[29] including the fragment relaxation terms[30] has been applied. Evaluation of the BSSE-corrected energy (ΔE^{BSSE}) thus requires the determination of four additional terms:

$$\Delta E^{\mathrm{BSSE}} = \Delta E + \{E_{\mathrm{CG}}^{\alpha}(\mathrm{A}) - E_{\mathrm{CG}}^{\alpha\cup\beta}(\mathrm{A})\} + \{E_{\mathrm{CG}}^{\beta}(\mathrm{B}) - E_{\mathrm{CG}}^{\alpha\cup\beta}(\mathrm{B})\}$$

TABLE 1: Bond Distances (Å), Uncorrected ($-\Delta E$), and BSSE-Corrected ($-\Delta E^{\mathrm{BSSE}}$) Interaction Energies (kcal/mol), Calculated with DFT (BP) and MP2 Methods[a]

	C−X		X···N		$-\Delta E$		$-\Delta E^{\mathrm{BSSE}}$	
	BP	MP2	BP	MP2	BP	MP2	BP	MP2
$CH_3I{\bullet}NH_3$	2.196 (2.180)	2.151 (2.147)	3.071	3.196	2.8	3.1	2.5	2.1
$CH_2FI{\bullet}NH_3$	2.201 (2.196)		3.040		3.5		3.2	
$CHF_2I{\bullet}NH_3$	2.209 (2.202)		2.978		4.7		4.3	
$CF_3I{\bullet}NH_3$	2.210 (2.192)	2.151 (2.148)	2.882	2.948	7.1	7.3	6.4	5.8
$CF_3Br{\bullet}NH_3$	1.972 (1.961)		2.817		5.0		4.7	
$CF_3Cl{\bullet}NH_3$	1.781 (1.783)		2.900		2.6		2.3	

[a] In all systems the optimized C−X···N angle deviates less than 3° from 180°. The C−X distances in the free monomers are indicated in parentheses

Even though there are some differences between DFT and MP2 results, the overall agreement in optimized bond distances and interaction energies is satisfactory. The BSSE is less important in DFT than in MP2 calculations, so that for our systems $|\Delta E|$ is larger at MP2 level while the opposite is true for $|\Delta E^{\mathrm{BSSE}}|$. According to both methods the BSSE-corrected binding energy increases from about 2 kcal/mol in the $CH_3I{\cdots}NH_3$ complex to about 6 kcal/mol in $CF_3I{\cdots}NH_3$. With amines whose electron-donating ability is greater than ammonia the interaction energies should be even stronger. The calculated value for the $CF_3I{\cdots}NH_3$ interaction compares well with experimental data, namely, (*i*) the 5.0 ± 0.1 kcal/mol for the association of CF_3I with 2,4,6-trimethylpyridine in cyclopentane solution by temperature dependent nmr spectroscopy,[31] and (*ii*) the value of 7.4 kcal/mol[19] for the 1-iodoperfluorohexane and liquid 2,2,6,6-tetramethylpiperidine measured with an adiabatic accelerating rate calorimeter. The energy values calculated for the ammonia adducts with CF_2HI, CF_3Br and CF_3I are comparable or even larger than strong hydrogen bonding. These results are consistent with experimental evidence on halogen bonding-driven self-assembly of iodoperfluorocarbons with hydrocarbon amines[16,18,19] and with competitive experiments where cocrystal formation is shown to be driven preferentially by halogen bonding rather than by hydrogen bonding.[19] The more effective screening of the nuclear charge and the lower polarizability imply a decrease of the interaction energy on moving from iodine to bromine to chlorine. Even in the latter case an attractive interaction is however predicted, comparable to that found in calculations involving the chlorocyanoacetylene dimer, formaldehyde with chlorocyanoacetylene[15] and nitromethane with 1-chloro-2-methylacetylene.[32]

The DFT results illustrate nicely how the progressive substitution of H with F leads to shorter I···N distances and increasing interaction energies. The I···N distance in $CF_3I{\cdots}NH_3$ is moreover in very good agreement with the value of 2.84 ± 0.03 Å, found by X-ray crystallography in cocrystals of α,ω-diiodoperfluoroalkanes with different diamines.[16,18] On the other hand, a I···N distance of 2.93 Å was estimated from the microwave spectrum of $CF_3I{\cdots}N(CH_3)_3$,[33] under the assumption

TABLE 2: DFT (BP) Atomic Charges q (e) in Monomers, Calculated by the AIM Methodology

	CH_3I	CH_2FI	CHF_2I	CF_3I	CF_3Br	CF_3Cl	NH_3
q(F)		−0.606	−0.601	−0.593	−0.590	−0.591	
q(C)	−0.227	0.374	0.986	1.617	1.754	1.868	
q(X)	0.009	0.030	0.082	0.165	0.018	−0.094	
q(H)	0.073	0.102	0.136				0.337
q(N)							−1.009

TABLE 3: Charge Variation (e), $\Delta q = q^{dim} - q^{mon}$, and Overall Charge Transfered from NH_3 upon Complex Formation (Q_T)

	$\Delta q(H_C)$	Δq(F)	Δq(C)	Δq(X)	Δq(N)	$\Delta q(H_N)$	Q_T
$CH_3I \bullet NH_3$	−0.018		−0.018	0.028	−0.001	0.015	0.045
$CH_2FI \bullet NH_3$	−0.020	−0.009	−0.043	0.040	0.000	0.018	0.053
$CHF_2I \bullet NH_3$	−0.022	−0.009	−0.061	0.039	0.000	0.021	0.063
$CF_3I \bullet NH_3$		−0.011	−0.080	0.031	−0.002	0.028	0.081
$CF_3Br \bullet NH_3$		−0.008	−0.075	0.031	0.010	0.019	0.067
$CF_3Cl \bullet NH_3$		−0.006	−0.051	0.027	0.006	0.012	0.042

that the monomer geometries remain unchanged upon complex formation. The distances between halogens and nitrogen are in all cases markedly shorter than the sum of van der Waals radii, considering both the values proposed by Bondi[34] (1.70, 1.76, 1.85, and 1.98 Å for N, Cl, Br, and I) and those established by Nyburg and Faerman[35] (1.60, 1.58, 1.54, and 1.76 Å for the same atoms). The latter taking into account the fact that halogens have a shorter radius along the X−C bond vector ("polar flattening").

In all adducts, with the exception of $CF_3Cl\cdots NH_3$, the interaction with ammonia yields an elongation of the C−X bond, more pronounced in CH_3I and CF_3I. The C−F bonds are also elongated by about 0.01 Å upon formation of the adduct. These bond elongation effects are consistent with a small charge transfer involving antibonding LUMO orbitals in the acceptor molecules (see below). A reduced effect is noticed in the MP2 results, probably indicating that the charge-transfer contribution to the intermolecular interaction is less significant at this level.[12]

The atomic charges were obtained from the DFT densities using the Atoms in Molecules methodology (AIM)[36] with the AIMPAC program package.[37] Those for the monomers are given in Table 2. Table 3 illustrates their variations and the net charge transferred from NH_3, upon complex formation. The latter, indicated with Q_T in Table 3, is larger for higher halogen atomic number and is enhanced by fluorine substitution. The net charge transfer might be expected to correlate either with the HOMO−LUMO gap or with the monomer polarizabilities, or both. A precise discrimination between these criteria would require a more extensive set of calculations, including systematic variations of the donor, along with a partitioning of the overall interaction energy into electrostatic, induction, dispersion, charge transfer,... contributions. Therefore we leave it to future work.

The electron charge lost by the ammonia hydrogen atoms (H_N) parallels that gained by the carbon so that they appear as the ultimate protagonists of the charge transfer. The negative nitrogen charge is almost constant in free NH_3 and in all iodide adducts, while it slightly decreases with Br and Cl. Iodine has a positive charge which increases significantly when more fluorine atoms are present, as expected. This effect is enhanced in the complexes, this being a signature of the charge polarization induced by the interaction with the NH_3 dipole. The charge is much less positive on bromine and becomes negative on chlorine, both in free CF_3Cl and its adduct with ammonia.

Density functional theory at the GGA level probably overestimates the charge-transfer interaction, as pointed out for dihalogen•donors systems,[12] for which the differences between DFT (BP) and MP2 intemolecular interactions were found to be quite large. We have carried out BP calculations on $I_2\cdots NH_3$ with the same methodology used for our systems and found the net charge on the monomers to be 0.144 e, thus markedly higher than in $CF_3I\cdots NH_3$. The charge-transfer contribution to the C−I···N interaction is therefore far less than in the $I_2\cdots N$ case. This explains the good agreement between BP and MP2 results found in our study, in contrast with the dihalogen situation.

In summary, we have described the results of quantum chemical calculations (DFT and MP2) on the intermolecular interaction involving a representative donor (ammonia) and halofluoromethanes. The energy values and the definite geometry of the interaction promise to make halogen bonding a very effective tool in the manipulation of perfluorocarbons.

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