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The Nature of Halogen···Halogen Interactions: Are Short Halogen Contacts Due to Specific Attractive Forces or Due to Close Packing of Nonspherical Atoms?[1a]

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The nature of halogen···halogen interactions in crystals has long been a matter of interest and debate.[2] Intermolecular interactions associated with distances shorter than the sum of the van der Waals radii of contacting atoms have been variously referred to earlier[3] as "donor–acceptor" interactions, "secondary" interactions, and "charge transfer" interactions and, more recently,[4–6] as interactions between the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals (HOMO–LUMO) or "incipient electrophilic and nucleophilic attack".[4,5] In all such interactions, it has been noticed[4,5] that there is a directional preference with which contacting groups position themselves relative to each other. For example, halogen···halogen contacts[4c,7] have two preferred geometries, type I ($\theta_1 = \theta_2$) or type II ($\theta_1 = 180°$, $\theta_2 = 90°$), where θ_1 and θ_2 are the two C–Cl···Cl angles. A delimma arises since these preferred geometries may result due to either (i) specific attractive forces in certain directions[4–5,8] (i.e., increased attraction) or (ii) nonspherical shapes with polar flattening[7,9] in a close-packed crystal (i.e., decreased repulsion). In the first case, it is implied that the short and directional halogen···halogen contacts are caused by the specific attractive forces, whereas in the second case, they are due to the close packing of nonspherical atomic moieties of molecules. Computationally, both alternatives have been modeled either with special bonding terms[8] or with anisotropic atom potentials for halogen atoms.[9] While these computational methods might permit a better fit of structure to observed properties of halogenated organic crystals, they do not provide real physical insight into the nature of these interactions. In this communication, we examine whether the halogen···halogen contacts are attractive or not.

Table I.[a] Intermolecular Contacts from Halogen Atoms to Halogen, Hydrogen, and Carbon Atoms in Halogenated Hydrocarbon Crystals

	contact type	distance, Å (less than)	no of contacts	correctn factor: *P*	corrected no. of contacts
fluorohydrocarbons (45)	F···F	2.94	25	0.19	132
	F···H	2.67	43	0.17	253
	F···C	3.22	46	0.64	72
chlorohydrocarbons (108)	Cl···Cl	3.52	147	0.27	544
	Cl···H	2.96	73	0.17	429
	Cl···C	3.51	74	0.56	132
bromohydrocarbons (58)	Br···Br	3.72	24	0.13	185
	Br···H	3.06	20	0.27	74
	Br···C	3.61	18	0.61	30
iodohydrocarbons (18)	I···I	3.96	12	0.31	39
	I···H	3.18	1	0.23	13
	I···C	3.73	7	0.46	15

[a] Van der Waals radii in Å: F, 1.47, Cl, 1.76, Br, 1.86, C, 1.75, H, 1.20.

There is evidence that indicates that the primary cause of directional halogen···halogen interactions is the specific attractive forces, and the nonspherical shapes or polar flattening is the resulting effect. The gas-phase molecular beam scattering experiments by Klemperer and co-workers[10] show that $(X_2)_2$ (X is a halogen) and F–Cl···F–H form complexes. Also, the "L" shape and the stereochemistry of the cluster and the complex not only follow the molecular orbital calculations[11] but also are in perfect agreement with the directional interactions seen in the solid state.[4c] Since close packing is not involved in deciding the gas-phase stereochemistry (which, incidentally, agrees with the solid-state stereochemistry), the dilemma is resolved in the gas phase and it is clear that the primary cause for the directional preferences of halogen···halogen interactions is the attractive forces.

To resolve the dilemma in the solid state, we have employed a statistical approach. In a close-packed crystal where no directional forces are invoked, it is reasonable to assume that the number of intermolecular contacts to any given atom is nearly proportional to the exposed surface area of that atom. If, in a group of compounds, halogen···halogen contacts are observed in numbers greatly out of proportion to the average ratio of halogen to total surface area, these interactions must be attractive in nature. Conversely, if these contacts are observed in numbers that approximately conform to the ratio of halogen to total area, the structures are close-packed and the observed intermolecular geometries must be due to the ellipsoidal shapes of the halogen moieties. *Though both the increased attraction and reduced repulsion give rise to the same geometry for C–X···X–C interactions, the number of such interactions in a given class of compounds will depend on the nature of the interaction.* So the key question is, Is the number of halogen···halogen contacts greatly out of proportion to the average ratio of halogen to total surface area or not?

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The Cambridge Database[12] was used to retrieve F···F, Cl···Cl, Br···Br, and I···I contacts from the halogen-substituted hydrocarbons. Molecules containing two different halogen atoms (for example, Cl and Br) were not chosen. For instance, the 1988 database (Version 3.1; 69 691 entries) yielded 108 high-precision ($R \leq 0.075$), fully ordered, diffractometer data based structures of compounds containing only carbon, hydrogen (optional), and chlorine atoms. Intermolecular Cl···Cl, Cl···H, and Cl···C contacts less than the corresponding van der Waals limits were computed for these structures with the program GEOSTAT88. The area-based "normalization or correction" factors for calculating Cl atom contacts to Cl, H, and C were derived as the average values of the atom stoichiometries, weighted by the respective atomic areas.[13] These weights were taken as the squares of the van der Waals radii (Table I). Similarly, 45 fluoro- and 58 bromo-containing structures were retrieved and the contacts computed. Because of the paucity of iodohydrocarbon structures, all the available 18 structures were accepted irrespective of error limits, disorder, or mode of data collection.

Table I shows the results of these geometrical calculations. Since the numbers of halogen contacts to halogen, hydrogen, and carbon have been corrected for the stoichiometry and surface areas of these atom types, the numbers in the last column should be comparable within each group (F, Cl, Br, I), if the contacts in the crystal structures are primarily determined by close packing. If the number of halogen···halogen contacts are much higher than the halogen contacts to other atoms, this excess number of contacts must imply some attractive halogen···halogen interaction. A comparison of the halogen···halogen with halogen···hydrogen contacts should be especially meaningful since both halogen and hydrogen atoms are situated at the molecular extremities. Examination of Table I shows that the numbers obtained for Cl, Br, and I are indicative of two chemical trends: (1) halogen···halogen contacts are attractive in nature and (2) halogen···hydrogen contacts are of the $\delta^-\cdots\delta^+$ type. While trend 1 is weakest for Cl and strongest for I, trend 2 is most pronounced for Cl and hardly important for I. For Cl, these two tendencies together result in nearly equal numbers of Cl···Cl and Cl···H contacts while for Br, Br···Br contacts far outnumber Br···H contacts due to the greater polarizability and lesser electronegativity of Br. The I···I and I···H contacts appear to confirm and extend these trends, but the number of structures is probably not statistically significant.

Contacts from F to F, to H, and to C are distinctive. The strongly dipolar character of the F···H interaction results in a greater number of these interactions relative to F···F interactions on both absolute and corrected scales. One must conclude, therefore, that F···F interactions do not have any additional stabilizing role in close packing unlike the other halogen–halogen interactions.

These results, we believe, constitute a strong demonstration of the attractive (and anisotropic) nature of Cl···Cl, Br···Br, and I···I but not of F···F interactions in molecular crystals. If hydrocarbon molecules in a close-packed crystal could be likened to slightly sticky globs, the surfaces of their chloro, bromo, and iodo derivatives would have a much stickier localized region corresponding to the halogen atoms.

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(13) (a) A typical calculation of probability correction factors *P*(Cl), *P*(H), and *P*(C) for the compound *cis*-1,2-dichloroacenaphthene, CCLACN, $C_{12}H_8Cl_2$, is as follows:

$$P(\mathrm{Cl}) = 2(1.76)^2/\{2(1.76)^2 + 8(1.2)^2 + 12(1.75)^2\}$$

$$P(\mathrm{H}) = 8(1.20)^2/\{2(1.76)^2 + 8(1.2)^2 + 12(12.75)^2\}$$

$$P(\mathrm{C}) = 12(1.75)^2/\{2(1.76)^2 + 8(1.2)^2 + 12(1.75)^2\}$$

These probabilities are averaged over each of the four groups of compounds in Table I to give the values in the fifth column of that table. (b) The squares of the atomic radii as the correction factor may not be the best one since they do not relate in a direct way to the exposed area, and to this extent, the numbers in the sixth column in Table I should be considered only as approximate, defining a range rather than particular values.

7-Bromoniabicyclo[2.2.1]heptane: A Stable 1,4-Bridged Bicyclic Bromonium Ion[1]

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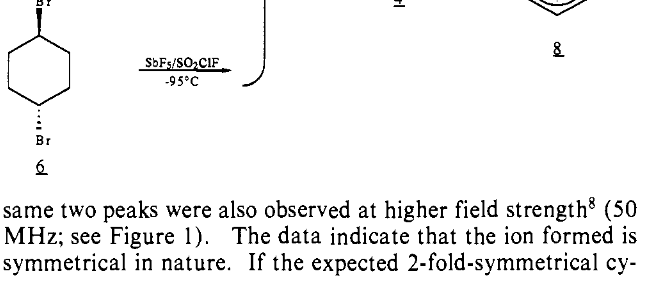
Recently we reported[2] the unusual β-fluorination of secondary cyclic and acyclic bromides in their reaction with $NO_2^+BF_4^-$ in pyridinium polyhydrogen fluoride[3] solution. The reaction in the case of bromocyclohexane, which gave *trans*-1-fluoro-2-bromocyclohexane (**1**) as the exclusive product, is in accordance with the formation of cyclohexene bromonium ion **2** as an intermediate, as shown in Scheme I. The mechanism proposed in Scheme I involving exclusive α-hydride abstraction by the nitronium ion was also supported by studies on α-deuterio-α-bromocyclohexane.[2] Although the cyclopentene bromonium ion **3** was well characterized in preceding studies under long lived stable ion conditions by ^{1}H and ^{13}C NMR spectroscopy,[4] the corresponding cyclohexane homologue **2** has never been observed. Consequently we embarked on a project for the possible preparation of **2** under long lived stable ion conditions. Our studies unexpectedly led to the preparation of a unique 1,4-bridged bicyclic bromonium ion, formed via transannular 1,4-bromine participation in the intermediate bromocyclohexyl cations.

Careful dissolution of a precooled solution of 1-fluoro-2-bromocyclohexane **1** in SO_2ClF in excess of SbF_5/SO_2ClF[5] solution at −95 °C[6] gave a pale yellow colored solution. The 20-MHz ^{13}C NMR spectrum[7] showed only two absorptions at $\delta(^{13}\mathrm{C})$ 118.7 ($J_{\mathrm{C-H}}$ = 172.1 Hz) and 37.4 ($J_{\mathrm{C-H}}$ = 135.5 Hz). Only the same two peaks were also observed at higher field strength[8] (50 MHz; see Figure 1). The data indicate that the ion formed is symmetrical in nature. If the expected 2-fold-symmetrical cy-



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(7) Spectra were obtained on a Varian Associates Model FT-80 NMR spectrometer equipped with a variable-temperature broad-band probe. Chemical shifts are referenced from an external capillary tetramethylsilane signal.

(8) Using Varian Associates Model VXR-200 NMR spectrometer equipped with a variable-temperature ^{1}H, ^{19}F broad-band probe.

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