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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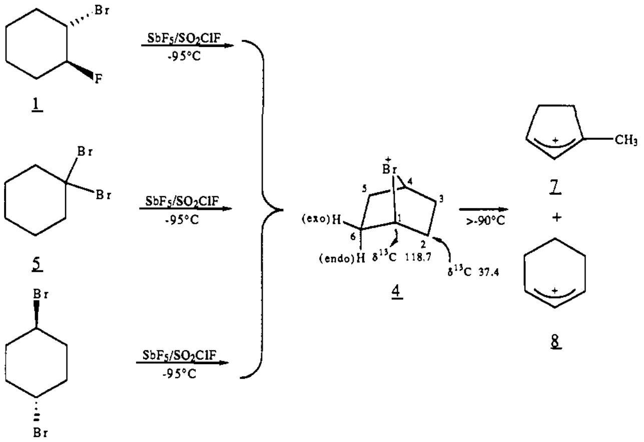
Recently we reported[2] the unusual β-fluorination of secondary cyclic and acyclic bromides in their reaction with $NO_2^+BF_4^-$ in pyridinium polyhydrogen fluoride[3] solution. The reaction in the case of bromocyclohexane, which gave *trans*-1-fluoro-2-bromocyclohexane (**1**) as the exclusive product, 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 ^1H 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 $\delta(^{13}C)$ 118.7 (J_{C-H} = 172.1 Hz) and 37.4 (J_{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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(1) Onium Ions. 38. Part 37: Olah, G. A.; Aniszfeld, R.; Prakash, G. K. S.; Williams, R. E.; Lammertsma, K.; Güner, O. F. *J. Am. Chem. Soc.* **1988**, *110*, 7885.

(2) Hashimoto, T.; Prakash, G. K. S.; Shih, J. G.; Olah, G. A. *J. Org. Chem.* **1987**, *52*, 931.

(3) For review on this reagent, see: Olah, G. A.; Shih, J. G.; Prakash, G. K. S. *J. Fluorine Chem.* **1986**, *33*, 377.

(4) Olah, G. A.; Liang, G.; Staral, J. *J. Am. Chem. Soc.* **1974**, *96*, 8112.

(5) Freshly distilled SbF_5 was used in 5-fold molar excess.

(6) A toluene/liquid nitrogen slush bath was used for cooling.

(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 ^1H, ^{19}F broad-band probe.

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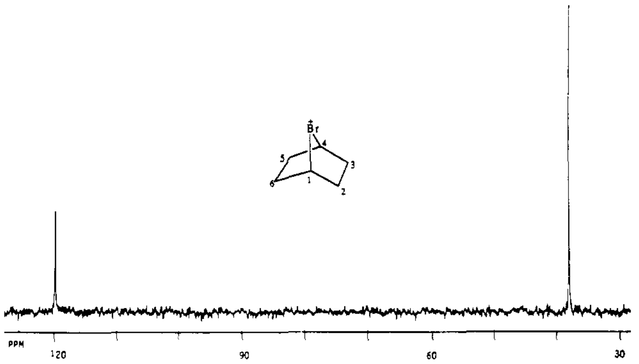
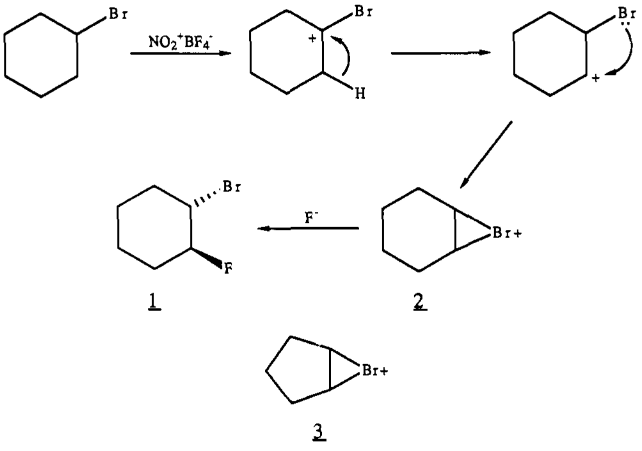


Figure 1. Proton-decoupled 50-MHz ^{13}C NMR spectrum of 7-bromoniabicyclo[2.2.1]heptane in SbF_5/SO_2ClF solution at −95 °C.

Scheme I



clohexene bromonium ion **2** had formed, it should have shown three distinct ^{13}C NMR absorptions instead of two. The observed spectrum, however, is still characteristic of a bromonium ion (based on the extent of ^{13}C deshielding of the α-carbon as well as an increase in the magnitude of the C–H coupling constant),[9] but with 4-fold symmetry. The only choice is the 4-fold-symmetrical ion 7-bromoniabicyclo[2.2.1]heptane (**4**). Formation of ion **4** can be best understood by successive 1,2-hydride shifts from the initially generated 2-bromocyclohexyl cation giving the 4-bromocyclohexyl cation, followed by transannular 1,4-bromine participation. The 200-MHz[8] ^{1}H NMR spectrum is also in agreement with the assigned structure with peaks at $\delta(^1H)$ 7.49 (br, 2 H, H_1 and H_4), 2.78 (d, $J_{H-H} = 9.0$ Hz, 4 H, endo, H_2, H_3, H_5, H_6), and 1.46 (d, $J_{H-H} = 9.0$ Hz, 4 H, exo, H_2, H_3, H_5, H_6). Interestingly, the same bicyclic bromonium ion **4** was formed by the ionization of 1,1-dibromocyclohexane (**5**),[10] which again involves successive 1,2-hydride shifts. Under no conditions attempted was the cyclohexene bromonium ion **2** formed, indicating that under long lived stable ion conditions **2** is not stable. To probe the suggested mechanism and assigned structure, we subsequently carried out ionization of *trans*-1,4-dibromocyclohexane (**6**)[11] in SbF_5/SO_2ClF at −95 °C, which very cleanly again yielded the same ion **4**, fully supporting the assigned structure and its formation path.

The unexpected 1,4-bridged bicyclic bromonium ion **4** is stable below −90 °C, above which it gives a mixture of 1-methylcyclopentenyl cation **7**[12] and cyclohexenyl cation **8**.[12] The observed unprecedented 1,4-transannular participation in the intermediate 4-bromocyclohexyl cation is rather interesting. No such participation in six-membered-ring systems is known. However, transannular participation in 7–11-membered rings is well recognized.[13] It appears that the bulky bromine atom is of the right size to effect such transannular participation in a six-membered ring through a boat type of transition state. Attempts to prepare the corresponding bicyclic chloronium ion by the ionization under a variety of conditions of both *trans*-1,2- and *trans*-1,4-dichlorocyclohexane were unsuccessful.[14] In these cases, the 1-methylcyclopentenyl cation was the only product. This shows that the smaller chlorine atom cannot readily induce similar transannular 1,4-participation in a six-membered ring.

To further rationalize the observed results, we also carried out semiempirical SCF-MO calculations. Using MNDO theory,[15] the C_{2v}-symmetrical **4** was found to be 2.6 kcal more stable than the C_s-symmetrical three-membered-ring bromonium ion **2**. Furthermore, the unbridged 4-bromocyclohexyl cations (both chair and boat forms) are also unstable compared to **4** by 2.9 and 3.8 kcal, respectively. On the other hand, the 1-bromocyclohexyl cation (chair form) is slightly more stable than **4** (by 1.1 kcal), although this ion was not observed under stable-ion conditions.

In conclusion, we have found under long lived stable ion conditions unprecedented 1,4-transannular participation in the 4-bromocyclohexyl cation leading to the unexpected persistent bicyclic bromonium ion **4**. Bromine appears to be of the proper size to effect such 1,4-participation in a six-membered ring. Smaller chlorine was found incapable of effecting such bridging. The observed experimental results are also in accord with semiempirical MNDO calculations.

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(10) Prepared by using the published procedure: Naopolitano, E.; Fiaschi, R.; Mastrorilli, E. *Synthesis* **1986**, 122.

(11) Purchased from Aldrich Chemical Company and used as such.

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(14) Ionizations carried out at −120 °C (using pentane/liquid N_2 slush) gave similar results.

(15) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. Full results of these calculations along with ab initio results will be the subject of a forthcoming paper.

Thermally Generated Benzannelated Trimethylenemethane Biradicals of the 2-Methylenecyclohexene-1,3-diyl Series Escape Capture by a New Rearrangement to Benzannelated Bicyclo[3.2.0]hept-1-enes

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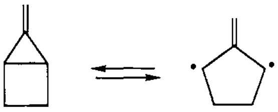
Because a finite energy barrier opposes intramolecular ring-closure of singlet 2-methylenecyclopentane-1,3-diyl biradicals (e.g., **2**) generated thermally from 5-methylenebicyclo[2.1.0]pentanes (e.g., **1**), it is possible to observe dimerization and intermolecular cycloaddition of these trimethylenemethane (TMM) species. These reactions are precluded in most TMM derivatives by fast intramolecular cyclization.[1,2] Thus, although a vinyl TMM



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