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Theoretical Approaches to Rearrangements in Carbocations. I. The Haloethyl System

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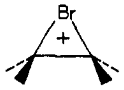
Abstract: *Ab initio* molecular orbital theory has been used to investigate the geometrical structures and energetic surface of the fluoro- and chloroethyl cations. The following points are of interest. The 1-haloethyl systems exhibit no conformational preference for the methyl group to eclipse or to stagger the carbon–halogen bond. The former arrangement would have been anticipated. The 2-haloethyl cations adopt eclipsed rather than bisected arrangements in agreement with earlier theoretical studies by Pople and Hoffmann and their collaborators. The preference is much stronger in the fluorine system. Fluorine- and chlorine-bridged ions geometrically resemble to a remarkable extent the isoelectronic three-membered rings ethylene oxide and sulfide and hence are best represented in terms of incorporation of a formally divalent and positively charged halogen rather than viewed as significantly delocalized. Of the forms considered only the 1-haloethyl and the halogen-bridged systems are found to be stable entities, all other structures collapsing to one or both without activation energy. For both fluorine and chlorine, the 1-haloethyl cations are found to be the minimum energy forms. Although the difference in stabilities of the two in the fluorine-substituted ion is large enough to make this conclusion firm, the corresponding theoretical difference in energy between the 1-chloroethyl- and chlorine-bridged ions is small and below the limits of reliability of the theory at this level. Comparison of our theoretical findings with Olah's superacid data on (primarily) the chloroethyl system is favorable. The effects of simple alkyl substituents in altering the energetic profile of the parent ions have been considered. 2-Haloethyl cations which were not minimum energy forms as parents may be stabilized in preference to other isomeric structures. Correspondingly, structures which were local minima on the parent surface (in particular the halogen-bridged ions) may be preferentially raised energetically. Comparison is made on many points with the rich literature on alkyl-substituted fluoro- and chloroethyl cations.



It was the daring proposal of a bridged bromonium ion by Roberts and Kimball[2] which provided organic chemistry with its first example of delocalized σ bonding. In the more than three decades since then, many further examples have been uncovered, and now it would seem that the existence of "nonclassical" bonding schemes among organic molecules is commonplace and widespread.[3] It must be admitted, however, that even after this lapse of time the details of structure and energetics of the bridged haloethyl cations are not in their entirety adequately understood. Although, primarily due to the work of Olah and his collaborators, cyclic cations containing iodine and bromine have been well characterized by proton and ^{13}C nmr for some time[4–8] (and the stable existence of open forms still very much in question), clear evidence for a bridged form of parent chloroethyl cation is only very recent.[9]

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(1) (a) University of California; (b) Université de Paris-Sud.

(2) I. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.*, **59**, 947 (1937).

(3) For reviews see (a) R. Breslow in "Molecular Rearrangements," Part I, Interscience, New York, N. Y., 1963, pp 233–294; (b) B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964); (c) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965; (d) M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967); (e) see also "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1972.

(4) (a) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967); (b) *ibid.*, **90**, 947 (1968).

(5) G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 2587 (1968).

(6) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(7) G. A. Olah and R. D. Porter, *J. Amer. Chem. Soc.*, **93**, 6877 (1971); see section C of the Results and Discussion.

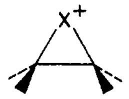
(8) G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. M. Brinich, *J. Amer. Chem. Soc.*, **94**, 1164 (1972).

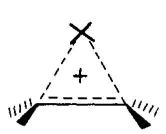
(9) G. A. Olah, D. A. Beal, and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 3387 (1973); for observations on open forms of parent chloroethyl cation, see also ref 10; on substituted chloroethyl systems, see ref 4, 5, and 8.

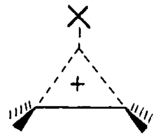
(10) G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Org. Chem.*, **37**, 1169 (1972).

Furthermore, even though attempts to detect bridging by fluorine using direct spectroscopic means have failed,[4] the accumulated chemical evidence for the existence of such species may not be passed over so easily.[11]

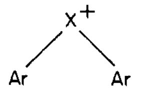
The nature of the bonding in the cyclic halogen cations is also a matter of considerable dispute,[12] as it has been represented both in terms of a purely hypervalent (divalent) halogen ion and within the framework of delocalized σ or three-center bonding theory.

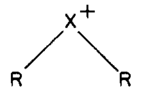


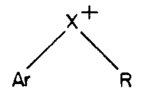




The former representation has received indirect experimental support in recent years with the observations, under long life conditions, of the acyclic diaryl, dialkyl, and mixed halogen cations,[13] molecules in







which σ delocalized bonding schemes are seemingly unrealizable.

In this paper we apply theoretical molecular orbital theory at the *ab initio* level in an attempt to answer such questions as have been posed above. Primarily we shall be interested in the predictions of the theory to indicate to us the relative stabilities of the acyclic and bridged forms of the halogen cations and to provide estimates of the barriers (if any) connecting them. The detailed structural predictions of the theory may enable us to discern between the two extremes of bonding or more likely provide an indication that an accurate description lies somewhere in the middle. To aid us in this task we shall also scrutinize the structural predictions of the theory regarding the acyclic halogen cations.

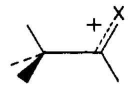
Quantum Mechanical Methods

Single determinant *ab initio* molecular orbital theory has been used throughout. We employ the minimal STO-3G basis functions,[14] whose use is primarily to establish molecular equilibrium (and transition state) geometries, and the split valence shell basis, 4-31G,[15] useful in accurately estimating relative molecular energies of the structures specified by the minimal set. We have found such tactics useful and reliable in prior studies. To supplement our own theoretical calculations we will be using the near Hartree–Fock results of Hariharan, Lathan, and Pople[16] on the parent open and bridged forms of the ethyl cation. These were derived from calculations in which the standard 6-31G extended basis[17] was supplemented by polarization functions on heavy atoms and hydrogens alike.[18] All calculations supported here have been performed using the GAUSSIAN 70 series of computer programs.[19]

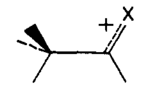
Results and Discussion

We shall divide our presentation into two sections. In the first we consider the nature of the geometric potential surface for the parent ions $C_2H_4X^+$ (X is a halogen) detailing each energetic minima and outlining to our best ability the possible modes of interconversion among them. The effects of simple alkyl substituents will be dealt with next, enabling direct comparison of our findings with the greater portion of the experimental (nmr) data. Hopefully such comparisons will be favorable enough to allow us to rationalize in terms of the theoretical model what is observed experimentally, and, more importantly, to lend credibility to the results of the theory in those areas where experimental observations have not as yet been made or have not been ammendable to ready interpretation. Our interest also lies in the possibility of specifying which substituents and which positions might preferentially stabilize one form of the halocations over another. In all our discussion we shall limit ourselves to the halogens fluorine and chlorine; extension to include elements beyond the second row is difficult at this time because of a lack of well developed theoretical methods. It is fortunate, however, that is is exactly the cations which at the present time pose the greatest mysteries.

A. Parent Ions. The 1-haloethyl cations may take on either eclipsed or staggered conformations (I and II, respectively), the former being the anticipated due to the observed[20] (and theoretically justified[23]) tendency of methyl groups to eclipse rather than to stagger (partial) double bonds. We will return to this later. It may be seen from the theoretical structures for eclipsed and staggered 1-fluoro- and 1-chloroethyl cations given in Table I that the carbon–fluorine and carbon–chlorine bond lengths are significantly shorter than normal single linkages[24] although the reduction



I
methyl eclipsed



II
methyl staggered

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(11) For a review, see R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).

(12) Recent work has tended to favor direct analogy with the normal three-membered ring molecules. See ref 5 for a discussion.

(13) (a) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **91**, 2113 (1969); (b) *ibid.*, **92**, 718 (1970); (c) *ibid.*, **92**, 2562 (1970); (d) G. A. Olah and E. G. Melby, *ibid.*, **94**, 6220 (1972); (e) G. A. Olah and Y. K. Mo, *ibid.*, **94**, 6864 (1972); (f) G. A. Olah and J. Shen, *ibid.*, **95**, 3582 (1973).

(14) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *ibid.*, **52**, 2191 (1970).

(15) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971); W. J. Hehre and W. A. Lathan, *ibid.*, **56**, 5255 (1972).

(16) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972).

(17) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).

(18) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).

(19) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(20) For example, propene[21] and acetaldehyde[22] prefer conformations in which one methyl hydrogen eclipses the double bond, the respective rotational barriers being 2.00 and 1.16 kcal/mol.

(21) D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957); E. Hirota, *ibid.*, **45**, 1984 (1966).

(22) W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *J. Chem. Phys.*, **26**, 1695 (1957).

(23) W. J. Hehre and L. Salem, *Chem. Commun.*, 754 (1973).

(24) STO-3G carbon–halogen bond lengths: C–F in CH_3F, 1.384 Å; C–Cl in CH_3Cl, 1.805 Å.

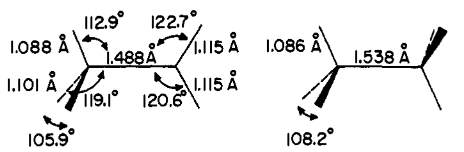
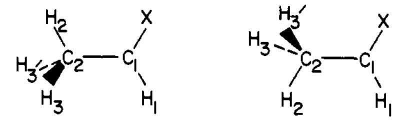


Figure 1. Theoretical (STO-3G) equilibrium geometries for the bisected ethyl cation and for staggered ethane: W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).

Table I. Theoretical (STO-3G) Geometries for the 1-Haloethyl Cations[a]



1-Fluoroethyl Cation (Eclipsed)	
$r(C_1C_2) = 1.510$	$\angle(FC_1C_2) = 122.4$
$r(C_1F) = 1.275$	$\angle(H_1C_1C_2) = 121.3$
$r(C_1H_1) = 1.124$	$\angle(H_2C_2C_1) = 111.6$
$r(C_2H_2) = 1.089$	$\angle(H_{33'}C_1C_2)^b = 119.7$
$r(C_3H_3) = 1.097$	$\angle(H_3C_2H_{3'}) = 107.8$
1-Fluoroethyl Cation (Staggered)	
$r(C_1C_2) = 1.511$	$\angle(FC_1C_2) = 122.3$
$r(C_1F) = 1.275$	$\angle(H_1C_1C_2) = 122.2$
$r(C_1H_1) = 1.123$	$\angle(H_2C_2C_2) = 111.5$
$r(C_2H_2) = 1.089$	$\angle(H_{33'}C_2C_1)^b = 119.9$
$r(C_2H_3) = 1.097$	$\angle(H_3C_2H_{3'}) = 107.8$
1-Chloroethyl Cation (Eclipsed)	
$r(C_1C_2) = 1.500$	$\angle(ClC_1C_2) = 124.0$
$r(C_1Cl) = 1.700$	$\angle(H_1C_1C_2) = 120.1$
$r(C_1H_1) = 1.117$	$\angle(H_2C_2C_1) = 112.7$
$r(C_2H_2) = 1.089$	$\angle(H_{33'}C_2C_1) = 119.0$
$r(C_2H_3) = 1.099$	$\angle(H_3C_2H_{3'}) = 107.2$
1-Chloroethyl Cation (Staggered)	
$r(C_1C_2) = 1.501$	$\angle(ClC_1C_2) = 123.9$
$r(C_1Cl) = 1.701$	$\angle(H_1C_1C_2) = 120.6$
$r(C_1C_1) = 1.116$	$\angle(H_2C_2C_1) = 112.6$
$r(C_2H_2) = 1.089$	$\angle(H_{33'}C_2C_1)^b = 119.2$
$r(C_2H_3) = 1.099$	$\angle(H_3C_2H_{3'}) = 107.0$

[a] Bond lengths in ångstroms, angles in degrees. [b] $H_{33'}$ is the line bisecting the plane formed by carbon 2 and hydrogens 3 and 3′.

is not as great as the 0.1–0.2 Å normally observed in going all the way to a double bond. The detailed geometrical structures of these cations may be understood in terms of a model based on the (unsubstituted) ethyl cation, the geometry of which is presented in Figure 1 along with that of neutral ethane for comparison.[25] Following the ideas of Radom, Pople, and Schleyer[26] and of Hoffmann and his collaborators[27] we consider the two-electron interaction of the (occupied) valence orbitals of methyl with the empty orbital of p symmetry at the carbonium center (Figure 2). To a first approximation, the symmetric component of the methyl pseudo π orbital (symmetric with respect to the plane of the paper) and the cationic center do not interact. The asymmetric component is, however, of the proper symmetry and acts as an electron donor, leading to an increase in the bond order between the two carbons at the expense of electron density in the bonding orbitals of the out-of-plane CH linkages. Thus we observe a shortening of the CC bond (from 1.538 Å in ethane to 1.488 Å in the bisected form of the ethyl cation) and an accompanying lengthening of the out-of-plane CH bonds (from 1.086 to 1.101 Å). Hydrogen–hydrogen repulsive forces between the two out-of-plane methyl H's are also lessened leading to a decrease in methyl HCH bond angle from 108.2° in ethane to 105.9° in the bisected ethyl cation. By the same reasoning we would expect the in-plane methyl bond length to be little altered from the ethane value, and this is indeed found to be the case, an elongation of only 0.002 Å being noted.

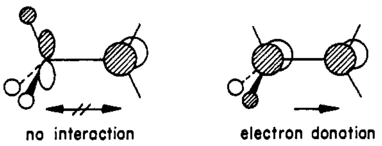


Figure 2. Interaction of the pseudo π orbitals on methyl with a cationic center.

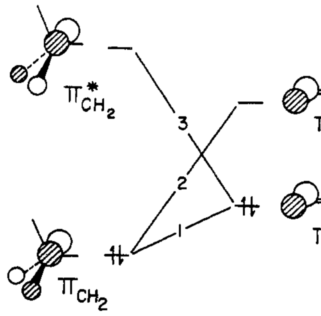
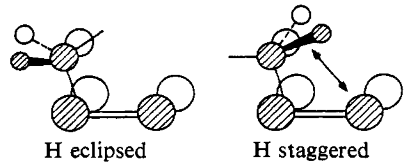


Figure 3. Interaction of the delocalized π orbitals of a nonpolar double bond with the pseudo-π-symmetry functions on a methyl group.

The structures of the 1-halogen-substituted cations given in Table I show similiar if only subdued geometrical distortions from what would be expected of the corresponding haloalkanes. Here π-electron donation by the directly bonded halogen atom renders interaction of the cationic center and pseudo π orbitals on methyl a less attractive (and necessary) affair.

As mentioned earlier, it is the normal preference for methyl groups directly bonded to unsaturated linkages to adopt eclipsed rather than staggered conformations.[20,23] The phenomenon may be explained in terms of the consequences of interaction of the orbitals of a double bond with those of π symmetry on the methyl (Figure 3). We review it only briefly here. The four-electron interaction (1) is net destabilizing;[28] the H-eclipsed conformer with the less overlap (the contribution from the out-of-plane methyl hydrogens overlapping with the component of the double bond centered on the terminal atom being smaller in the eclipsed form) is the one less disfavored. Similarly, the same secondary overlap dictates that the eclipsed form will


H eclipsed H staggered

secondary overlap increases destabilizing four-electron interaction

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(25) Theoretical STO-3G geometries from W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).

(26) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 5935 (1972), and references therein.

(27) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, **94**, 6221 (1972).

(28) L. Salem, *J. Amer. Chem. Soc.*, 90, 543 (1968); K. Müller, *Helv. Chim. Acta*, **53**, 1112 (1970).

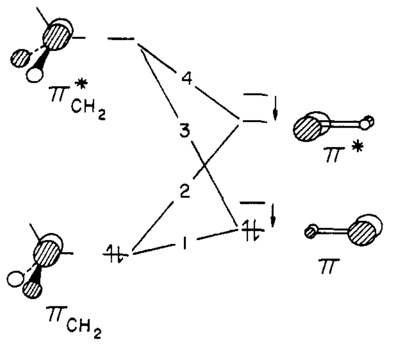
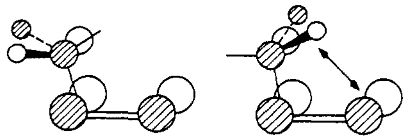


Figure 4. Interaction of the now localized π orbitals of a polar (partial) double bond with the pseudo-π-symmetry functions on a methyl group.

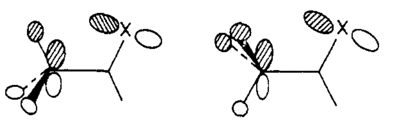
also be the preferred for maximizing the total positive overlap in the stabilizing two-electron interactions (2) and (3), for example, as in interaction (2) between π and $\pi_{\mathrm{CH_3}}{}^*$.



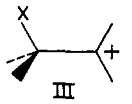
negative secondary overlap decreases stabilizing two-electron interaction

At least two significant factors distinguish the 1-haloethyl cations from the model systems described above. Firstly the double bond orbitals in the polar C=X linkage (the halogen X being much more electronegative than carbon) are no longer fully delocalized. Rather the filled π orbital is centered primarily on the (more electronegative) halogen while the empty π* function remains for the most part on carbon. Figure 4 depicts the resulting interaction diagram. At first glance it would appear that although the secondary (and according to our model, conformational determining) component of the two-electron interaction (2) decreases, those of interactions (1) (four electron) and (3) (two electron) actually increase. The net change due to bond localization would seem to be little and if any certainly in the direction of enhanced conformational preference (for the eclipsed structure). We must also consider, however, that the increased electronegativity over carbon of the halogen lowers the energies of both π and π* double bond orbitals. Thus, interaction (2), weak in conformational preference, takes on added importance, while the conformationally dictating effects of the third term are weakened. The effects of stabilization of the π levels on the magnitude of the four-electron interaction (1) are not apparent.

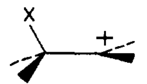
In addition to a change in degree of localization of the π bond we can expect from our 1-haloethyl cations some degree of interaction between the filled and high-lying σ lone pairs on halogen and the methyl group orbitals of appropriate symmetry. The conformational dependence here is very difficult to ascertain for it involves deciding in which of two arrangements, H eclipsed or staggered, total orbital overlap will do the most good (or least harm). We offer no opinion at this time.



Two conformational possibilities also exist for the 2-haloethyl cations, eclipsed and bisected, forms III and IV, respectively. In the unsubstituted ethyl cation

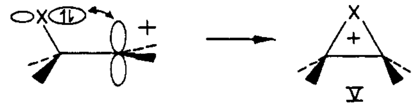


III



IV

the two are nearly equal in energy;[29] that is to say that the (sixfold) rotational barrier is essentially zero. As recently detailed by Radom, Pople, and Schleyer[26,30] and by Hoffmann and his collaborators,[27] however, a significant (twofold) rotational barrier is to be expected with the eclipsed conformer preferred when one of the methyl hydrogens is replaced by a group X of greater electronegativity.[31,32] We shall not reproduce the theoretical argument (for this the reader is referred to the work of Hoffmann[27]) but only mention that the magnitude of the barrier (preference for the eclipsed conformer) is expected to depend foremost on the relative electronegativity of carbon and the halogen X. Thus, following the electronegativity scale suggested by Pauling,[33] we would predict the barriers in the 2-haloethyl cations to fall in the order (greatest to smallest) F > Cl > Br > I. Unfortunately, these rotational barriers are not amenable to direct experimental measurements as the bisected form of the 2-haloethyl cation itself is unstable with respect to skeletal rearrangement in the direction of halogen bridging. Here direct through space interaction of the lone pair orbitals on the halogen with the vacant p orbital at the carbonium center leads to collapse *without activation energy* to a halogen-bridged structure (V).[34] Such



V

behavior is reminiscent of our previous experience with

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(29) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969); J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **92**, 2141 (1970); J. E. Williams, V. Buss, and L. C. Allen, *ibid.*, **93**, 6867 (1971).

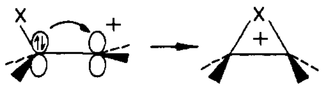
(30) See also L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 2371 (1972).

(31) More correctly stated it is the electronegativity of the group X with respect to the carbon to which it is bonded which is of concern here.

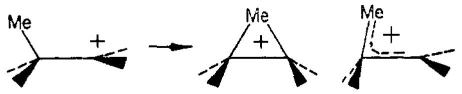
(32) The conformational preferences of the 2-fluoroethyl and related cations have already undergone extensive study by Radom, Pople, and Schleyer, ref 26.

(33) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960; halogen electronegativities: F, 4.10; Cl, 2.83; Br, 2.74; I, 2.21.

(34) A second and independent interaction between the pseudo π orbital on the β carbon and the vacant p orbital is also suspected to lead to bridging. Thus, even the *n*-propyl cation, where no lone pair–empty



orbital interactions can exist, is found to be bridge (or at least distorted from a normal acyclic form): L. Radom, J. A. Pople, V. Buss, and

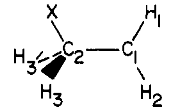


P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 311 (1972), and references therein. Recent studies seem to favor a symmetrically methyl-bridged ion (corner protonated cyclopropane) over asymmetric forms: P. C. Hariharan, L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, **95**, 6531 (1973).

the homoallyl[35] and 2-phenylethyl[36] cations. Here interaction of the primary carbonium center with the π orbitals of ethylene (or the aromatic π system in the case of the 2-phenylethyl cation) led to collapse of the open ions toward bridged forms without any activation at all required. We will see the phenomena again in our theoretical treatment of neighboring cyclopropyl participation.[37] The size of the rotational barriers in the 2-haloethyl cations can be investigated theoretically, if we constrain the geometry of the bisected form so as not to allow bridging. Thus, as reported by Hoffmann,[27] the eclipsed form of the 2-fluoroethyl cation is favored by 8.4 kcal/mol over the bisected;[38] the corresponding barrier in the chlorine analog is but 1.5 kcal/mol.

The detailed geometrical structures for the eclipsed forms of the 2-fluoro- and 2-chloroethyl cations are given in Table II. As before the geometrical distortions found in these molecules (with respect to say ethane as a model) are very similar to those in the (unsubstituted) ethyl cation. Here the β halogen is not as effective as a directly bonded atom in altering the interaction of the pseudo π orbitals on methyl with the carbonium center.

Table II. Theoretical (STO-3G) Geometries for the 2-Haloethyl Cations[a]



2-Fluoroethyl Cation	
$r(C_1C_2) = 1.511$	$\angle(FC_2C_1) = 113.2$
$r(C_2F) = 1.371$	$\angle(H_1C_1C_2) = 120.0$
$r(C_1H_1) = 1.117$	$\angle(H_2C_1C_2) = 120.0$
$r(C_1C_2) = 1.115$	$\angle(H_{33'}C_2C_1)^b = 115.8$
$r(C_2C_3) = 1.114$	$\angle(H_3C_2H_{3'}) = 105.8$
2-Chloroethyl Cation	
$r(C_1C_2) = 1.499$	$\angle(ClC_2C_1) = 113.9$
$r(C_2Cl) = 1.786$	$\angle(H_1C_1C_2) = 122.3$
$r(C_1H_1) = 1.118$	$\angle(H_2C_1C_2) = 120.0$
$r(C_1H_2) = 1.117$	$\angle(H_{33'}C_2C_1) = 118.3$
$r(C_2H_3) = 1.107$	$\angle(H_3C_2H_{3'}) = 106.0$

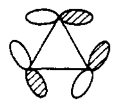
[a] Bond lengths in ångstroms, angles in degrees. [b] $H_{33'}$ is the line bisecting the plane formed by carbon 2 and hydrogens 3 and 3′.

The geometrical structures of the halogen-bridged fluoro- and chloroethyl cations are presented in Table III. The corresponding quantities for the isoelectronic neutral analogs ethylene oxide and ethylene sulfide are also included for comparison. Our results clearly indicate that the bridged halonium ions correspond closely to normal three-membered rings, incorporating a formally divalent and positively charged halogen (but see below) rather than a loose complex between ethylene and the halogen as has often been supposed. In this respect the calculations strongly support the opinions recently voiced by Olah and his coworkers.[39] The carbon–carbon bond lengths we report for the bridged fluoro- and chloroethyl ions are nearly identical with those calculated (and observed) for the analogous neutral molecules. The fact that the carbon–carbon lengths in the two bridged ions and in neutral ethylene oxide are *shorter* than those in cyclopropane (1.502 Å at STO-3G[40]) may be rationalized by considering the effects of the increased electronegativity (over carbon) of the fluorine, chlorine, and oxygen heteroatoms.[41] The antisymmetric component of the Walsh orbital in cyclopropane[42,43] serves to destabilize (and hence lengthen) one of the carbon–carbon bonds, while strengthening the other two (in cyclopropane itself the effects are, of course, exactly compensated for by participation of the other member of the Walsh pair). If the electronegativity of the apical heteroatom is greater than carbon (as is the case in the bridged fluoro- and chloroethyl cations and in ethylene oxide) then electron density will accumulate on that center at the expense of the antibonding character of the basal carbon–carbon bond. Correspondingly, if the heteroatom X is less electronegative than carbon, as is the case for

Table III. Theoretical (STO-3G) Geometries for Bridged Fluoro- and Chloroethyl Cations and Their Oxygen and Sulfur Analogs[a]

Bridge Fluoroethyl Cation	
$r(CC) = 1.488$	$\angle(H_2CC)^b = 167.3$
$r(CF) = 1.486$	$\angle(HCH) = 117.8$
$r(CH) = 1.099$	
Ethylene Oxide[c]	
$r(CC) = 1.483\ (1.472)$	$\angle(H_2CC)^b = 155.3\ (159.4)$
$r(CO) = 1.433\ (1.436)$	$\angle(HCH) = 115.5\ (116.7)$
$r(CH) = 1.088\ (1.082)$	
Bridged Chloroethyl Cation	
$r(CC) = 1.482$	$\angle(H_2CC)^b = 164.0$
$r(CCl) = 1.927$	$\angle(HCH) = 117.9$
$r(CH) = 1.099$	
Ethylene Sulfide[d]	
$r(CC) = 1.507\ (1.492)$	$\angle(H_2CC)^b = 146.7\ (151.6)$
$r(CS) = 1.774\ (1.819)$	$\angle(HCH) = 112.8\ (116.0)$
$r(CH) = 1.083\ (1.078)$	

[a] Bond lengths in ångstroms, angles in degrees. Experimental values given in parentheses. [b] H_2C is the line bisecting the plane formed by the carbon and its two attached hydrogens. [c] Theoretical data taken from ref 51; experimental determination: G. L. Cunningham, Jr., A. W. Boyd, R. J. Myers, W. D. Gwinn, and W. I. LeVan, *J. Chem. Phys.*, **19**, 676 (1951). [d] Experimental determination: G. L. Cunningham, Jr., A. W. Boyd, R. J. Myers, W. D. Gwinn, and W. I. LeVan, *ibid.*, **19**, 676 (1951).



antisymmetric Walsh orbital in cyclopropane

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(35) W. J. Hehre and P. C. Hiberty, *J. Amer. Chem. Soc.*, **94**, 5917 (1972).

(36) W. J. Hehre, *J. Amer. Chem. Soc.*, **94**, 5919 (1972).

(37) W. J. Hehre, manuscript in preparation. For a different viewpoint on the importance of geometrical relaxation in systems such as these, see T. C. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971), and references therein.

(38) The difference between this and the value of 9.3 kcal/mol reported by Radom, Pople, and Schleyer (ref 26) is due solely to differences in molecular geometries used.

(39) See ref 4–8 (especially 5) for discussions on this point.

(40) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 5339 (1971).

(41) Pauling electronegativities: C, 2.50; O, 3.50; F, 4.10; S, 2.44; Cl, 2.83.

(42) For a discussion of the orbitals of cyclopropane, see R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, **93**, 5699 (1971); W. J. Hehre, *ibid.*, **94**, 6592 (1972); W. Jorgensen and L. Salem, "An Organic Chemists Book of Orbitals," Academic Press, New York, N. Y., 1973.

(43) The arguments we present here have their roots in the work of Hoffmann and of Günther in their treatment of substituent effects on the norcaradiene-cycloheptatriene equilibrium: R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970); H. Günther, *ibid.*, 5173 (1970).

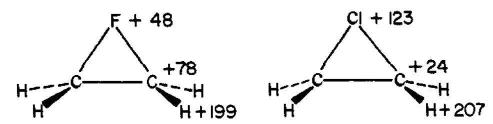
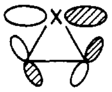
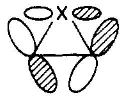


Figure 5. Theoretical (STO-3G wave functions) Mulliken charges for bridged fluoro- and chloroethyl cations (× 10^3 electrons).



X more electronegative than carbon

sulfur, density would be pushed away from this center and into the antibonding region. A lengthening of the basal carbon–carbon bond is predicted and theoretically but not experimentally observed, in this case.



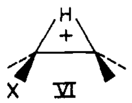
X less electronegative than carbon

The carbon–halogen bond lengths in the bridged cations fit nicely with data on acyclic species. Thus a lengthening of 0.102 Å is noted in going from methyl fluoride (C–F = 1.384 Å) to the (F) protonated form (C–F = 1.486 Å).[44] Note that this latter value is identical with that which we report for the fluorine-bridged ion, although we might have anticipated a (slight) shortening due to a difference in hybridization between cyclic and acyclic ions. Similarly, whereas the carbon–chlorine bond length in methyl chloride increases by 0.137 Å upon (Cl) protonation (from 1.805 to 1.942 Å), there is little difference between the latter value and that in our bridged chloronium ion. Indeed here the expected shortening is observed.[45]

In conclusion the accumulated evidence on the geometrical structure of the bridged haloethyl cations leaves little doubt that they may be mistaken for complexes incorporating but a slightly perturbed ethylenic moiety.

A theoretical Mulliken population analysis[46] (Figure 5) indicates, contrary to chemical notions, that very little of the positive charge is actually borne by the halogen itself. Rather it is delocalized throughout the molecular framework, the greater share being taken by the ethylenic hydrogens.

Finally we have investigated the possibility of fluorine- and chlorine-substituted bridged ethyl cations (VI).



VI

Here we have not determined the geometrical structures theoretically (because of lack of molecular symmetry a complete optimization would be too costly) but have performed only single calculations using the geometry of the bridged ethyl cation[25] and attaching the halogen substituent at the same angles as the hydrogen it replaced. Connecting bond lengths of 1.37 and 1.79 Å have been used for fluorine and chlorine substituents, respectively.

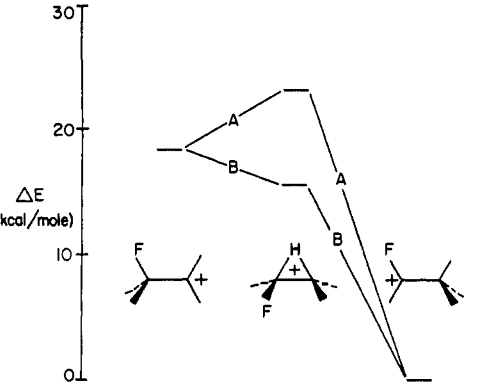


Figure 6. Interconversion of 2-fluoroethyl and 1-fluoroethyl cations. See text for explanation of A and B pathways.

B. Pathways to Interconversion. STO-3G and 4-31G total energies for the haloethyl cations discussed in the previous section are given in Table IV. In addition we include previously published STO-3G, 4-31G, and polarization basis 6-31G** data on the open eclipsed and bridged ethyl cations.[16] We will employ this latter information to aid us in obtaining more accurate estimates of relative molecular energetics.

Table IV. Theoretical Energy Data for Parent Haloethyl Cations[a]

Cation	STO-3G	4-31G	6-31G**[b]
Eclipsed ethyl	−77.40806	−78.19496	−78.31688
Bridged ethyl	−77.38986	−78.18418	−78.31831
Eclipsed 1-fluoroethyl	−174.89880	−176.91897	
Staggered 1-fluoroethyl	−174.89883		
Eclipsed 2-fluoroethyl	−174.84083	−176.88977	
F-bridged fluoroethyl	−174.87214	−176.87146	
H-bridged fluoroethyl	−174.83646	−176.88210	
Eclipsed 1-chloroethyl	−531.40808	−536.59460	
Staggered 1-chloroethyl	−531.40809		
Eclipsed 2-chloroethyl	−531.37944	−536.57275	
Cl-bridged chloroethyl	−531.40978	−536.58738	
H-bridged chloroethyl	−531.36469	−536.56390	

[a] Energies in hartrees. [b] Theoretical data taken from ref 16.

In the preceding section we pointed out that the bisected forms of the 2-fluoro- and 2-chloroethyl cations (IV) were unstable with respect to collapse to halogen-bridged structures (V). Also it was commented that these forms represented energy maxima on the rotational of the 2-haloethyl system, the eclipsed structures (III) actually being the stable conformers. It now remains for us to show the energy disposition of the eclipsed 2-haloethyl systems and in particular their stability with respect to halogen-substituted hydrogen-bridged ethyl cations (VI) and to the 1-haloethyl cations (I and II).

Pathway A of Figure 6 illustrates the predictions of the extended 4-31G basis regarding the interconversion of eclipsed 2-fluoroethyl and eclipsed 1-fluoroethyl cations proceeding *via* a base fluorine-substituted hydrogen-bridged ethyl cation. An activation energy of 4.8 kcal/mol is required (the energy of the hydrogen-bridged structure above that of 2-fluoroethyl cation),

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(44) Theoretical STO-3G geometry data from W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Progr. Phys. Org. Chem.*, 11, 175 (1974).

(45) Similar behavior is noted in comparison of the C–O and C–S bond lengths between the acyclic–cyclic pairs methanol–ethylene oxide and thiomethanol–ethylene sulfide. Whereas the carbon–oxygen bond length is the same in the two (1.433 Å, using the STO-3G basis), a shortening of 0.023 Å is noted in going from the acyclic to cyclic sulfur systems.

(46) R. S. Mulliken, *J. Chem. Phys.*, 23, 1833 (1955).

but due to the approximate geometry used for the intermediate hydrogen-bridged ion this figure no doubt represents an upper bound for the method. Furthermore because it is known that the 4-31G basis underestimates the stability of the parent hydrogen-bridged ethyl cation relative to open forms[47] (and relative to the predictions of the theory at the Hartree–Fock limit) it is desirable to pursue the potential surface for this interconversion one step further. Although we are not able to perform better calculations on systems of this complexity at the present time, we can estimate with some degree of reliability the effects of an improved atomic basis (in particular the inclusion of polarization type functions on all centers) by a simple variant of a procedure used by us for some time. The energy of reaction 1 provides us with some indication of the

$$CH_2FCH_2^+ + CH_4 \longrightarrow CH_3CH_2^+ + CH_3F \tag{1}$$
$$\Delta E(\text{4-31G}) = -14.0 \text{ kcal/mol}$$

effectiveness of a 2-fluorine substituent in stabilizing (or in this instance destabilizing) the eclipsed form of the ethyl cation. Likewise the energy of reaction process 2 gives us an estimate of the corresponding effect

$$CH_3CHF^+ + CH_4 \longrightarrow CH_3CH_2^+ + CH_3F \tag{2}$$
$$\Delta E\,(\text{4-31G}) = +4.3 \text{ kcal/mol}$$

of a 1-fluorine substituent. An analogous scheme (eq 3)

$$\overline{CHFCH_2H}^+ + CH_4 \longrightarrow \overline{CH_2CH_2H}^+ + CH_3F \tag{3}$$
$$\Delta E\,(\text{4-31G}) = -12.0 \text{ kcal/mol}$$

demonstrates the destabilizing nature of fluorine on the bridged form of ethyl cation. Previous experience has suggested that the energies of such *isodesmic* processes[48] (processes in which equal numbers and kinds of chemical bonds appear on both sides of the arrow) as (1), (2), and (3) are well described by single-determinant molecular-orbital theory at the *ab initio* level, even with basis sets as simple as 4-31G. Indeed, previous studies involving upwards of 100 individual examples (neutral and cationic species alike) have placed an error limit of between 2 and 5 kcal/mol for the energies of such reactions.[26,49] Combining our fluorine substituent effect data with the best available set of relative energies for the unsubstituted open and bridged ethyl cations (and setting the energy of the resulting most stable form, the 1-fluoroethyl cation, to zero) we see (pathway B of Figure 6) that the fluorine-substituted hydrogen-bridged ion is actually lower in energy than eclipsed 2-fluoroethyl cation. No doubt it represents an intermediate point (of no special significance) to 2-fluoroethyl-1-fluoroethyl interconversion. Thus it would appear that neither bisected nor eclipsed conformers of the 2-fluoroethyl cation represent true energy minima.

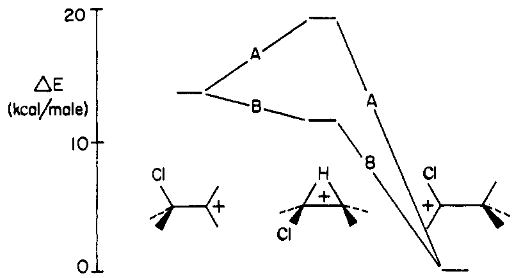

Figure 7. Interconversion of 2-chloroethyl and 1-chloroethyl cations. See text for explanation of A and B pathways.

Pathway A of Figure 7 displays the 4-31G predictions regarding the 2-chloroethyl-1-chloroethyl interconversion process. As was the case in the fluorine-substituted ion, a small activation energy (of 5.6 kcal/mol) is required. The corresponding effects of chlorine substituents on the ethyl cation energies are given by the *isodesmic* reactions 4, 5, and 6. Combined as before with the 6-31G** results on the unsubstituted ethyl cations they are represented as pathway B of Figure 7. Again the 4-31G findings (pathway A) are altered and again we shed doubt on the stable existence of a 2-haloethyl (this time 2-chloroethyl) cation.

$$CH_2ClCH_2^+ + CH_4 \longrightarrow CH_3CH_2^+ + CH_3Cl \tag{4}$$
$$\Delta E(\text{4-31G}) = -14.4 \text{ kcal/mol}$$

$$CH_3CHCl^+ + CH_4 \longrightarrow CH_3CH_2^+ + CH_3Cl \tag{5}$$
$$\Delta E(\text{4-31G}) = -0.7 \text{ kcal/mol}$$

$$\overline{CHClCH_2H}^+ + CH_4 \longrightarrow \overline{CH_2CH_2H}^+ + CH_3Cl \tag{6}$$
$$\Delta E(\text{4-31G}) = -13.2 \text{ kcal/mol}$$

The picture we now support for the parent fluoro- and chloroethyl cations is the very simple one depicted in Figure 8. Arrows indicate transformations which occur without activation energy. Two stable local minima coexist; the 1-haloethyl form (I) (both for the fluorine- and chlorine-substituted ions being the more stable of the 4-31G level) and the halogen-bridged ion (V). We have suggested that one way they may interconvert is *via* the rather lengthy process I ← VI ← III ← IV → V, a bisected 2-haloethyl cation being to a first approximation the transition state.[50] Perhaps more direct pathways exist, but we have not been able to deal realistically with such possibilities here.

At this point it is useful to assess the accuracy of the theory (at the 4-31G level which we have applied) in assigning the relative stabilities of the 1-haloethyl and halogen-bridged cationic forms. Perhaps the only straightforward way of accomplishing this is to consider the predictions of the theory, regarding relative stability of isomers, in a case (hopefully closely related to the system of interest) where experimental data are available. One such example meets these requirements. The 4-31G basis finds acetaldehyde to be 37.8 kcal/mol

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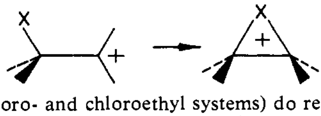
(47) Thus, whereas the 4-31G basis finds eclipsed ethyl cation to be 6.8 kcal/mol more stable than the hydrogen-bridged form, inclusion of polarization functions reverse the prediction resulting in the bridged ion being the favored form by 0.9 kcal/mol.[16] Although the ground state geometry of the ethyl cation has not been unambiguously assigned experimentally, it is known that either the ion is bridged *or* undergoes hydrogen migration with a very low activation; see P. Ausloos, R. E. Rebbert, L. W. Seick, and T. O. Tiernan, *J. Amer. Chem. Soc.*, **94**, 8939 (1972); J. H. Vorachek, G. G. Meisels, R. A. Geanangel, and R. H. Emmel, *ibid.*, **95**, 4078 (1973).

(48) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970).

(49) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 289 (1971).

(50) We have investigated the process. The transition state structures (both for fluoro- and chloroethyl systems) do resemble to a great extent bisected haloethyl cations. Approximate activation required: from eclipsed 2-fluoroethyl cation, 7.4 kcal/mol; from eclipsed 2-chloroethyl cation, 0.8 kcal/mol. Thus, the total activation energies for 1-fluoroethyl cation to fluorine-bridged ethyl cation and from 1-chloroethyl cation to chlorine-bridged ethyl cation are on the order of 26 and 14 kcal/mol, respectively. Activation required for the reverse reactions is more difficult to accurately estimate, but see text following.



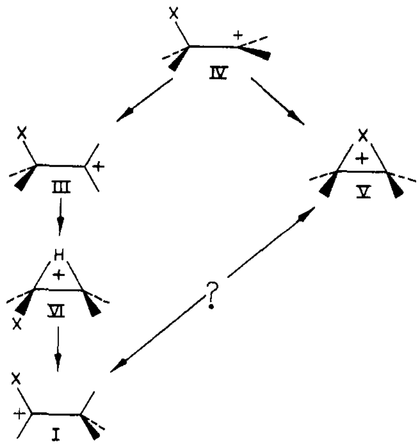


Figure 8. Energy surface for interconversion of haloethyl cations. Arrows indicate direction of transformations which occur without activation energy.

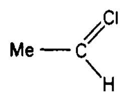
lower in energy than ethylene oxide.[51] Experimentally, the same ordering is found but the difference in stability is only 27.6 kcal/mol. If we transfer this correction for the discrepancy between theory and experiment our 29.8 kcal/mol difference in stability between 1-fluoroethyl and fluorine-bridged ethyl cation is reduced to 19.6 kcal/mol, a quantity still large enough that our predictions of a ground state form remain unambiguous. Transference directly to the chloroethyl cations is a more risky affair (the analogous pair would be thiaacetaldehyde–ethylene sulfide, but here thermochemical data are lacking) and because of the small energy difference between open and bridged forms the consequences are more severe. Thus we cannot at this time state a clear prediction for the ground state geometry for parent chloroethyl cation. What is apparent is that the two competing forms are nearly equal in stability and that even moderate substituent effects might have considerable significance in altering the delicate equilibria.

Olah has postulated the 1-fluoroethyl cation to be formed as a result of fluoride abstraction from 1,1-difluoroethane by SbF_5.[9,10] Evidence for the existence of the $MeCHF^+\cdots SbF_6^-$ counterion pair is not based

$$MeCHF_2 + SbF_5 \rightleftarrows MeCHF^+ + SbF_6^-$$

on direct observation but rather on the temperature dependence of the proton magnetic resonance spectra interpreted as indicating rapid fluorine exchange between the two partners. Direct structural evidence on this parent species is lacking, and other forms of fluoroethyl cation (in particular a fluorine-bridged moiety) remain to be experimentally characterized.

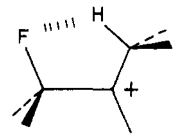
The experimental situation regarding chloroethyl cation is more interesting. Here, upon addition of 1-chloro-2-fluoroethane to an admixture of antimony pentafluoride and sulfuryl chloride (another variant of "magic acid") an nmr spectrum consistent with the presence of two products, the 1-chloroethyl cation and the chlorine-bridged ethyl cation, is observed. The observation of the two together (that is under identical experimental conditions) might well be taken to imply their closeness in energy (but see discussion below). In addition Olah suggests the ^{13}C results on the 1-chloroethyl cation to be interpretable in terms of significant participation of resonance forms, consistent with our findings of a short carbon–chlorine bond. Perhaps most intriguing is Olah's observation that the two stable ions do not (readily) interconvert.[52] Thus our notion of a significant potential separating the two is supported.



C. Effects of Alkyl Substituents. In this section we consider the effects of simple alkyl substituents in altering the energetic profile of the haloethyl cation potential surface. Our interest is twofold. In the first instance we shall be interested in learning to fabricate stable (and thus, we hope, observable) alkyl-substituted forms of a given parent tautomer, structures which without the benefit of such substituents would have no stable existence. In particular we will be on the lookout for substituted 2-haloethyl cations. Our second interest stems from the rich literature on alkyl-substituted fluoro- and chloroethyl cations. We will have a much better opportunity here than we did with the parent ions to confirm or contest many aspects of our theoretical observations.

Because of the size of the alkyl-substituted ions in which we are interested, theoretical molecular orbital calculations even at the 4-31G level are (economically) infeasible at this time. As before we shall have to rely on the ability of simple levels of theory (this time the minimal STO-3G basis will be our solitary probe[53]) to realistically estimate the energies of the *isodesmic* processes which we shall employ to describe the energetic effects of substituent groups on the parent moieties.

STO-3G total energies for alkyl-substituted fluoro- and chloroethyl cations are presented in Table V. Note that a 1-methyl substituent preferentially adopts a syn relationship to the halogen in the substituted 2-fluoroethyl cation, perhaps indicative of the formation of a weak hydrogen bond.[54] In the corresponding



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(51) L. Radom, W. A. Lathan, P. C. Hariharan, W. J. Hehre, and J. A. Pople, *Fortschr. Chem. Fortsch.*, 40, 1 (1973).

(52) Although the ratio of the two products is temperature dependent it is only the concentration of 1-chloroethyl cation and not the bridged ion which is affected. Olah has demonstrated that the former species is in equilibrium with the 1-fluoroethyl cation.

$$\begin{tikzcd}
MeCHCl^+ \arrow[r, shift left, "SbF_6^-"] & MeCHClF \arrow[l, shift left, "SbF_5"] \arrow[d, shift left, "SbF_5"] \\
MeCHF_2 \arrow[r, shift left, "SbF_6^-"] & MeCHF^+ \arrow[l, shift left, "SbF_5"] \arrow[u, shift left, "Cl^-"]
\end{tikzcd}$$

(53) Even at the STO-3G level the energies of *isodesmic* processes such as those considered here seem to be well described. For a survey, see L. Radom, W. J. Hehre, and J. A. Pople, *J. Chem. Soc. A*, 2299 (1971).

(54) Experimental evidence regarding this point is mixed. Thus, while the neutral saturated analog of the 1-methyl-2-fluoroethyl cation, *n*-propyl fluoride, does indeed adopt a gauche as opposed to trans ground state conformation,[55] so too does *n*-propyl chloride.[56] For a theoretical discussion of possible intramolecular hydrogen bonding in these and related systems, see L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **95**, 693 (1973).

(55) E. Hirota, *J. Chem. Phys.*, 37, 283 (1962).

(56) T. N. Sarachman, *J. Chem. Phys.*, **39**, 469 (1963).

Table V. Theoretical (STO-3G) Energy Data for Alkyl-Substituted Haloethyl Cations

Position and nature of substituents	Halogen	
	Fluorine	Chlorine
1-Haloethyl cations		
1-Methyl	−213.51460	−570.02123
1-Ethyl	−252.09747	−608.60434
1-Isopropyl	−290.67993	−647.18700
1-*tert*-Butyl	−329.26143	−685.76361
2-Haloethyl cations[a]		
syn-1-Methyl	−213.46058	−569.99803
anti-1-Methyl	−213.45878	−579.99841
2-Methyl	−213.43042	−569.96789
1,1-Dimethyl	−252.07205	−608.61015
syn-1,2-Dimethyl	−252.04867	−608.58500
anti-1,2-Dimethyl	−252.04295	−608.58209
2,2-Dimethyl	−252.01763	−608.55433
1,1,2-Trimethyl	−290.65521	−647.19287
syn-1,2,2-Trimethyl	−290.63464	−647.17022
anti-1,2,2-Trimethyl	−290.62517	−647.16415
Tetramethyl	−329.23562	−685.77402
Halogen bridged ethyl cations		
Methyl	−213.47326	−570.00922
1,1-Dimethyl	−252.07199	−608.60665
syn-1,2-Dimethyl	−252.06586	−608.60001
anti-1,2-Dimethyl	−252.07288	−608.60738
Trimethyl	−290.66349	−647.19652
Tetramethyl	−329.25305	−685.78469
Halomethyl cations		
Ethyl	213.48411	−569.99294
Isopropyl	252.06815	−608.57763

[a] The labels syn and anti refer to the relationship between the halogen and the methyl substituent on the 1 position.

chlorine system the syn and anti conformers are within a fraction of a kilocalorie of each other, the latter being the favored this time. Syn orientations are also the favored for the 1,2-dimethyl- and 1,2,2-trimethyl-2-fluoro- and chloroethyl cations, an effect, in addition to the hydrogen-bonding possibilities discussed above, which is no doubt due in part to a minimization of steric repulsions. Similarly steric effects dictate that vicinal methyl substituents on the halogen-bridged ethyl cations take on an anti as opposed to syn orientation.

Four basic types of *isodesmic* processes are required in order to represent the stabilizing effect of one or more alkyl substituents on the parent haloethyl cation forms. Thus, for example, the effect of a single alkyl substituent R (methyl, ethyl, isopropyl, or tertiary butyl) directly bonded to the positively charged center of a 1-haloethyl cation is given by the energy of the *isodesmic* process 7. Correspondingly, the added stabilization resulting from the replacement of a methyl group by a larger alkyl substituent R is given by (8).

$$\mathrm{MeCRX^+ + CH_4 \longrightarrow MeCHX^+ + CH_3R} \quad (7)$$

$$\mathrm{RC^+HX + CH_4 \longrightarrow CH_3C^+HX + RH} \quad (8)$$

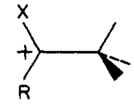
Similarily the ability of methyl substituents (this time from 1 to 4 of them) to stabilize the parent 2-haloethyl ions is represented by reaction scheme 9. Finally substituent effects (again from one to four attached methyls) in the halogen-bridged ions are given by (10).

$$\mathrm{CMe}_m\mathrm{H}_{2-m}\mathrm{XCMe}_n\mathrm{H}_{2-n}{}^+ + (m+n)\mathrm{CH_4} \longrightarrow \mathrm{CH_2XCH_2}^+ + (m+n)\mathrm{CH_3Me} \quad (9)$$

$$\overline{\mathrm{CMe}_m\mathrm{H}_{2-m}\mathrm{CMe}_n\mathrm{H}_{2-n}\mathrm{X}}^+ + (m+n)\mathrm{CH_4} \longrightarrow \overline{\mathrm{CH_2CH_2X}}^+ + (m+n)\mathrm{CH_3Me} \quad (10)$$

The resulting stabilization energies for the four processes 7 through 10 are listed in Tables VI–IX, respectively. Combined with our best values for the

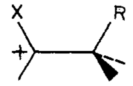
Table VI. (1) Alkyl-Substituent Effects on 1-Haloethyl Cations[a]



R	X: F	Cl
Me	23.2	21.6
Et	25.3	23.7
i-Pr	26.8	25.4
t-Bu	27.8	23.3

[a] Energies (kcal/mol) of the *isodesmic* reactions $\mathrm{MeCRX^+ + CH_4 \rightarrow MeCHX^+ + CH_3R}$. Theoretical (STO-3G) energies used taken from Table IV and V and: methane, −39.72670; ethane, −78.30549; isopropane, −116.88512; isobutane, −155.46511; neopentane, −194.04507.

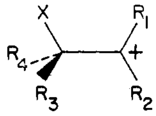
Table VII. (2) Alkyl Substituent Effects on 1-Haloethyl Cations[a]



R	X: F	Cl
Et	4.1	3.8
i-Pr	6.9	7.0

[a] Energies (kcal/mol) of the *isodesmic* reactions $\mathrm{RCHX^+ + CH_4 \rightarrow CH_3CHX^+ + RH}$. Theoretical (STO-3G) energies used taken from Tables IV and V and: methane −39.72670; ethane; −78.30549; isopropane; −116.88512.

Table VIII. Methyl-Substituent Effects on 2-Haloethyl Cations[a]



X = F	
R_1 = Me	25.7*
R_3 = Me	6.8
$R_1 = R_2$ = Me	46.2*
$R_1 = R_3$ = Me	31.5
$R_3 = R_4$ = Me	12.1
$R_1 = R_2 = R_3$ = Me	49.0*
$R_1 = R_3 = R_4$ = Me	36.0
$R_1 = R_2 = R_3 = R_4$ = Me	50.5*
X = Cl	
R_2 = Me	24.9*
R_3 = Me	5.7
$R_1 = R_2$ = Me	45.9*
$R_1 = R_3$ = Me	30.1
$R_3 = R_4$ = Me	10.9
$R_1 = R_2 = R_3$ = Me	48.0*
$R_1 = R_3 = R_4$ = Me	33.8
$R_1 = R_2 = R_3 = R_4$ = Me	49.5*

[a] Energies (kcal/mol) of the *isodesmic* reactions ($\mathrm{CR_3R_4XCR_1R_2^+ + \mathit{n}CH_4 \rightarrow CH_2XCH_2^+ + CH_3R_1 + \ldots}$) where *n* is the number of R methyl substituents. Unless specified otherwise R_1, R_2, R_3, and R_4 are hydrogens. Theoretical (STO-3G) energies used taken from Tables IV and V and: methane, −39.72670; ethane, −78.30549.

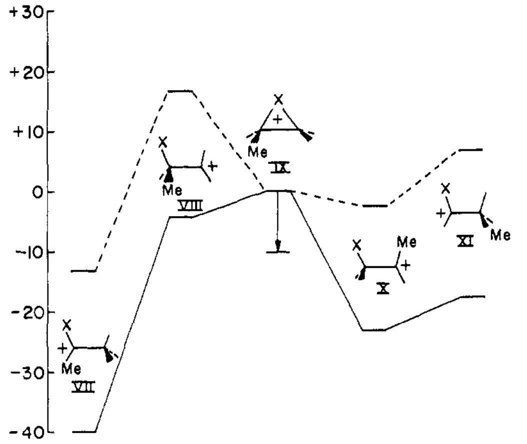
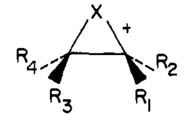


Figure 9. Energy map (kcal/mol), relative to the methyl-substituted halogen-bridged ethyl cations (IX)) for monomethyl-fluoro- and chloroethyl cations.

Table IX. Methyl-Substituted Effects on Halogen-Bridged Ethyl Cations[a]



X = F	
R_1 = Me	14.0*
R_1 = R_2 = Me	26.5
R_1 = R_4 = Me	27.1*
R_1 = R_2 = R_3 = Me	34.5*
R_1 = R_2 = R_3 = R_4 = Me	41.3*
X = Cl	
R_1 = Me	13.0*
R_1 = R_2 = Me	24.7
R_1 = R_4 = Me	25.1*
R_1 = R_2 = R_3 = Me	31.6*
R_1 = R_2 = R_3 = R_4 = Me	37.5*

[a] Energies (kcal/mol) of the *isodesmic* reactions

$$\overline{\mathrm{CR_1R_2CR_3R_4X}} + n\mathrm{CH_4} \rightarrow \overline{\mathrm{CH_2CH_2X}} + \mathrm{CH_3R_1} + \ldots$$

where n is the number of R methyl substituents. Unless otherwise specified R_1, R_2, R_3, and R_4 are hydrogens. Theoretical (STO-3G) energies taken from Tables IV and V and: methane, −39.72670; ethane, −78.30549.

relative energies of the parent haloethyl species (4-31G and 6-31G**) they provide reasonable theoretical estimates for the stabilities of a diverse range of alkyl-substituted ions. The results of such a treatment are displayed pictorially in Figures 9–13.

The potential surface for interconversion among the various isomers of monomethyl-substituted fluoro- and chloroethyl cations is considered first (Figure 9). Here, as in the examples which follow, energies are presented relative to those of the methyl-substituted halogen-bridged ions as given by the 4-31G basis. Correction of the "zero" value for its anticipated deviation from experiment is indicated by a lowering of 10.2 kcal/mol. As commented previously, whereas such a correction (based on energy differences between theory and experiment for the ethylene oxide–acetaldehyde pair of isomers) is expected to be reasonably appropriate for the isoelectronic fluorine-substituted ions, its value in improving the chloroethyl cation data is questionable. Certainly (for reasons explained earlier) it represents a maximum correction, and hence resulting bridged ion energies a lower bound. In this figure and in the diagrams which follow, solid lines connect fluoroethyl cations while dashes string together the chloroethyl tautomers.

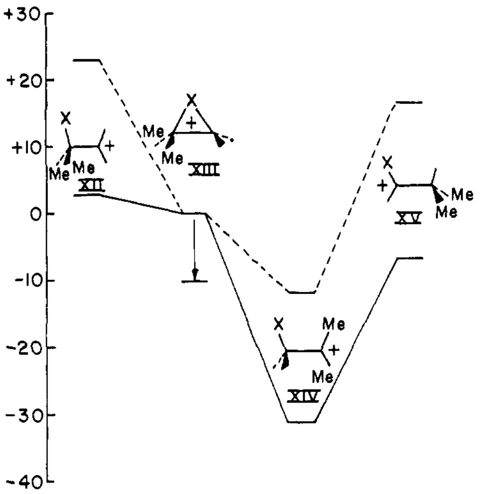


Figure 10. Energy map (kcal/mol, relative to the 1,1-dimethyl-substituted halogen-bridged ethyl cations (XIII)) for 1,1-dimethyl-fluoro- and chloroethyl cations.

Considering the methyl-substituted cations first we see that the 1-methyl-1-fluoroethyl structure (VII) is the lowest energy form. The 4-31G basis results would have us believe that the energy of the fluorine-bridged structure (IX) is above that of the 2-methyl-2-fluoroethyl form (VIII),[57] rendering the former unstable with respect to geometrical distortion (but not necessarily guaranteeing the stability of VIII), but the finding is upset if we correct for basis improvement. Both levels of theory do predict, however, that the 1-methyl-2-fluoroethyl cation (X) falls in an energy well between the bridged ion (IX) and the 2-methyl-1-fluoroethyl cation (XI), providing us with the simplest example of a situation where a 2-haloethyl cation might be trapped and subsequently observed.

Our treatment of methyl-substituted chloroethyl cation leaves little doubt as to the instability of 2-chlorine-substituted forms. Taking into account the full brunt of the correction for improved basis set description (although in fact only a small fraction of this correction is necessary in order for our contentions to hold), the most stable structure found is the 1-methyl-1-chloroethyl cation (VII), followed closely by the chlorine bridged ion (IX).

The most stable form of geminally substituted dimethyl fluoroethyl cation is XIV (Figure 10). In all likelihood all other structures collapse to it with little or no activation. 1,1-Dimethyl-2-chloroethyl cation (XIV) is also predicted to be the favored isomer, although here the energy of the bridged ion (XIII) is probably not much higher. Here again, in both of these cases the possibility for detection of stable 2-haloethyl systems seems great.

Opposite behavior is suggested by the theory for the vicinal dimethyl-substituted fluoro- and chloroethyl

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[57] For reasons of clarity we shall refer to our alkyl-substituted systems as derivatives of the parent ethyl cations, rather than in the usual manner based on derivatives of the longest carbon chain. Thus, a 2-methyl-substituted 3-haloethyl cation is referred to by exactly that name rather than as a 2-halopropyl ion.

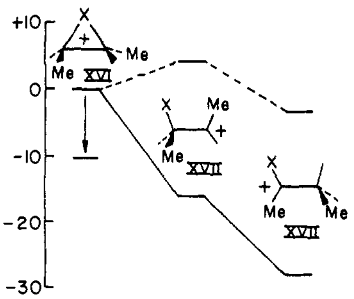


Figure 11. Energy map (kcal/mol, relative to the 1,2-dimethyl-substituted halogen-bridged ethyl cations (XVI)) for 1,2-dimethylfluoro- and chloroethyl cations.

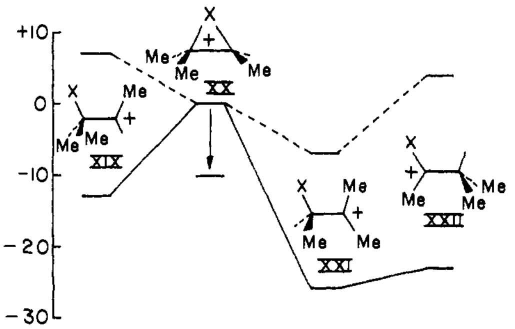


Figure 12. Energy map (kcal/mol, relative to the trimethyl-substituted halogen-bridged ethyl cations (XX)) for trimethylfluoro- and chloroethyl cations.

cations (Figure 11). Whereas only the acyclic 1,2-dimethyl-1-fluoroethyl cation (XVII) is indicated to be a stable entity (assuming as we have free interconversion between neighboring forms) both the analogous chlorine structure and the bridged chloronium ion (XVI) are seen to be local minima of similar energy. One possible barrier to their interconversion may be thought of as the energy of the dimethyl-substituted 2-chloroethyl system (XVII).

Two trimethyl-substituted fluoroethyl cations are slated for existence by the theory (Figure 12), the secondary 1,2,2-trimethyl-2-fluoroethyl cation (XIX) and the analogous tertiary system (XXI). The bridged ion (XX) is seen to be only slightly higher in energy than the former, however, and if we assume that it is one possible transition state for their interconversion, conditions under which XIX would actually be observable would indeed be difficult to achieve.

As before the corresponding chloroethyl series of cations exihibit an entirely different pattern of behavior. The chlorine-bridged ion (XX) and the acyclic tertiary species (XXI) are, it would appear, too close in energy for a clear prediction to be made concerning the geometrical structure of the ground state form.

Finally the acyclic tetramethyl-substituted fluoroethyl cation (XXIV) is more stable than the bridged system (XXIII) (Figure 13), while the energy ordering in the analogous chlorine-containing ions is probably the opposite.

A comparison of the over-all effects of alkyl groups in stabilizing each of the three isomeric forms of the fluoroethyl cation as a function of the number of such substituents is given in Figure 14.[58] As before we consider the stability of substituted ions to be represented as the relative stability of the parents (with respect to the 1-fluoroethyl cation as a standard) plus the energy of the appropriate *isodesmic* process depicting substitution. Both data based on relative parent energies as given by the 4-31G basis and that corrected for the probable effects of an improved orbital description are presented for the alkyl-substituted cyclic cations, the latter being represented by the lower of the two parallel curves. Methyl substitution in bridged fluoroethyl cation follows an approximately additive pattern. While the first two substituents contribute 14.0 and 13.1 kcal/mol, respectively, toward the stability of the parent, the energetic effect of the final methyls is somewhat less (7.8 and 6.8 kcal/mol for the third and forth group, respectively). This is, no doubt, due in part to steric crowding and would, we think, be partially relieved if a complete geometric optimization of the methyl-substituted ions had been performed.

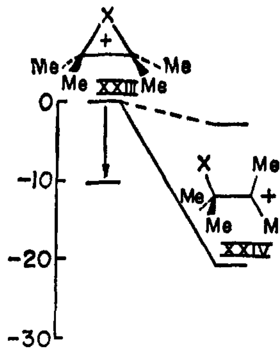


Figure 13. Energy map (kcal/mol, relative to the tetramethyl-substituted halogen-bridged ethyl cations (XXIII)) for tetramethylfluoro- and chloroethyl cations.

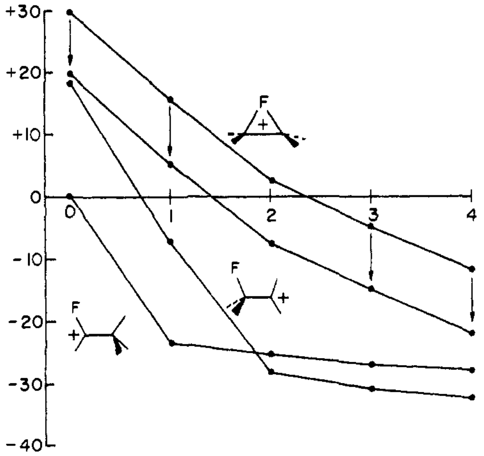


Figure 14. Relative stability of isomeric forms of alkyl-substituted fluoroethyl cations. Lower curve for bridged ions represents probable correction for improved basis description.

The initial pair of methyl groups on the 2-fluoroethyl cation (both directly attached to the positively charged center) provide almost the total possible stabilization. Indeed further methyl substitution at the two available 2 positions contributes but an additional 4.3 kcal/mol.

The substitution curve for the 1-fluoroethyl cation represents the effect of increase in size of a single alkyl substituent directly bonded to the cationic center.

[58] Theoretical data needed in the construction of this and the proceding figure are taken from Table IV (for the parent ions) and from the starred values of Tables VI, VIII, and IX.

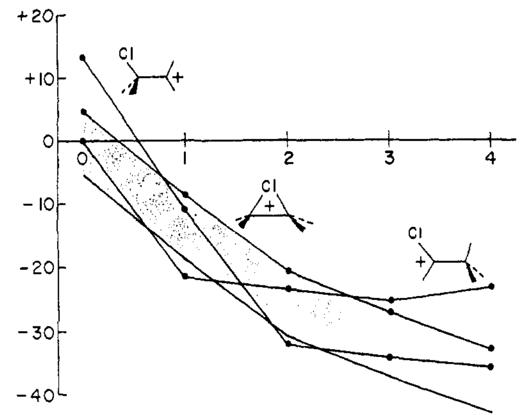
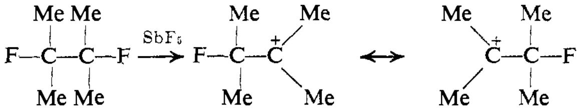


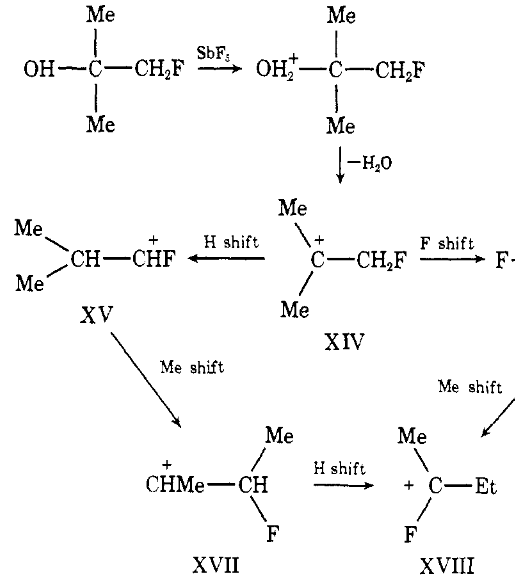
Figure 15. Relative stability of isomeric forms of alkyl-substituted chloroethyl cations. Shaded area represents probable energy limits for bridged ions.

As expected initial substitution by the simplest alkyl substituent, a methyl, is important (a stabilization of 23.2 kcal/mol is found), while progression to a tertiary butyl substituent results in but a 4.6 kcal/mol further energy stabilization. The size of the differential inductive effect here (difference in stabilizing abilities of the methyl and tertiary butyl substituents) is similar indeed to that of 3.1 kcal/mol found for "para" alkyl groups on the stability of protonated benzene.[59]

Thus far the nmr spectra of only two alkyl-substituted fluoroethyl cations have been reported. The "magic acid" ($SbF_5 \ldots FSO_4$) ionization of 2,3-dimethyl-2,3-difluorobutane results in an ion the nmr spectrum of which is interpretable in terms of a rapidly equilibrating pair of open tetramethyl-substituted 2-fluoroethyl cations, rather than a static-bridged fluoronium ion.[3] The theory agrees in assigning the acyclic 2-fluoroethyl cations at least 10 kcal/mol lower in energy than the cyclic counterpart.



Protonation of 1-fluoro-2-methyl-2-propanol followed by loss of water results in a species the nmr spectrum of which has been interpreted by Olah as characterizing the methyl ethyl fluorocarbonium ion (XVIII).[4] Reaching such a structure from the initially formed 1,1-dimethyl-2-fluoroethyl cation (XIV) would seem to require a series of F and Me (or H and Me) shifts. The theory suggests the closeness in energy of XIV and XVII (although the 1,1-dimethyl-2-fluoroethyl system is predicted to be 3 kcal/mol the more stable) but also implies any such rearrangement processes as those described above would require considerable activation.[60] The matter requires further scrutiny.



The theory is in agreement with the nonobservation of cyclic fluoronium ions. The calculations indicate that the nearest in energy they come to the most stable acyclic form is the 10 kcal/mol difference between tetramethyl fluoronium and 2-fluoroethyl cations, XXIII and XXIV, respectively.

Figure 15 depicts the corresponding substituent effects on the three isomeric forms of chloroethyl cation. This time a shaded area extends below the line representing substitution on the bridged chloronium ion indicating the range of uncertainty for corrections to the theory in order to reproduce the experimental data on the parents. The comments made previously for substitution in the fluoroethyl cations equally well apply here. Thus, a near additive behavior is noted for continued methyl substitution on bridged chloronium ion, tapering off somewhat in the final stages probably due in part to steric crowding. As before the first two methyl substituents on the 2-chloroethyl system (both directly bonded to the carbonium center) provide us with the greater part of the total stabilization energy, and again the magnitude of the differential inductive effect (comparing the stabilities of 1-methyl and 1-*tert*-butyl-1-chloroethyl cations) is small. This time a slight destabilizing effect is noted in progressing from an isopropyl to tertiary butyl alkyl substituent, probably a remnant of steric crowding due to a poor choice of molecular geometry.

The experimental situation regarding alkyl-substituted chloroethyl cations is much more complete than the fluoroethyl story. Ionization of either of 2,3-dimethyl-2,3-dichloro- or 2-methyl-2,3-dichlorobutane results in ions the spectra of which have been interpreted in terms of static-bridged structures, corresponding no doubt to XXIII and XX, respectively. The nmr spectrum of the latter (trimethyl substituted) species is interesting in that the geminal methyl groups appear to be equivalent. This may be due to an accidental degeneracy or as a result of the involvement of a (freely rotating) acyclic 2-chloroethyl cation.[4] Although, because of a failure to detect any temperature dependence in the magnetic resonance spectrum, the authors prefer the former interpretation, that progression through the tertiary 2-chloroethyl cation (XXI) should indeed be a facile process can be seen by its closeness in energy to

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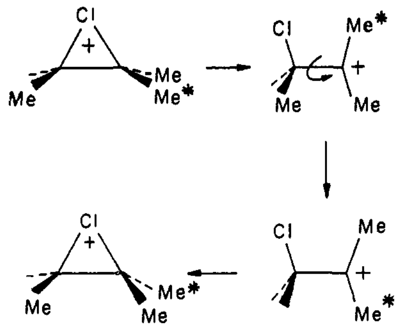
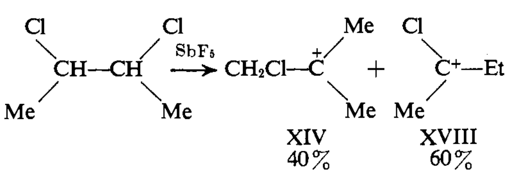
(59) W. J. Hehre, R. T. McIver, Jr., J. A. Pople, and P. v. R. Schleyer, manuscript in preparation; see also ref 26.

(60) Thus we can estimate the energy of XII (the approximate transition state for the right-hand path) to be 34.1 kcal/mol above XIV and the highest energy point proceeding *via* the left-hand mechanism (structure XV) to lie some 24.3 kcal/mol above. Considering the right-hand pathway, the midpoint for fluorine (or fluoride) shift lies intermediate in energy between reactant and product structures (XIV and XII, respectively) and that for methyl migration no doubt between XII and XVIII. It is conceivable, however, turning to the route on the left, that the transition state for hydrogen (or hydride) migration is higher in energy than either reactant or product species (XIV and XV, respectively), thus increasing somewhat our proposed 24.3 kcal/mol value for the activation required in order to reach XVIII.

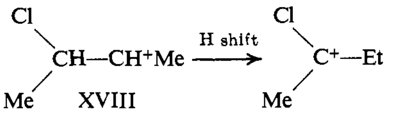


the trimethyl chloronium ion XX. A labeling experiment could prove of some use here. Upon "magic acid" ionization of 2-methyl-2,3-dichloropropane the spectrum of the open ion (XIV) is recorded,[5] in agreement with the theory's suggestion for the most stable dimethyl-substituted chloroethyl cation. Dissolution of isomeric 2,3-dichlorobutane, however, results in an admixture of two product ions. The methylethyl



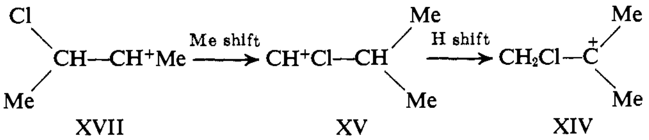
$$\mathrm{Cl(Me)CH{-}CH(Me)Cl} \xrightarrow{\mathrm{SbF_5}} \underset{\substack{\mathrm{XIV}\\ 40\%}}{\mathrm{CH_2Cl{-}\overset{+}{C}Me_2}} + \underset{\substack{\mathrm{XVIII}\\ 60\%}}{\mathrm{Cl(Me)C^+{-}Et}}$$

chlorocarbonium ion XVIII is easily derived from the initially formed secondary ion (XVII) by a hydrogen shift (a process which as detailed previously should require no activation), but the formation of the 1,1-dimethyl-2-



$$\underset{\mathrm{XVIII}}{\mathrm{Cl(Me)CH{-}CH^+Me}} \xrightarrow{\text{H shift}} \mathrm{Cl(Me)C^+{-}Et}$$

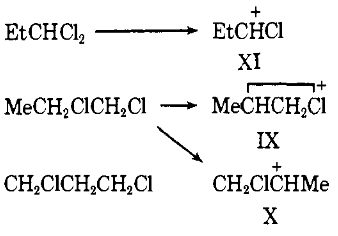
chloroethyl cation (XIV) requires a sequence of methyl and then hydrogen shifts. The intermediate ion (XV)



$$\underset{\mathrm{XVII}}{\mathrm{Cl(Me)CH{-}CH^+Me}} \xrightarrow{\text{Me shift}} \underset{\mathrm{XV}}{\mathrm{CH^+Cl{-}CHMe_2}} \xrightarrow{\text{H shift}} \underset{\mathrm{XIV}}{\mathrm{CH_2Cl{-}\overset{+}{C}Me_2}}$$

formed as a result of such a sequence is some 14.2 kcal/mol higher in energy than XVII, so discounting any additional energy in order to achieve the transition states for methyl and hydrogen migration, at least that amount of activation is required.

Upon acid ionization of 1,1-, 1,2- or 1,3-dichloropropane, an nmr spectrum corresponding to an admixture of three methyl-substituted chloroethyl cations results. It is clear that while ionization of the 1,1-dihaloalkane leads directly to XI and that of 1,2-



$$\mathrm{EtCHCl_2} \longrightarrow \underset{\mathrm{XI}}{\mathrm{Et\overset{+}{C}HCl}}$$

$$\mathrm{MeCH_2ClCH_2Cl} \longrightarrow \underset{\mathrm{IX}}{\mathrm{MeCHCH_2Cl^+}}$$

$$\mathrm{CH_2ClCH_2CH_2Cl} \qquad \underset{\mathrm{X}}{\mathrm{CH_2Cl\overset{+}{C}HMe}}$$

dichloropropane to both IX and X, the ion initially formed from the 1,3-halogen-substituted alkane must undergo extensive skeletal rearrangement. The theoretical results support the experimental observation of the coexistence of IX and X, explaining it in terms of the closeness in energy of the two (the bridged ion predicted to be the more stable species). Theory and experiment disagree, however, on one and possibly two important points. First, the 2-methyl-1-chloroethyl cation XI is energetically speaking not competitive with the other two nor is it envisioned by the theory as being isolated by a sizable potential barrier. Second, the theory predicts that the most stable isomer of monomethylchloroethyl cation is none of the species considered here but rather the 1-methy-1-chloroethyl system (VII). Further investigation is warranted.

Conclusion

We have presented a theoretical *ab initio* molecular orbital study of the structures and energetics of the fluoro- and chloroethyl cations and their simple alkyl-substituted derivatives. The following interesting features have come to light.

1. The energetic potential surface for both ions contains but two minimum energy forms. For the lighter halogen system, the acyclic 1-fluoroethyl cation is the absolute minimum, the halogen-bridged structure also being stable but falling somewhat higher in energy. The 2-fluoroethyl cation is unstable with respect to distortion in the direction of either of these two, and hence may be thought of as one possible transition state for their interconversion. Similarily, hydrogen-bridged structures are found not be be stable. The same two potential minima appear in the chloroethyl system although in this instance their respective energies are too close to permit a clear assignment by the theory of the ground state equilibrium geometry. As before, 2-halogen-substituted forms as well as hydrogen-bridged structures are unstable with respect to distortion toward one or both of the energy minima.

2. The 1-haloethyl cations exihibit no conformational preference for the methyl group to eclipse or to stagger the carbon–halogen bond. The former arrangement would have been expected. 2-Haloethyl cations are found to prefer eclipsed as opposed to bisected arrangements of the carbonium center about the halogen bond in agreement with the predictions of simple perturbation theoretic agruments.

3. Fluorine- and chlorine-bridged ethyl cations are seen to be well described in terms of formally divalent and positively charged halogens rather than in the language of delocalized σ or three-center bonding theory. Geometrical parameters are close indeed to what one would expect from investigations of the structures of the acyclic halogen cations, molecules in which delocalized bonding schemes would not seem to be applicable.

4. By invoking specific alkyl-substitution patterns any given form of the fluoro- and chloroethyl cations may be stabilized in preference to all others. In particular, the 2-haloethyl cations, not stable as parent forms, can be made to become the predominant species.

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