Tetrahedron Vol. 44, No. 24, pp. 7489 to 7498, 1988
Printed in Great Britain

0040-4020/88 $3.00 + .00
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REEXAMINATION OF THE $C_2H_4F^+$ POTENTIAL SURFACE. THE STATUS OF THE CLASSICAL 2-FLUOROETHYL CATION: A LOCAL MINIMUM OR TRANSITION STRUCTURE? †

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(*Received in USA* 3 *April* 1988)

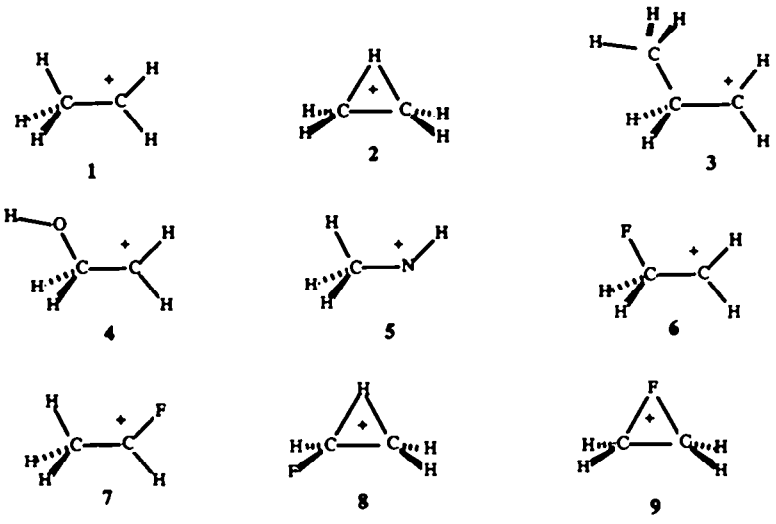
Abstract: According to *ab initio* molecular orbital calculations carried out with full geometry optimization at the MP2/6-31G** level, the classical 2-fluoroethyl cation, $FCH_2CH_2^+$, is a transition structure for H-scrambling in CH_3CHF^+. Single point MP4/6-31G** calculations at the optimized geometries predict the cyclic ethylene fluoronium ion to lie 24.2 kcal mol^{-1} above CH_3CHF^+ and 5.4 kcal mol^{-1} below the 2-fluoroethyl cation. $\Delta G^{\ddagger}$ for ring opening of the cyclic fluoronium ion at -60° is estimated to be *ca* 15 kcal mol^{-1}. This barrier is largely attributable to the powerful negative fluorine hyperconjugation in the transition state as described by Hoffmann and coworkers. When electron correlation effects are ignored a qualitatively different potential surface is obtained on which the 2-fluoroethyl cation is calculated to be a local minimum separated from the stable 1-fluoroethyl cation by an H-bridged transition state.

INTRODUCTION

While the transient existence of primary alkyl carbenium ions in solution can sometimes be inferred from isotopic scrambling experiments,[1] the primary ions, unlike their secondary and tertiary relatives, have so far eluded detection under stable-ion conditions.[2] In the gas-phase, primary carbenium ions have been similarly elusive.[3-5] The ethyl cation (1) formed on photoionization of the corresponding radical, for example, rearranges spontaneously to the "non-classical" bridged structure 2.[3] The 1-propyl cation (3), formed on radiolysis of alkanes, is converted in less than 10^{-10} sec to the 2-propyl cation and protonated cyclopropane derivatives.[5]

A clearer understanding of the structures and energies of gaseous carbocations has been a long standing goal in which theoretical calculations have played central a role.[6-7] The MINDO/3 method introduced by Dewar and coworkers[8] in 1975 proved especially successful in this area.[9-12] The relative energetics of

† Dedicated to Professor M. J. S. Dewar in the year of his 70th birthday.



alternative species on both the $C_2H_5^+$ and $C_3H_7^+$ potential surfaces predicted by this method,[10,11] for example, agree well with what is known experimentally[3,4] and with high level *ab initio* molecular orbital calculations by Pople and coworkers[13] employing polarized basis sets and extensive corrections for electron correlation. Both the semiempirical and *ab initio* methods correctly predict the primary ions to be higher in energy than the secondary or non-classical ions. More interestingly, examination of the MINDO/3 and *ab initio* HF/6-31G* force constant matrices for 1[13,14] and 3[15,16] show both to be transition structures and not local minima.

We recently found a similar situation for the 2-hydroxyethyl cation (4). At the *ab initio* HF/6-31G* level, this is also predicted to be a transition structure.[17] The same is true of the singlet nitrenium ion 5, which is isoelectronic with 1.[18] Together these results seemed to suggest that electron deficient primary cations do not generally[19] correspond to potential minima, but to transition states. It was therefore with surprise that we discovered[16] the classical 2-fluoroethyl cation (6) to be a local minimum at this level, especially since the β-fluorine is expected to *destabilize* the already unstable primary ion.[20]

That 6 might be a local minimum was particularly intriguing since the transition state for its conversion to the stable 1-fluoroethyl cation (7) should be a structure akin to 8, a fluorine substituted analog of 2. The bonding in such "non-classical" species has been significantly clarified by M. J. S. Dewar who pointed out their relationship to alkene π-complexes many years ago[21] and has subsequently provided much enlightening discussion.[9-11,22,23] An essential feature of such bonding is electron donation from the highest filled orbital of the alkene to a vacant *s* or *sp* type orbital of the apical atom.[23] The destabilization of 8 by the strongly electron withdrawing fluorine atom bound directly to the basal alkene moiety therefore seems entirely plausible. A hydrogen bridged species of this kind had indeed been considered in two previous theoretical studies[24,25] although both were carried out at a time when adequate theoretical procedures for its evaluation were unavailable.

The cyclic fluoronium ion (9), an isomer of 6 and 7, has attracted considerable theoretical interest.[15,24,27] Unlike the higher halo analogs, all attempts to detect this species under stable ion conditions have failed.[28] To varying degrees, previous theoretical studies in this area[15,24-27] have focussed on the energetic relationships between the open and cyclic ions. However, with one exception,[15] these studies have entirely ignored the effects of electron correlation, now known to be essential if even relative energetics are to be predicted correctly.[15]

With our interest piqued by the HF/6-31G* results for the primary fluoroethyl cation mentioned above, we decided to carry out a complete reevaluation of this potential surface at a level of theory comparable to that used by Pople and coworkers in their study of the C_2 and C_3 cations.[13]

METHODOLOGY

All calculations were performed using the GAUSSIAN82 program system.[29] Geometries were optimized at the Hartree-Fock level using the split valence 6-31G* and 6-31G** basis sets[30] and with the inclusion of electron correlation via second order Moller-Plesset theory[31] (MP2) using the 6-31G** basis set. Force constant calculations were carried out on all HF/6-31G* geometries thereby characterizing them as either equilibrium structures or saddle points on the basis of the number of negative eigenvalues. The significantly more computationally intensive force constant calculations at the MP2/6-31G** level were carried out only in selected cases. Single point calculations with valence shell correlation corrections at the Moller-Plesset third[32] (MP3), and partial fourth[33] (MP4(SDQ)) order were performed on the MP2/6-31G** geometries.

RESULTS

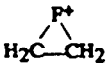
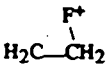
Calculated total energies using the HF/6-31G* and MP2/6-31G** optimized geometries are collected in Tables 1 and 2. Where force constant calculations were carried out the number of negative eigenvalues of the force constant matrices are shown in parentheses following the energy. The HF/6-31G* geometries changed very little on refinement at the HF/6-31G** level while the corresponding total energies were virtually indistinguishable from those obtained in the single point calculations. The HF/6-31G*//HF/6-31G* data were therefore not included in the Tables but may be obtained from the authors on request. The transition structure (8) for interconversion of 6 and 7 was initially located using MNDO[34] followed by refinement at the HF/6-31G* level. However, no stationary point of this kind appears to exist on the MP2/6-31G** surface. All attempts to further refine this structure at the higher level of theory led directly to 7.

Table 1. Total Energies (a.u.) Using HF/6-31G* Geometries.[a]

Molecule		Symmetry	HF/6-31G*	HF/6-31G**	MP2/6-31G*	MP2/6-31G**
$FCH_2CH_2^+$	(6)	C_s	-177.13552 (0)	-177.14331	-177.53071	-177.56027
CH_3CHF^+	(7)	C_s	-177.17465 (0)	-177.18218	-177.58086	-177.61069
	(8)	C_1	-177.13338 (1)	-177.14220	-177.53563	-177.56630
	(9)	C_{2v}	-177.12763 (0)	-177.13485	-177.54227	-177.57197
	(10)	C_1	-177.11989 (1)	-177.12711	-177.51299	-177.54267
CH_3CHF^+	(11)	C_s	-177.17401 (1)	-177.18143	-177.57981	-177.60953

[a] The number of negative roots of the force constant matrix is given in parentheses following the energy.

Table 2. Total Energies (a.u.) Using MP2/6-31G** Geometries.[a]

Molecule	Symmetry	HF	MP2	MP3	MP4(SDQ)
$FCH_2CH_2^+$ (6)	C_s	-177.14163	-177.56207 (1)	-177.58415	-177.59297
CH_3CHF^+ (7)	C_s	-177.18117	-177.61185	-177.62944	-177.64011
 (9)	C_{2v}	-177.13447	-177.57250 (0)	-177.58918	-177.60161
 (10)	C_1	-177.12605	-177.54391 (1)	-177.56629	-177.57654

[a] The number of negative roots of the force constant matrix is given in parentheses following the energy.

Table 3. Relative Energies (kcal mol^{-1}) Using HF/6-31G* Geometries.

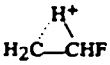
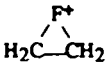
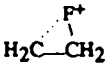
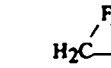
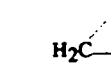
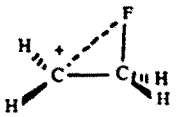
Molecule	Symmetry	HF/6-31G*	HF/6-31G**	MP2/6-31G*	MP2/6-31G**
$FCH_2CH_2^+$ (6)	C_s	24.6	24.4	31.5	31.6
CH_3CHF^+ (7)	C_s	0	0	0	0
 (8)	C_1	25.9	25.1	28.4	27.9
 (9)	C_{2v}	29.5	29.7	24.2	24.3
 (10)	C_1	34.4	34.6	42.6	42.7
CH_3CHF^+ (11)	C_s	0.4	0.5	0.7	0.7

Table 4. Relative Energies (kcal mol^{-1}) Using MP2/6-31G** Geometries.

Molecule	Symmetry	HF	MP2	MP3	MP4(SDQ)
$FCH_2CH_2^+$ (6)	C_s	24.8	31.2	28.4	29.6
CH_3CHF^+ (7)	C_s	0	0	0	0
 (9)	C_{2v}	29.3	24.7	25.3	24.2
 (10)	C_1	34.6	42.6	39.6	39.9

Transition structure **10** was obtained by linear interpolation between the geometries of **6** and **9** followed by HF/6-31G* and MP2/6-31G** optimizations. An alternative C_s structure of the 1-fluoroethyl cation (**11**) was also calculated. This corresponds to a transition state for methyl rotation in **7**. However, since this structure is somewhat peripheral to our main interest, and the preference for the eclipsed form (**7**) is well understood[25] an optimization beyond the HF/6-31G* level was not performed.



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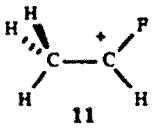

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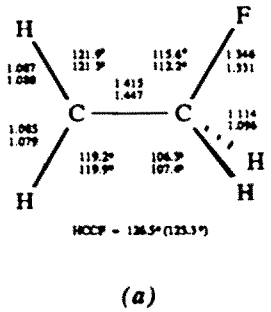
The HF/6-31G* and MP2/6-31G** geometries are shown in figure 1. The two structures for which only HF/6-31G* geometries were obtained are shown in figure 2. The relative energies (kcal mol-1) of **6**-**11** using the HF/6-31G* geometries are summarized in Table 3. Of special interest is the dramatic effect seen on inclusion of electron correlation at the MP2 level. In particular the primary fluoroethyl cation (**6**), which is more stable than both **8** and **9** on the HF surface, is less stable than either when electron correlation is



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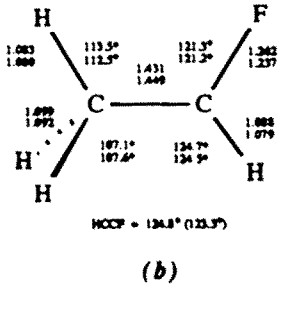

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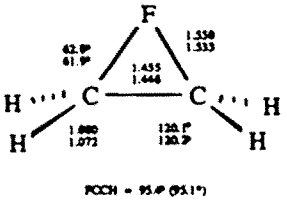

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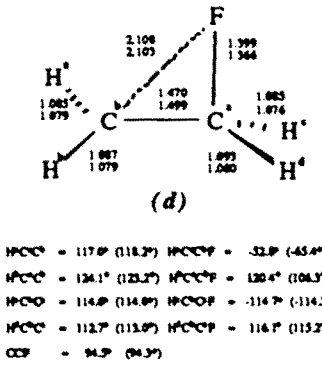


(d)

Fig. 1. Calculated HF/6-31G* (lower, or parenthesized values) and MP2/6-31G** geometries. (a) 2-fluoroethyl cation, **6**; (b) 1-fluoroethyl cation, **7**; (c) ethylene fluoronium ion, **9**; (d) transition structure **10**.

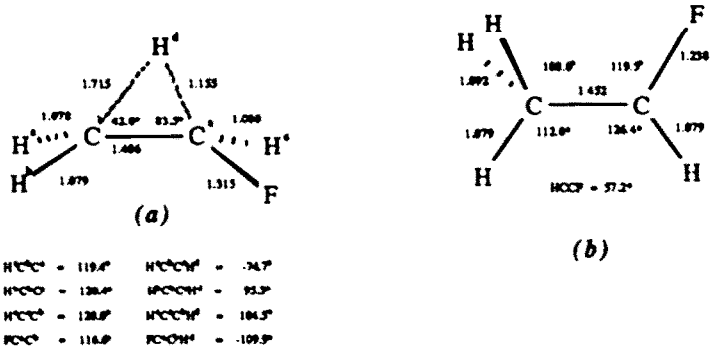
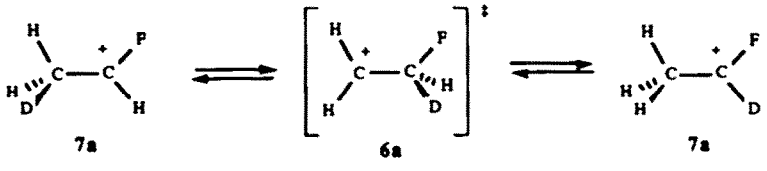


Fig. 2. Calculated HF/6-31G* geometries. (a) transition structure 8; (b) rotational transition structure 11.

included. This qualitative order persists throughout subsequent refinements of the theoretical model. Indeed, while the total energies naturally become more negative with addition of hydrogen polarization functions to the 6-31G* basis set, geometry optimization at the MP2 level, and inclusion of third, and fourth order correlation corrections, the *relative* energies change rather little (Table 4).

DISCUSSION

According to our higher level calculations, the primary fluoroethyl cation (6) is a not a local minimum, on the $C_2H_4F^+$ potential surface, but a transition state for hydrogen scrambling in the 1-fluoroethyl cation (7). The atomic motions associated with the imaginary frequency in 6 are shown in figure 3.



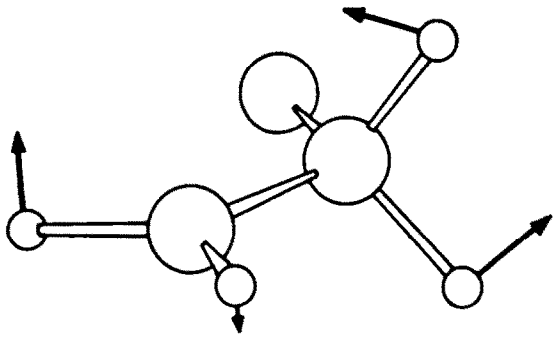
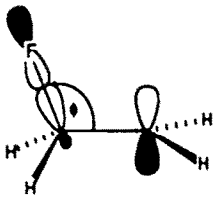


Fig. 3. Calculated (MP2/6-31G**) transition vector for structure 6.

As first pointed out by Hoffmann and coworkers[35] there should be a substantial barrier to rotation about the CC bond in **6** due to the unfavorable hyperconjugative interaction between the CF bond and the vacant 2p(C^+) orbital. In a qualitative sense this his has been amply verified.[20,25-27] However, a quantitative value for this barrier cannot be unambiguously defined since the "perpendicular" geometry, **12**, is not a stationary point but instead collapses to the cyclic fluoronium ion (**9**) without activation.[25,36] This was verified in the present work by optimizing the C_s structure **12** at the HF/6-31G* level for a series of angles ϕ, followed by single point MP2/6-31G* calculations. For ϕ = 110° for example, **12** is calculated to be 18.7 kcal mol^{-1}



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higher than **6** at this level. The actual barrier separating **6** and **9** is closer to 10 kcal mol^{-1} and corresponds to passage across a transition state involving simultaneous ring closure and methylene rotation (*c.f.* Figures 1 and 4). Of special note is that, while both the CCF bond angle and the methylene torsion angles are roughly intermediate between their values in **6** and **9**, the CC bond is markedly longer than in either. This again is presumably a manifestation of the highly unfavorable interaction between the CF bond and vacant sp(C^+) orbital as they come into alignment prior to bond formation.

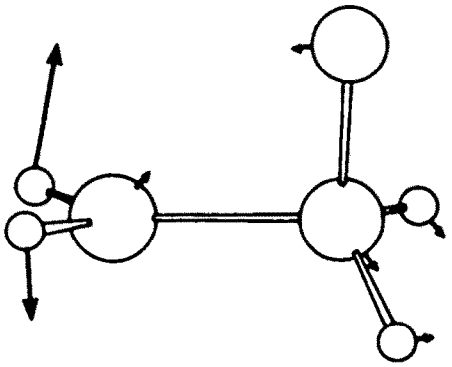


Fig. 4. Calculated (MP2/6-31G*) transition vector for structure **10**.

The relative energetics of the $C_2H_4F^+$ ions at the MP4/6-31G**//MP2/6-31G** level are shown schematically in figure 5 The most stable species is the 1-fluoroethyl cation (**7**) in which the the CF bond eclipses one of the CH bonds of the methyl group.[25] The cyclic fluoronium ion (**9**) lies in a fairly deep potential well 24.2 kcal mol^{-1} higher in energy. Using the calculated moments of inertia and scaled[38] vibrational frequencies to correct the MP4/6-31G** energies, the activation free energy ($\Delta G^{\ddagger}$) for escape from this well via **10** is estimated to be 14.5 kcal mol^{-1} at -60°. This corresponds to a half life of *ca* 2 min.

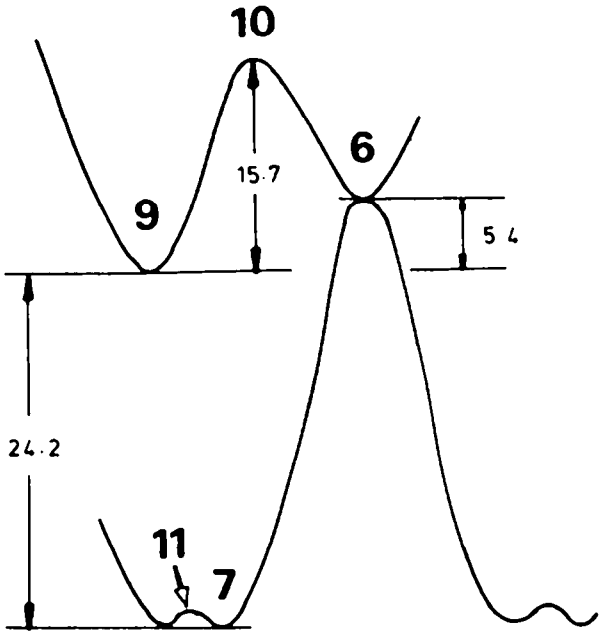
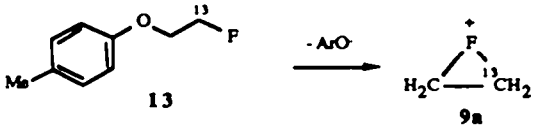


Fig. 5. Calculated (MP4(SDQ)/6-31G**//MP2/6-31G**) relative energies in kcal mol^{-1} on the $C_2H_4F^+$ potential surface.

Thus, if similar energetics apply in superacid media, as seems likely,[39] once formed, the lifetime of 9, at least with respect to unimolecular decomposition, should be sufficient to permit its observation. Unfortunately, the methods that have been successful for other ethylene halonium ions[28] are not applicable here. Thus, the essentially adiabatic entry to the $C_2H_4F^+$ surface via formal precursors of 6 under these conditions is expected to lead directly to 7, while the barrier to formation of 9 from 7 is for practical purposes insurmountable. The situation in the gas-phase is somewhat different. Here the surface can be entered via precursors of 6 with sufficient energy to reach the region of the potential surface corresponding to 9. This appears to have been accomplished recently by Ciommer and Schwarz[40] who observed scrambling of the ^{13}C label in the gas-phase dissociative ionization of 13:



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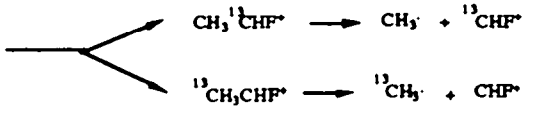
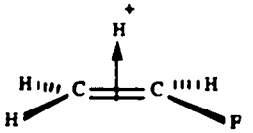


The inclusion of electron correlation has a profound qualitative effect on the calculated potential surface. At both the HF/6-31G* and HF/6-31G** levels the cyclic fluoronium ion (9) is calculated to be higher in energy than the 2-fluoroethyl cation (6). Inclusion of electron correlation at the MP4 level lowers the relative energy of the cyclic ion by 10.7 kcal mol^{-1}, an amount similar to that (11.6 kcal mol^{-1}) seen in the CEPA calculations of Lischka and Kohler,[15] and sufficient to reduce its energy to a point below that of 6.

The most interesting effect of electron correlation concerns the classical 2-fluoroethyl cation itself. This is transformed from a local minimum at both the HF/6-31G* and HF/6-31G** levels to a saddle point at MP2/6-31G**. The transition state, 8, found on the HF surface is evidently an artifact of the incorrect curvature of the potential surface resulting from the neglect of correlation effects. As can be seen from Table 1 its MP2 energy is already slightly more negative than that of the primary ion even prior to geometry optimization. Our search for a stationary point in this region of the potential surface led directly to the stable 1-fluoroethyl cation. Examination of the progress of the optimization revealed the starting point to be at the top of a long downward sloping plateau corresponding to passage of the migrating hydrogen across the "top"



14

of the basal "fluoroethylene" moiety in a series of the π-complex-like structures akin to 14. The energy of an arbitrary point on this pathway was obtained by optimizing one of these geometries subject to the constraint that the bridging hydrogen lie mid-way between the two carbon atoms. From the calculated energetics of the isodesmic process:

$$14 + CH_4 \rightarrow 2 + CH_3F$$

$$\Delta E\ (MP2/6\text{-}31G^*//HF/6\text{-}31G^*) = 1.0\ \text{kcal mol}^{-1}$$

the estimated[25,41] effects of fluorine substitution in 2 are quite modest and evidently insufficient to generate a barrier between 6 and 7 when the effects of electron correlation are included.

Acknowlegement: We thank the National Institutes of Health for financial support for this research through grant No. CA 38473 (to GPF) and SMU for a generous allocation of computer time on the IBM 3081D at the Bradfield Computer Center. We are also grateful to Professor C. Parkanyi (University of Texas at El Paso) and the University of Texas Center for High Performance Computing (UTCHPC) for computational resources on the Cray XMP/24.

REFERENCES

1. M. Saunders, P. Vogel, E. L. Hagen, and J. Rosenfeld, *Acc. Chem. Res.*, **1973**, *6*, 53.
2. G. A. Olah, G. K. S. Prakash, and J. Sommer, *Superacids*, Wiley: New York, 1985, p. 65-176.
3. F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, **1979**, *101*, 4067.
4. J. C. Schultz, F. A. Houle, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **1984**, *106*, 3917.
5. D. M. Shold and P. Ausloos, *J. Am. Chem. Soc.*, **1978**, *100*, 7915.
6. For summaries of *ab initio* molecular orbital studies see: W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley: New York, 1986, pp. 379-400. W. J. Hehre, *Applications of Electronic Structure Theory*, H.F. Schaeffer, III, ed., Plenum: New York, 1977, pp. 277-331.
7. For summaries of semiempirical molecular orbital studies see: M. J. S. Dewar, *Chem. Brit.*, **1975**, *11*, 97. See also refs 9-11.
8. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **1975**, *97*, 1285, 1294, 1302, 1307. M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *ibid.*, **1975**, *97*, 1311.
9. M. J. S. Dewar and K. M. Merz, Jr. *J. Am. Chem. Soc.*, **1986**, *108*, 5634. M. J. S. Dewar and M. K. Holloway, *ibid.*, **1984**, *106*, 6619. M. J. S. Dewar and C. H. Reynolds, *ibid.*, **1984**, *106*, 6388. M. J. S. Dewar and C. H. Reynolds, *ibid.*, **1982**, *104*, 3244.

10. M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **1977**, *99*, 7432.
11. P. K. Bischof and M. J. S. Dewar, *J. Am. Chem. Soc.*, **1975**, *97*, 2278.
12. See also ref 2*a-h* in: G. P. Ford and J. D. Scribner, *J. Comput. Chem.*, **1983**, *4*, 594.
13. K. Raghavachari, R. A. Whiteside, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **1981**, *103*, 5649.
14. D. Heidrich, M. Grimmer, and H.-J. Kohler, *Tetrahedron*, **1976**, *32*, 1193.
15. H. Lischka and H. J. Kohler, *J. Am. Chem. Soc.*, **1978**, *100*, 5297.
16. G. P. Ford, unpublished HF/6-31G* force constant calculations.
17. G. P. Ford and C. T. Smith, *J. Am. Chem. Soc.*, **1987**, *109*, 1325.
18. G. P. Ford and P. S. Herman unpublished work.
19. We exclude such π-stabilized ions as allyl, benzyl and cyclopropylcarbinyl from this generalization.
20. Y. Apeloig, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, **1977**, *99*, 5901.
21. M. J. S. Dewar, *Nature*, **1945**, *156*, 784. M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **1951**, C71.
22. M. J. S. Dewar and R. C. Dougherty, *The PMO Theory of Organic Chemistry*, Plenum: New York, 1975, pp. 285-306.
23. M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **1979**, *101*, 783.
24. D. T. Clark and D. M. J. Lilley, *J.C.S. Chem. Commun.*, **1970**, 1042.
25. W. J. Hehre and P. C. Hiberty, *J. Am. Chem. Soc.*, **1974**, *96*, 2665.
26. D. T. Clark and D. M. J. Lilley, *J.C.S. Chem. Commun.*, **1970**, 603.
27. A. C. Hopkinson, M.H. Lien, K. Yates and I. G. Csizmadia, *Theor. Chim. Acta*, **1975**, *38*, 21.
28. G. A. Olah, J. M. Bollinger, *J. Am. Chem. Soc.*, **1968**, *90*, 947. G. A. Olah, J. M. Bollinger, and J. M. Brinich, *J. Am. Chem. Soc.*, **1968**, *90*, 2587. G. A. Olah, D. A. Beal, and P. W. Westerman, *J. Am. Chem. Soc.*, **1973**, *95*, 3387. G. A. Olah, P. Schilling, P. W. Westerman, and H. C. Lin, *J. Am. Chem. Soc.*, **1974**, *96*, 3581.
29. GAUSSIAN 82 program package: J. S. Binkley, M. Frisch, K. Raghavachari, E. Fluder, R. Seeger, and J. A. Pople, Carnegie-Mellon University, 1984.
30. P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **1973**, *28*, 213.
31. J. S. Binkley and J. A. Pople, *Int. J. Quantum Chem.*, **1975**, *9*, 229.
32. J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem.Symp.*, **1976**, *10*, 1.
33. R. Krishnan and J. A. Pople, *Int. J. Quantum Chem.*, **1978**, *14*, 91.
34. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **1977**, *99*, 4899, 4907.
35. R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **1972**, *94*, 6221.
36. The existence of a local minimum corresponding to 12 on the MNDO potential surface[37] is presumably associated with its general tendency to underestimate the stabilities of hypervalent bridged species. *c.f.* M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **1979**, *101*, 5558.
37. M. J. S. Dewar and G. P. Ford, *J. Mol. Struct.*, **1979**, *51*, 281.
38. R. F. Hout, Jr., B. A. Levi, and W. J. Hehre, *J. Comput. Chem.*, **1982**, *3*, 234.
39. E. M. Arnett and N. J. Pienta, *J. Am. Chem. Soc.*, **1980**, *102*, 3329.
40. B. Ciommer and H. Schwarz, *Z. Naturforsch.*, **1983**, *38b*, 635.
41. Additional data from: R. A. Whiteside, M. J. Frisch, J. A. Pople, *The Carnegie-Mellon Quantum Chemistry Archive*, Carnegie Mellon University, Pittsburgh, 1983.