

flicting results for the geometry and relative stability of the conformers. When these two semiempirical methods are applied to ethylene ozonide (a 1,2,4-trioxolane), the CNDO/2 accurately predicts the experimental conformation while EHT does not. These two results clearly indicate that earlier studies of primary ozonide conformation and the associated conclusions concerning the mechanism of ozonolysis of olefins need to be reconsidered. This reconsideration included the use of a more reliable geometry for the primary ozonide ring. The improved relative stabilities of the primary ozonide conformers are similar to those obtained using the crude geometry and confirm that conformers with

pseudo-axial and pseudo-equatorial substituent positions are present in concentrations similar to conformers with clearly defined axial and equatorial positions. These conclusions raise questions concerning the ozonolysis mechanism proposed by Bailey, *et al.*

Acknowledgments. I thank Robert W. Murray for many helpful discussions which led to these calculations, John R. Sabin for the CNDO/2 computer program, and Robert L. Kuczkowski for making the microwave structure of ethylene ozonide available before publication. The University of Missouri—St. Louis Computer Center provided a grant under which these calculations were performed.

Electronic Structure of Reactive Intermediates. The Nitrenium Ions NH_2^+ , NHF^+ , and NF_2^+ ¹

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Abstract: The nitrenium ions NH_2^+ , NHF^+ , and NF_2^+ have been studied using *ab initio* techniques and have been compared with the isoelectronic carbenes CH_2 , CHF , and CF_2 . We find the triplet ground state of NH_2^+ (150°) 45 kcal/mol below the singlet (120°), while the singlet ground state of NF_2^+ (105°) is 33 kcal/mol below the triplet (122°). The ordering of the multiplicities is essentially in accord with the isoelectronic carbenes and as in CHF the singlet and triplet states of NHF^+ are essentially degenerate, the triplet (135°) lying 4 kcal/mol below the singlet (107°), an inversion of the carbene order. We find that although fluorine substitution destabilizes both the singlet and triplet states the triplets are destabilized to a greater extent. The effects contributing to the destabilization are analyzed and quantified. Finally, an analysis of the charge distribution indicates that the charge on the N atom varies from +0.10 to +0.96 as we go from NH_2^+ to NF_2^+ .

Nitrenium ions³ are compounds bearing a positive charge and containing a formally divalent nitrogen atom. For every nitrenium ion there is an isoelectronic carbene obtained by decreasing the divalent nitrogen's atomic number from 7 to 6. There is also an isomorphous relationship between nitrenium ions and primary and secondary carbonium ions, the former being obtained from the latter by coalescing a proton and the carbon nucleus formally associated with the carbonium ion center. The resulting nitrenium ion is isoelectronic with the parent carbonium ion and also hosts a positive charge. Whether one traces the nitrenium ion's lineage to a carbene or carbonium ion one anticipates that insight into the chemistry of the nitrogen species will accrue from a careful analysis of the parent-offspring electronic structure.

In this study we will concern ourselves with the nitrenium ions NH_2^+ , NHF^+ , and NF_2^+ and the corresponding isoelectronic carbenes CH_2 , CHF , and CF_2 .

Calculations

For N and F we use the gaussian-lobe function representation of Huzinaga's⁴ 9s,5p set contracted to

4s,2p while for H we use his 4s set contracted to 2s. All contractions are as recommended by Dunning.⁵ A common scale factor of 1.2 was obtained for both hydrogen functions by optimizing the SCF energy for the ¹A₁ state of NH_2^+ . This scale factor will be used in all calculations reported.

A N-H distance of 1.9055 au was obtained by optimizing the SCF energy of the ¹A₁ state of NH_2^+ while a N-F distance of 2.5766 au was assumed. The Hartree-Fock-Roothaan⁶ equations were solved for the lowest doubly occupied singlet state of NH_2^+ , NHF^+ , and NF_2^+ in the previously described basis as a function of angle. The results are presented in Figure 1 along with the results for the isoelectronic carbenes.⁷

In all cases the highest occupied MO has a significant nitrogen lone-pair component, and we will refer to this orbital as the σ_1 MO. So in NH_2^+ , $\sigma_1 \equiv 3a_1$, in NHF^+ , $\sigma_1 = 7a'$, while in NF_2^+ it is $6a_1$. Also, the lowest empty MO is essentially a N p orbital perpendicular to

(1) Supported in part by a grant from Research Corporation.

(2) National Science Foundation Undergraduate Research Participant, summer 1971.

(3) P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

(4) (a) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965). (b) By "lobe function representation" we mean that each nuclear centered p orbital is replaced with an antisymmetric combination of 1s gaussians, the exponent (α) being the same as that of the p function being mimicked while the lobe separation is taken as $0.03 \alpha^{-1/2}$ following J. D. Petke, *et al.*, *J. Chem. Phys.*, **51**, 256 (1969).

(5) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).

(6) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(7) J. F. Harrison, *J. Amer. Chem. Soc.*, **93**, 4112 (1971).

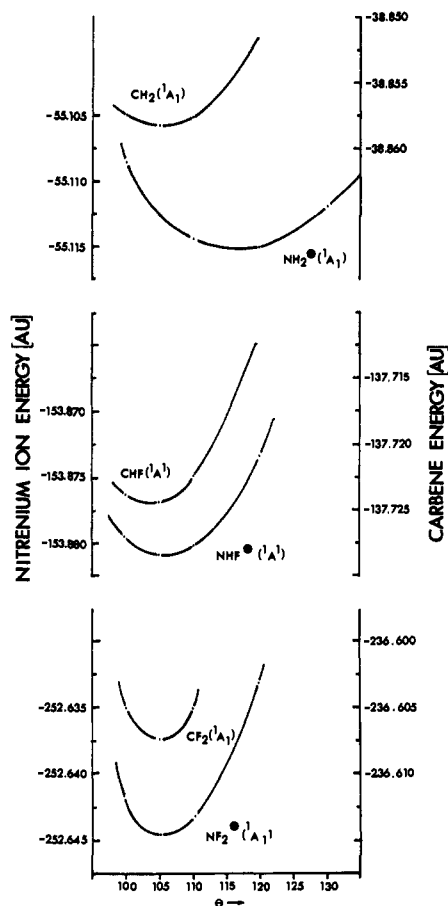


Figure 1. Self-consistent field results for the lowest singlet states of the carbenes and nitrenium ions.

the molecular plane and we will refer to this as the p_1 MO.⁸

If we refer to all orbitals below σ_1 as core we have the representation

$$\psi_{\text{SCF}} = (\text{core } \sigma_1 | \text{core } \sigma_1) \equiv \psi(\sigma_1^2)$$

where all orbitals on the left of the vertical bar have α spin while those to the right host β spins. If we excite one electron from a σ to a p orbital we may form

$${}^3\psi(\sigma_1 p_1) = (\text{core } \sigma_1 | \text{core } p_1) - (\text{core } p_1 | \text{core } \sigma_1)$$

and

$${}^1\psi(\sigma_1 p_1) = (\text{core } \sigma_1 | \text{core } p_1) + (\text{core } p_1 | \text{core } \sigma_1)$$

We may further improve the representation of the low-lying states by allowing some configuration interaction and writing

$$\psi(\sigma^2) = \sum_{i,j}^N \psi(\sigma_i \sigma_j) C_{ij}^\sigma + \sum_{i,j}^M \psi(p_i p_j) C_{ij}^p$$

$${}^3\psi(\sigma p) = \sum_{i=1}^N \sum_{j=1}^M {}^3\psi(\sigma_i p_j) b_{ij}$$

$${}^1\psi(\sigma p) = \sum_{i=1}^N \sum_{j=1}^M {}^1\psi(\sigma_i p_j) a_{ij}$$

and determining the linear coefficients variationally. In constructing the small configuration interactions we

(8) This notation was first introduced by Hoffmann, *et al.*, in a study of carbene structure: R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).

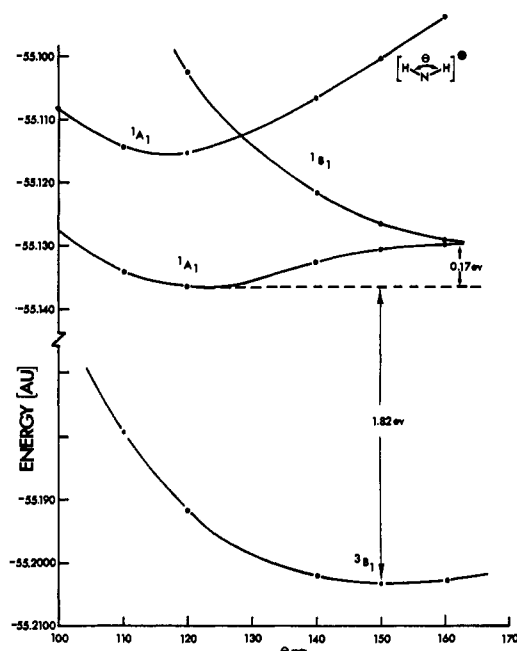
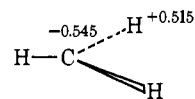


Figure 2. A configuration interaction study of the low-lying states of NH_2^+ . Top 1A_1 curve is SCF result.

used the three lowest unoccupied p orbitals ($M = 3$) for NF_2^+ and NHF^+ and (the only) two for NH_2^+ ($M = 2$), while for σ_1 we used the highest occupied orbital and then generated two additional σ orbitals as linear combinations of the unoccupied σ orbitals with the coefficients in the expansion chosen to optimize the exchange integral with σ_1 . The results of the subsequent calculations are given in Figures 2-4.

Charge Distribution. In Figure 5 we present the charge distribution (Mulliken gross charges⁹) in the lowest singlet and triplet states of the nitrenium ions. The electron shift from F and H to N as we go from the carbene to the isoelectronic nitrenium ion is qualitatively in accord with our intuition. This electron migration continues until the energy gain in changing the electron's environment is no longer favorable, stopping when the fluorines are essentially neutral and the hydrogens host a positive charge of 0.5. The net result is a dramatic change in the charge hosted by the N atom as a function of fluorination in both the singlet and triplet sequence. We should contrast the essentially neutral nitrogen in NH_2^+ with the negative carbon in the methyl cation¹⁰ in CH_3^+ .



The similarity of the hydrogen charge¹¹ in CH_3^+ and NH_2^+ prompts the speculation that in CF_3^+ the entire positive charge would be localized on the carbon with the obvious intermediate results for CH_2F^+ and CHF_2^+ .

Looking at the charge distribution within the singlet or triplet sequence indicates that about 0.5 electron is lost from the in-plane N orbitals each time a fluorine

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

(10) J. E. Williams, V. Buss, and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 6867 (1971).

(11) S. T. Lee and K. Morokuma, *J. Amer. Chem. Soc.*, **93**, 6863 (1971).

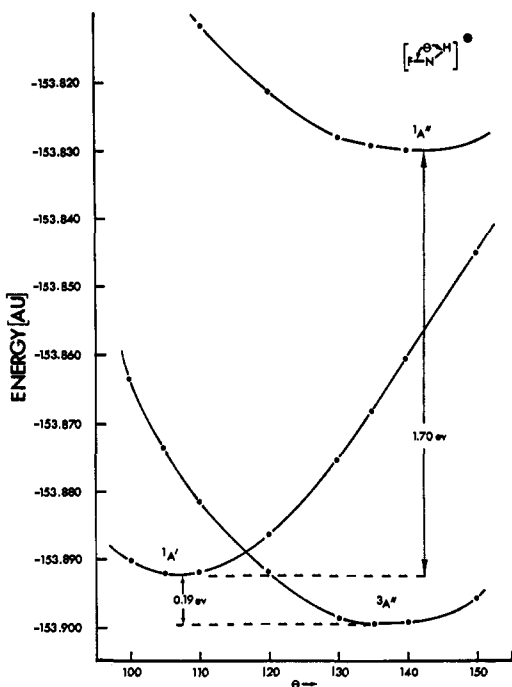


Figure 3. A configuration interaction study of the low-lying states of NHF^+ .

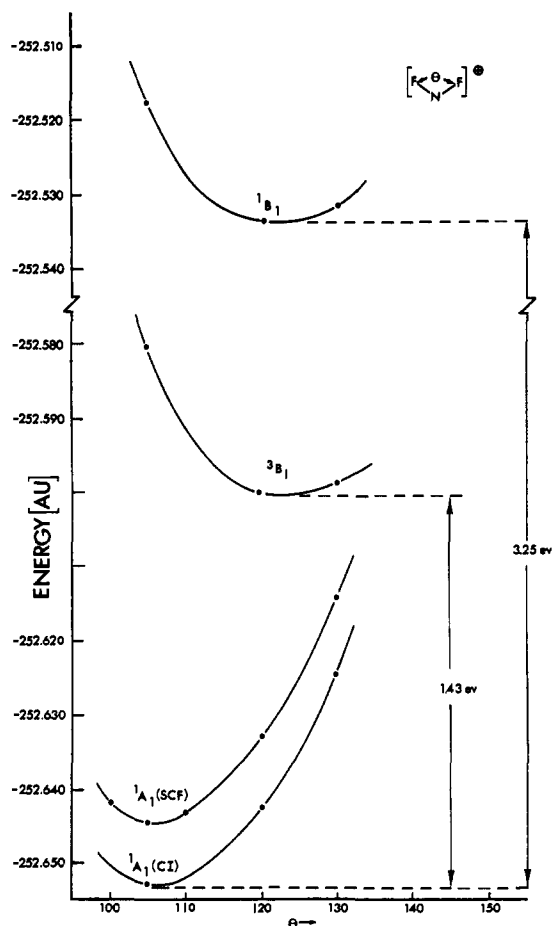


Figure 4. A configuration interaction study of the low-lying states of NF_2^+ .

replaces a hydrogen while the nitrogen p orbital gains electrons. A qualitatively similar effect was noted in our study of the isoelectronic carbenes.⁷

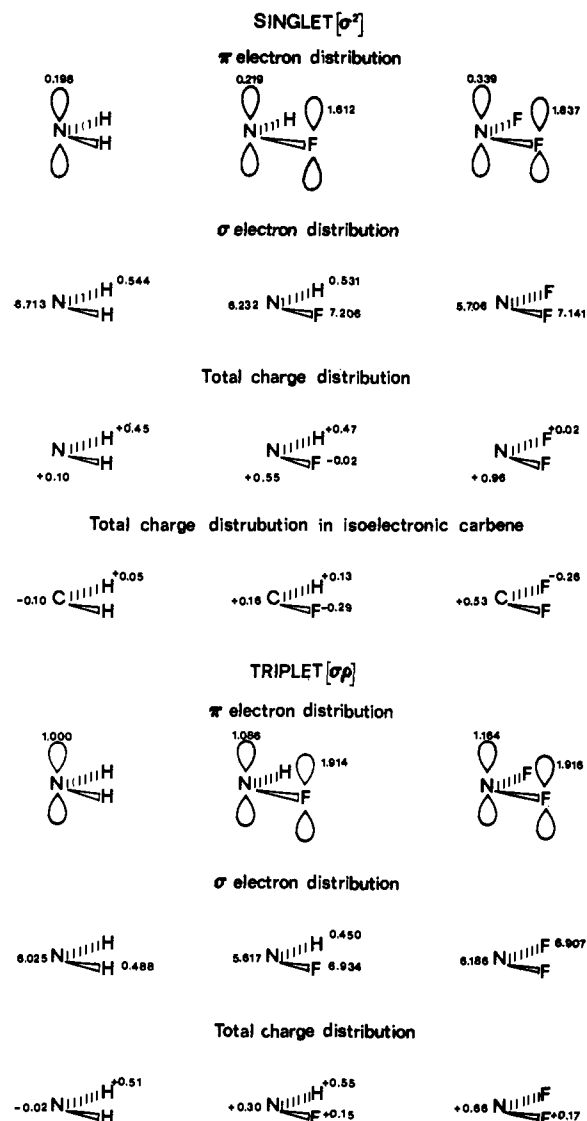


Figure 5. Charge distribution in the lowest singlet and triplet states.

The difference between the singlet and triplet charge distribution is easily understood by noting that the triplet is formally obtained from the singlet by removing an electron from the σ orbital and depositing it in the lowest π orbital. The σ orbital is delocalized over the entire molecule (see Figure 6) while the π orbital is localized primarily on N. Nitrogen invariably gains electrons while F and H invariably lose electrons resulting in a less positive N atom in the triplet state.

Finally, in Figure 6 we present contour maps of the electron density associated with the highest occupied in-plane orbital (σ) for the nitrogen ions as well as the gross atomic and the overlap population. Note the substantial decrease in the electron density associated with the N atom relative to the carbon in the isoelectronic carbene.⁷ This decrease is so striking in NF_2^+ as to call into question the conceptual utility of regarding the σ orbital as a nitrogen lone pair.

Bond Angles. From Figure 1 we see that in going from CHF and CF_2 to the isoelectronic nitrogen ions (in the lowest singlet state) the bond angle is remarkably constant, while NH_2^+ and CH_2 differ by 17° . The bond angles in the carbene sequence have been

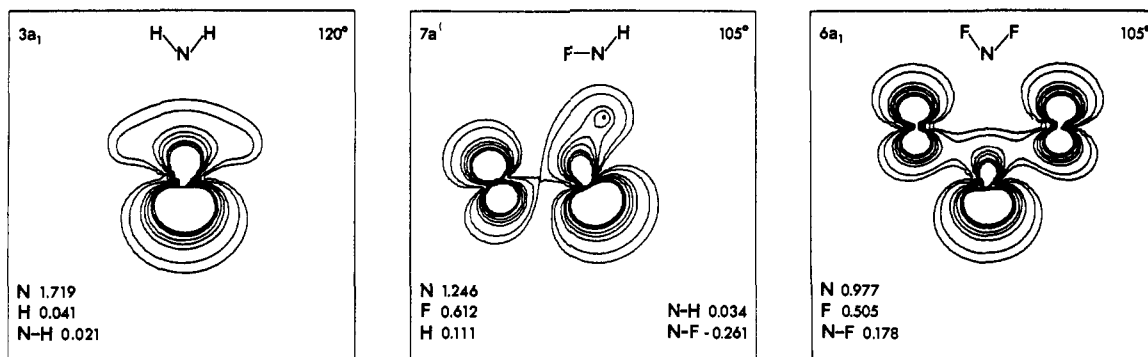


Figure 6. Contour maps of the electron density associated with the σ orbital in the carbenes and nitrenium ions.

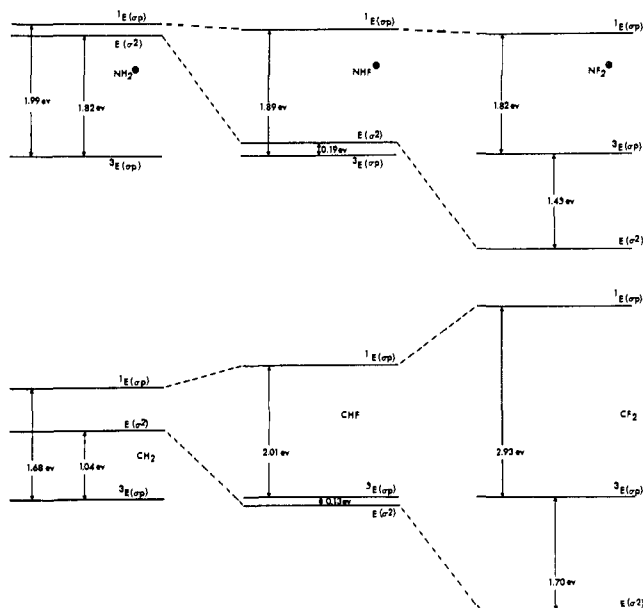


Figure 7. Energies of the calculated 0-0 transitions.

rationalized^{7,8,12} in terms of a balance between the increase in stabilization of the lone-pair (σ) orbital upon bending away from the linear geometry and a concomitant decrease in the stability of those molecular orbitals associated with the CH and CF bonds (bond-bond repulsion).

Plotting the one-electron energies of the σ and highest b_2 orbitals of the nitrenium ions along with those of the carbenes as a function of angle indicates that the same mechanism is operative in the nitrenium ion sequence.

The slight increase in the NH_2^+ angle relative to CH_2 is then associated with the increased positive charge hosted by the hydrogen atoms. That the charge on the ligand is effective in changing the NH_2^+ angle relative to CH_2 and of little consequence in the NHF^+ and NF_2^+ cases is due to the much larger ligand-ligand distance in the fluorinated nitrenium ions.

Coupling the similarity of the bond angles in the isoelectronic carbenes and nitrenium ions with the interpretation that the increase in the stability of the σ MO upon bending is due to an increased s orbital contribution, we might expect the nitrenium ion sequence to exhibit a % s character in the lone-pair density com-

parable to the carbene. If we define the % s character associated with these orbitals as

$$\% s = \frac{\text{gross s population on N atom}}{\text{gross s} + \text{gross p population on N atom}} \times 100$$

then the magnitude of this index for the nitrenium ion sequence is NH_2^+ (120°) 10.7, NHF^+ (105°) 18.3, and NF_2^+ (105°) 29.2, while the corresponding index for the isoelectronic carbenes is CH_2 (105°) 25.0, CHF (105°) 29.6, and CF_2 (105°) 55.2. Most intriguing is the greatly reduced s character in the nitrenium ion sequence. Apparently if we want to retain the above interpretation of the stability of the σ MO we must ascribe a comparable stabilizing effect to "lone pairs" containing less s character if they are in the field of a significantly increased positive charge.

The dominant configuration in $^1\psi(\sigma p)$ and $^3\psi(\sigma p)$ differs from $\psi(\sigma^2)$ in that one electron has been removed from the σ_1 orbital and placed in the p_1 orbital, the energy of which is essentially constant with angle. The larger bond angle found for these two states relative to the σ^2 state is therefore not unexpected. Table I compares our theoretical results and the available

Table I. Theoretical and Experimental Angles for the Carbenes and Nitrenium Ions

	CH_2^a	NH_2^+	CHF^a	NHF^+	CF_2^a	NF_2^+
	105 (102.4) ^b	122	104 (101.6)	107	104.9 (105)	105
Singlet σ_p	180 (140)	180	128 (127.2)	142	122.5 (122.3)	120
Triplet σ_p	132.5 (136)	150	122	135	120	122

^a Reference 7. ^b Experimental angles in parentheses. See ref 7 for details.

experimental angles (in parentheses) for the carbenes and nitrenium ions. (There are no experimental data for the nitrenium ions.)

Relative Energies of Singlets and Triplets. The Figure 7 representation of the energies of the 0-0 transitions for the molecules under consideration indicates that fluorination first preferentially lowers the σ^2 singlet relative to the σp triplet and secondly results in a slight decrease in the σp singlet-triplet separation for the nitrenium ions and a substantial increase for the carbenes.

As a possible rationale for the latter observation we note that the σp singlet-triplet separation is given by $2K_{\sigma p}$ where

$$K_{\sigma p} = \int \sigma(1)p(1)(1/r_{12})\sigma(2)p(2) dV(1,2) \quad (1)$$

(12) J. F. Harrison in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1971.

Table II. Theoretical ΔE 's and $\Delta\Delta H_f^\circ$ for the Carbenes and Nitrenium Ions

Reaction ^a	X≡C				X≡N ⁺			
	ΔE		$\Delta\Delta H_f^\circ$		ΔE		$\Delta\Delta H_f^\circ$	
	SCF	CI	SCF	CI	SCF	CI	SCF	CI
(1) XH ₂ (s) + F → XHF(s) + H	10.2	12.2	-23.6	-21.6	84.3	90.5	50.5	56.7
(2) XHF(s) + F → XF ₂ (s) + H	-0.2	-0.9	-34.0	-34.7	85.6	87.1	51.8	53.3
(3) XH ₂ (T) + F → XHF(T) + H		36.7		2.9		128.0		94.2
(4) XHF(T) + F → XF ₂ (T) + H		38.0		4.2		124.8		91.0
(5) XH ₂ (s) + F → XHF(s, No π_x) + H	29.8		-4.0		108.4		74.6	
(6) XHF(s, No π_x) + F → XF ₂ (s, No π_x) + H	17.8		-16.0		107.1		73.3	

^a All energies are in kilocalories/mole.

and, if we assume that one-center terms dominate this integral, we may write

$$K_{\sigma p} = K_{\sigma p}(C) + K_{\sigma p}(F) \quad (2)$$

If we further assume that these single-center contributions may be expressed as a standard exchange integral (each orbital singly occupied) weighted by the actual occupation we may write

$$K_{\sigma p} \sim \eta_\sigma(C)\eta_p(C)K_{\sigma p}^0(C) + \eta_\sigma(F)\eta_p(F)K_{\sigma p}^0(F) \quad (3)$$

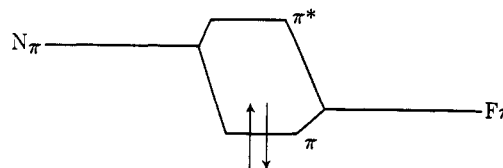
with a similar expression for the nitrenium ions. Since ${}^1E(\sigma p) - {}^3E(\sigma p)$ is 1.99 eV for NH₂⁺ and 1.68 eV for CH₂ we infer $K_{\sigma p}^0(N) > K_{\sigma p}^0(C)$ and extrapolate this to

$$K_{\sigma p}^0(F) > K_{\sigma p}^0(N) > K_{\sigma p}^0(C) \quad (4)$$

So, as we fluorinate the carbene both the carbon σ and p orbitals lose electrons to F, and from eq 3 this decreases the first term and increases the second resulting in an increase in the singlet-triplet separation. When we consider the nitrenium ions we have the added feature of an increased positive charge on the nitrogen atom which would increase $K_{\sigma p}^0(N)$. Our numerical results are consistent with this being increased until it is approximately equal to $K_{\sigma p}^0(F)$.

In order to understand the mechanism operative in the preferential lowering of the σ^2 singlet relative to the σp triplet, we investigated the relative stabilities of the carbenes and nitrenium ions as a function of fluorine substitution. In Table II we list a series of reactions along with the computed ΔE and $\Delta\Delta H_f^\circ$ (the difference between the enthalpies of formation of the two compounds involved in the reaction). These numbers are obtained using molecular energies from this work and ref 7 and the atomic energies of Whitten¹³ and Dunning.⁵ A positive ΔE indicates that fluorine substitution for hydrogen is destabilizing and it is interesting that all nitrenium ions listed and all but the singlet state of CHF are destabilized with the triplet states being more destabilized than the singlets, in complete agreement with the pattern displayed in Figure 7.

We anticipate that both the singlet and triplet states are subject to the inductive σ destabilizing ($-I_\sigma(F)$) and the inductive π stabilizing ($+I_\pi(F)$) effects of the fluorine atom.¹⁴ In the singlet system under consideration we may think of the I_π effect as resulting from the orbital pattern displayed below, while in the triplets we also occupy the π^* orbital, resulting in additional destabilization. This last destabilization mechanism is mathematically a consequence of orthogonality or more physically the Pauli principle; *i.e.*, a singly occupied AO, the N (or carbon) p_π overlapping a doubly



occupied orbital, the fluorine p_π , results in two electrons with the same spin occupying the same region of space and therefore suffering an increased repulsion. This we will call the Pauli effect, and it seems to be the main distinction between the singlet σ^2 and triplet σp stabilities. To quantify these effects we deleted the N and C p_π orbitals from our basis (thus eliminating the opportunity for an I_π stabilizing effect) and repeated the SCF calculations for the singlets. The ΔE 's computed with this constraint are listed in Table II for reactions 5 and 6 and indicate that the 84.3 kcal/mol destabilization of NHF⁺ relative to NH₂⁺ is a composite of a 108.4 kcal/mol destabilization energy, the $-I_\sigma(F)$ effect, and 24.1 kcal/mol stabilization energy, the $+I_\pi(F)$ effect. If we assume these effects are operative with comparable magnitudes in the triplet states, then we estimate the Pauli effect in triplet NHF⁺ as 128.0 - 84.3 or 43.7 kcal/mol. Continuing along these lines we construct Table III. We see that while the various

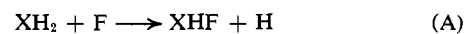
Table III. Factors Contributing to the Stability of the Fluorinated Carbenes and Nitrenium Ions^a

Compd ^b	$-I_\sigma(F)$		$+I_\pi(F)$		Pauli		ΔE^d	
	C	N ⁺	C	N ⁺	C	N ⁺	C	N ⁺
XHF(s)	29.8	108.4	-19.6	-24.1	0	0	10.2	84.3
XF ₂ (s)	47.6	215.5	-37.6	-45.6	0	0	10.0	169.9
XHF(T)	29.8 ^c	108.4 ^c	-19.6 ^c	-24.1 ^c	26.5	43.7	36.7	128.0
XF ₂ (T)	47.6 ^c	215.5 ^c	-37.6 ^c	-45.6 ^c	64.7	82.9	74.7	252.8

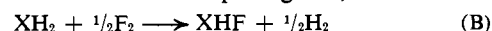
^a Stabilization is measured relative to the parent carbene or nitrenium ion in the appropriate spin state. ^b Energies in kilocalories/mole; singlets are from SCF results; triplets are from CI results. ^c Assumed to be the same as corresponding singlets. ^d Relative to XH₂(S;T).

"effects" for the nitrenium ions are additive, *i.e.*, two fluorines have twice the effect as one, those for the carbenes are not.

Finally, we should comment on our choice of



as a reference reaction for computing ΔE , rather than



The ΔE of reaction A is given by

$$\begin{aligned} \Delta E_A &= \Delta H_f^\circ(\text{XHF}) + \Delta H_f^\circ(\text{H}) - \\ &\quad \Delta H_f^\circ(\text{XH}_2) - \Delta H_f^\circ(\text{F}) \\ &= \Delta E_B + \Delta H_f^\circ(\text{H}) - \Delta H_f^\circ(\text{F}) \end{aligned}$$

(13) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).

(14) See, for example, J. N. Murrell, S. F. A. Kettle, and J. M. Teder, "Valence Theory," Wiley, New York, N. Y., 1965, p 309.

Table IV. Summary of NH₂⁺ Energetics^a

State	Peyerimhoff, <i>et al.</i> ^b		Lee and Morokuma (MZ) ^c		Lee and Morokuma (DZ) ^d		Present work ^e		Hayes, <i>et al.</i> ^f	
	Angle	Energy	Angle	Energy	Angle	Energy	Angle	Energy	Angle	Energy
¹ A ₁	120	-55.0853	106	-55.0582	115	-55.2014	122	-55.1365	120	-55.1530
³ B ₁			146	-55.1268	180	-55.2732	150	-55.2032	140	-55.2102
¹ B ₁			150	-55.0241	180	-55.1887	180	-55.1300	180	-55.1357

^a All energies in hartrees; angles in degrees. ^b Reference 15 SCF calculation. ^c Reference 16 MZ refers to minimal ζ . Full CI with 1s on N doubly occupied. No bond length given. ^d Reference 16 DZ refers to double ζ . Full CI with 1s on N doubly occupied. No bond length given. ^e Details given in text. ^f Reference 17. CI with 1s on N doubly occupied. Bond length 2.0 bohrs.

Using 36.6 and 104.2 kcal/mol for the binding energy of F₂ and H₂, respectively,¹⁵ we compute

$$\Delta E_A = \Delta E_B + 33.8 \text{ kcal/mol}$$

or

$$\Delta E_A = \Delta \Delta H_f^\circ + 33.8 \text{ kcal/mol}$$

Using the difference in the standard enthalpy of formation as an index of relative stability could be very misleading because of the 33.8 kcal/mol bias required for the reference state. For example, while ΔE would indicate that CHF(s) was destabilized relative to CH₂(s) by 10.2 kcal/mol, $\Delta \Delta H_f^\circ$ would indicate that it was stabilized by 23.6 kcal/mol. Clearly, if we are interested in the relative stability when we change one atom for another in a molecule we should not employ $\Delta \Delta H_f^\circ$ s.

Comparison with Previous Work. Not discussed in ref 7 are four recent *ab initio* calculations^{11,16-18} of the geometry and singlet-triplet separation in CH₂. The most recent and most extensive of these, by Bender, *et al.*,¹⁸ is characterized by the inclusion of polarization functions on the carbon (a set of d orbitals) and H (a set of p orbitals). Using this basis and the iterative natural orbital technique they constructed CI wave functions which predicted a singlet-triplet separation of 11.0 ± 2.0 kcal/mol, about 8 kcal/mol lower than that suggested in ref 7. In the nitrenium ion sequence

(15) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

(16) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **13**, 30 (1972).

(17) S. Y. Chu, A. K. Siu, and E. F. Hayes, *J. Amer. Chem. Soc.*, **94**, 2969 (1972).

(18) C. F. Bender, H. F. Schaeffer III, D. R. Franceschetti, and L. C. Allen, *J. Amer. Chem. Soc.*, **94**, 6888 (1972).

only the parent compound NH₂⁺ has received prior attention and then there have been only three *ab initio* studies. The first was by Peyerimhoff, *et al.*,¹⁹ and was an SCF study of the ¹A₁ state using a gaussian-lobe function basis. The second by Lee and Morokuma¹¹ was a complete CI (with the 1s on N constrained to be doubly occupied) with a minimal and double ζ basis. The third was a CI study by Hayes, *et al.*,¹⁷ in which they employed a basis very similar to that used by us in the current study. Both Hayes, *et al.*, and Lee and Morokuma studied the energy variation with bond angle for the ¹A₁, ³B₁, and ¹B₁ states and their results along with those of ref 19 and the current study are summarized in Table IV. We see that we agree very well with the predictions of Hayes, *et al.*, but note an ostensibly large discrepancy between our work and Lee and Morokuma's best (DZ) CI in which the angle in the ³B₁ state differs from our result by 30°. However, since our barrier to linearity in the ³B₁ state is less than 2 kcal/mol we do not consider this a significant difference. Further, we both predict the ³B₁-¹A₁ separation to be 45 kcal/mol (Hayes, *et al.*, suggest 36 kcal/mol) and agree that the ¹A₁-¹B₁ separation should be very small (we estimate 4 kcal/mol as do Hayes, *et al.*, while Lee and Morokuma suggest 8 kcal/mol).

Having our NH₂⁺ results agree with the much more extensive Lee and Morokuma calculation increases our confidence in the accuracy of the results for NHF⁺ and NF₂⁺. However, since there are no experimental data available for these ions our calculated geometries, energy level patterns, and 0-0 transition energies must stand as predictions.

(19) S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966).