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Ground States of Molecules. 40.
MNDO Results for Molecules Containing Fluorine

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Abstract: Heats of formation, molecular geometries, first ionization potentials, and dipole moments are calculated by the MNDO method for a wide range of compounds containing fluorine. Major improvement, in comparison with MINDO/3, is obtained for most properties. The relative energies of conformational and geometrical isomers are in agreement with experiment and in some cases the results are superior to those obtained by ab initio methods. The calculated properties of the polyfluoromethane radical cations agree well with the observed stabilities. Good agreement is also obtained for higher vertical ionization energies, and particularly for species such as F_2, where the highest occupied molecular orbitals are correctly predicted to be of π_g, π_u, and Σ_g^+ symmetry, respectively. Calculated proton and electron affinities agree well with experimental values. Singlet-triplet separations for fluorocarbenes and fluoronitrene are discussed.

Introduction

Previous papers[1-3] of this series have described a new semiempirical SCF MO procedure (MNDO), based on the NDDO approximation, and its application to a wide variety of molecules derived from the elements H, B, C, N, and O. The results were almost uniformly much better than those from MINDO/3,[4] particularly for compounds containing pairs of adjacent heteroatoms. This was not unexpected because the INDO approximation (on which MINDO/3 was based) fails in such cases as a result of the neglect of one-center differential overlap.[4a] Similar problems also arose in attempts[4c] to extend MINDO/3 to compounds of fluorine, as again might have been expected since fluorine contains three pairs of unshared electrons. Here we report an extension of MNDO to fluorine and the results of calculations for a wide range of fluorine compounds.

Parametrization

The method previously described[1] was used in obtaining the fluorine parameters given in Table I. Initial estimates, obtained by linear extrapolation of the C, N, and O parameters,[1] were refined by fitting 50 selected properties of 12 fluorine molecules (marked * in the tables of results). The previously optimized atomic parameters for H, B, C, N, and O[1,3] were held constant during this procedure. The final fluorine parameters were close to the extrapolated values, which suggests that the MNDO method as a whole is suitably self-consistent. It is also interesting to note that optimized orbital exponents are regularly about 0.3 greater than Clementi's values[5] and that the one-

Table I. Optimized MNDO Parameters for Fluorine

Parameter	Value	Derived parameters	Value
U_{ss}, eV	−131.071548	ΔH_f^A, kcal mol^{-1}	18.860
U_{pp}, eV	−105.782137	E_{el}^A, eV	−476.683781
ζ, au	2.848487	D_1, Å	0.2681377
β_s, eV	−48.29046	D_2, Å	0.2275224
β_p, eV	−36.50854	ρ_0, Å	0.425492
α, Å^{-1}	3.419661	ρ_1, Å	0.243849
		ρ_2, Å	0.255793

Table II. Mean Absolute Errors $\Delta(\Delta H_f^\circ)$ in the Heats of Formation of Fluorine Compounds

Class of compd	No.	$\Delta\Delta H_f^\circ$, kcal mol^{-1}	
		MNDO	MINDO/3
All compounds	71	9.80	24.8
Only CHF^a	23	7.1	6.4
Only CHFO	8	8.8	16.6
Only CHFN	6	11.8	58.2
CHBNOF	11	12.5	40.1
Carbenes	2	14.5	30.5
Cations	9	8.0	24.9
Anions	3	14.3	39.5
Radicals	6	14.3	30.5
Radical cations	3	8.0	19.1^b

^{a} Closed shell neutral compounds, not including carbenes. ^{b} 1 SCF calculation on the MNDO optimized geometry.

Table III. Heats of Formation of Closed Shell Fluorine Compounds by MNDO

Compd	$\Delta H°$ obsd, kcal mol⁻¹	$\Delta H°$ calcd, kcal mol⁻¹	Error	Ref	Compd	$\Delta H°$ obsd, kcal mol⁻¹	$\Delta H°$ calcd, kcal mol⁻¹	Error	Ref
HF	−65.1	−59.8	5.3	a	N₂F₄ (trans)	−2.0	−18.3	−16.3	a
CH₃F	−56.8*	−60.9	−4.1	b	HNF₂		−19.9		
CH₂F₂	−107.7	−111.8	−4.1	a	CH₃NF₂		−16.1		
CHF₃	−166.6	−163.9	2.7	a	F \ C=N / H (structure)		−34.5		
CF₄	−223.0*	−214.3	8.7	a					
CH₃CH₂F	−62.9	−65.1	−2.2	c					
CH₃CHF₂	−119.7	−113.5	6.2	c	F \ C=N \ H (structure)		−32.0		
CH₂FCH₂F (gauche)		−110.1							
CH₂FCH₂F (trans)		−109.8			F₂C=N=N		−22.2		
CH₃CF₃	−178.2	−164.5	13.7	c					
CF₃CF₃	−321.2	−299.8	21.3	a	F₂C (structure, N ring)		−21.2		
(CH₃)₂CHF	−69.4	−65.2	4.2	d					
△−F (structure)		−256.3			F₂NCN		39.9		
☐−F (structure)	−355.7	−360.4	−4.7	e	F—CN	8.6*	−2.7	−11.3	a
CH₂=CHF	−32.5*	−34.6	−2.1	f	CF₃CN	−118.4	−113.7	4.7	a
CHF=CHF (cis)		−83.75		g	C₃N₃F₃ (1,3,5)		−105.1		
CHF=CHF (trans)		−83.25			(structure) −F pyridine		−196.1		
CH₂=CF₂	−80.4	−84.2	−3.8	d					
CHF=CF₂	−117.3	−131.2	−13.9	d	FNO	−15.0*	−24.8	−9.8	a
CF₂=CF₂	−157.4*	−175.8	−18.4	a	CF₃NO		−153.7		
☐−F (structure)		−242.6			FNO₂	−26.0	0.6	26.6	a
=·=F₂		−52.4			FONO₂	2.5	28.0	25.5	a
C₆H₅F	−26.5	−25.4	1.1	d	F₃NO	−39	22.8	61.8	a,l
C₆H₄F₂ (1,2)	−70.3	−70.8	−0.5	d	F₂NOF		0.1		
C₆H₄F₂ (1,3)	−74.0	−71.1	2.9	d	BF₃	−271.4*	−261.1	10.3	a
C₆H₄F₂ (1,4)	−73.3	−71.2	2.1	d	B₂F₄ (D₂d)	−342.2	−339.4	2.8	a
C₆H₃F₃ (1,3,5)		−115.9			HBF₂	−175.4	−177.1	−1.7	a
C₆HF₅	−192.5	−201.8	−9.3	d	CH₃BF₂	−199	−191.5	7.5	m
C₆F₆	−228.5	−244.3	−15.8	d	F₂BCH=CH₂	−171	−166.7	4.3	m
(structure) F...F cyclopropene		−1.4			F₂BC≡CH		−131.6		
FC≡CH	5.0	15.0	10.0	a	FB=O	−144.0	−140.5	3.5	a
HOF	−23.5	−18.7	4.8	h	F₂BOH	−259.0	−253.4	5.6	a
CH₂FCH₂OH (gauche)		−109.0			(BOF)₃	−565.3	−525.8	39.8	a
CF₃CH₂OH (gauche)	−220.6ⁱ	−208.4	12.2ⁱ	j	F₂B=NH₂		−199.0		
CF₃OF	−182.8	−163.5	19.3	a	(BNF)₃ (1,3,5)		−386.0		
F₂O	5.9*	18.2	12.3	a	F₂	0.0*	7.3	7.3	
HCOF	−90.0	−88.9	1.1	a	CH₂F⁺	200.3	182.7	−17.5	n
CH₃COF	−106.4	−96.5	9.9	d	CHF₂⁺	142.4*	132.3	−10.1	n
F₂CO	−152.7*	−138.8	13.9	a	CF₃⁺	99.3	100.7	1.2	n
CF₃COCH₃		−189.9			CH₃CHF⁺	166	164.7	−1.3	o
CF₃COCF₃	−325.2	−322.3	2.9	k	CH₃CF₂⁺	107	116.5	9.4	o
CF₃CO₂H (trans)	−255ⁱ	−238.4	16.6ⁱ	d	CH₂FCF₂⁺	81	84.3	3.3	o
					CF₃CH₂⁺	114	121.1	7.1	o
F—(ring)—CO₂H (structure)	−118.2	−111.9	6.3	d	CH₂FCH₂⁺	>166	187.3		o
					CH₂FCHF⁺	>127	130.8		o
NF₃	−31.4*	−34.1	−2.7	a	CHF₂CHF⁺	>81	97.3		o
FN=NF (cis)	16.4	−2.2	−18.6	a	BF₂⁺	87	84.2	−2.8	a
FN=NF (trans)	19.4	2.5	−16.9	a	NF₂⁺	284	264.3	−19.7	a
					CF₃⁻	−163.4	−178.9	−15.5	p
					NF₂⁻	−29.5	−43.6	−13.1	p
					BF₂⁻	−191.7	−177.4	14.2	q

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center one-electron integrals U_{pp} are about 2 eV more positive than the values given by Oleari.[6] Finally, the use of atomic parameters reduces the number of adjustable constants required for the elements C, H, B, N, O, and F from 61 in MINDO/3 to 31 in MNDO.

Results and Discussion

A. Heats of Formation. Tables II and III compare the calculated and observed heats of formation at 25 °C (ΔH_f) for a representative selection of molecules containing fluorine.

Table IV. Heats of Formation of Open-Shell Fluorine Compounds by the Half-Electron Method[7]

Compd	$\Delta H°_{obsd}$, kcal mol^{-1}	$\Delta H°_{calcd}$, kcal mol^{-1}	Error	Ref
$CH_2F\cdot$		-33.3		
$CHF_2\cdot$		-88.4		
$CF_3\cdot$	-112.4	-137.2	-24.8	a,b
$CF_3CH_2\cdot$	-123.6	-129.8	-6.2	c
$NF_2\cdot$	10.1	-14.8	-24.9	a
$FO\cdot$	26.1	32.5	6.4	d
$FO_2\cdot$	3.0	24.1	21.1	a
$BF_2\cdot$	-139	-136.8	2.2	b
$\cdot CHF$ ($^3A''$)		14.5		
$\cdot CF_2$ ($^3B_1$)		-31.3		
$\cdot NF$ ($^3\Sigma^-$)		31.6		
$:CHF$ ($^1A'$)	30.0	21.5^e $(19.1)^f$	-8.5	a
$:CF_2$ ($^1A_1$)	-45	-65.2 (-66.4)	-20.2	g
$:NF$ ($^1\Delta$)		68.7 (56.3)		
$CH_3F^+\cdot$	233.3	223.2	-10.1	h
$CH_2F_2^+\cdot$	185.2	178.3	-6.9	h
$CHF_3^+\cdot$	151.9	158.7	6.9	h
$CF_4^+\cdot$		(119.6)		i

^{a} D. R. Stull and H. Prophet, "JANAF Thermochemical Tables", 2nd ed, NSRDS-NBS 37, 1971. ^{b} R. D. Srivastava, O. M. Uy, and M. Farber, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1033 (1974). ^{c} E. C. Wu and A. S. Rodgers, *J. Phys. Chem.*, **78**, 2315 (1974). ^{d} J. Berkowitz, P. M. Dehmer, and W. A. Chupka, *J. Chem. Phys.*, **59**, 925 (1973). ^{e} Obtained from a RHF S_0 calculation. This value should be used in comparison with experimental values, since MNDO is parametrized without inclusion of CI. ^{f} Lowest root of a 3 × 3 CI, based on the S_1 half-electron eigenvectors. ^{g} J. Vogt and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 6682 (1975); E. N. Okafo and E. Whittle, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1366 (1974). ^{h} R. J. Blint, T. B. McMahon, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 1269 (1974). ^{i} Dissociates to CF_3^+ and $F\cdot$.

Results for open-shell molecules, calculated by the "half-electron" method,[7] are listed in Table IV. For 71 molecules where reasonably accurate data are available, the mean absolute error in ΔH_f is reduced from 24.8 kcal/mol (MINDO/3) to 9.8 kcal/mol. The largest improvement is, as expected, for compounds of fluorine with nitrogen and oxygen. Indeed, for compounds of CH and F only, MINDO/3 is slightly superior, probably as a result of the use of bond rather than atomic parameters. Major improvements are seen for carbenes, cations, anions, and radicals, where the mean errors are not significantly greater than the overall error. In the case of radicals, the calculated heats of formation seem to be systematically too negative, a tendency that had previously been noted for radicals containing no fluorine.

In the set of 71 molecules analyzed, only two show errors of greater than 30 kcal in ΔH_f. For one of these ($F_3B_3O_3$), the experimental value may be in error, whereas the other (F_3NO) may be a case where the 2s, 2p orbital basis set used needs extension with polarization functions. The error in the calculated heat of formation (62 kcal) is certainly quite exceptionally large (cf. ref 1-3) and it should also be noted that MNDO gave quite a good result for FNO (error, -9.8 kcal/mol). For this reason, we did not include F_3NO in the statistical analysis.

The only other significant errors occur for highly fluorinated compounds such as C_2F_6, which tend to be too unstable. This systematic deviation seems to be due to an overestimation of the fluorine-fluorine repulsions, which also leads to too small a calculated decrease in the CF bond length with multiple substitution by fluorine at a given carbon atom (see below).
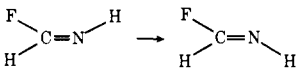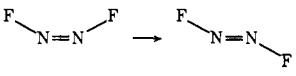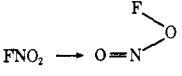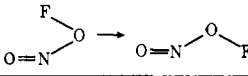
Relative energies of conformational and geometrical isomers come out very well, the propensity of fluorine for cis or gauche

conformations being very well reproduced. In the case of 2-fluoroethanol, this effect is apparently reinforced by weak hydrogen bonding, resulting in the gauche/gauche conformer being the most stable. 2,2,2-Trifluoroethanol is similar, preferring a conformation where the OH bond is gauche with respect to the C–C bond, the length from the hydrogen to the nearest fluorine being 2.8 Å. It should be emphasized that in cases such as this, where the molecule has no symmetry, *all* geometrical variables should be fully optimized. In contrast to the fluoro alcohols, the trans conformer of trifluoroacetic acid is 4 kcal/mol more stable than the cis. There does not appear to be any experimental evidence for this system. The only two examples given in Table V which appear to contradict the experimental evidence are B_2F_4 and N_2F_4. It seems likely that for N_2F_4, the experimental estimate,[8] based on a conformational population measured by electron diffraction, may not be very accurate, and the same may be true for B_2F_4. In the latter case our calculation agrees with a recent ab initio one.[9] Rather surprisingly, ab initio calculations, using the 4-31G basis set, erroneously predict *trans*-1,2-difluoroethylene to be more stable than the cis isomer[10] and *trans*-1,2-difluoroethane to be more stable than the gauche conformer.[11] Also, *cis*-difluorodiazine is only 1 kcal more stable than the trans isomer (full geometry optimization using a 4-31G basis set[10]), the experimental value being about 3 kcal/mol and the MNDO value being 4.7 kcal. One possible weakness of the MNDO method may be in cases involving strong hydrogen bonds. The heat of formation of FHF^- from F^- and HF is predicted to be too positive ($\Delta H_{calcd} = -28.4$ kcal/mol, $\Delta H_{obsd}^{12} = -44$ to -50 kcal/mol), and the energy of most weak hydrogen bonds is underestimated.[13]

The calculated geometries and energies of the molecular ions of the fluoromethanes are interesting. Thus in $H_3CF^+\cdot$ and $H_2CF_2^+\cdot$ the C–H distances are particularly long (1.20–1.21 Å), while in $HCF_3^+\cdot$ the C–H bond length has the large value of 1.38 Å. Curiously, the bound state of the latter is endothermic with respect to $H\cdot$ and CF_3^+ (5.9 kcal/mol) or $F\cdot$ and HCF_2^+ (7.5 kcal/mol). The activation energy for the dissociation to $H\cdot$ and CF_3^+ is only 1.8 kcal/mol (the H–C bond length in the transition state being 1.8 Å), compared with 14.1 kcal/mol for dissociation to $F\cdot$ and HCF_2^+. This is consistent with the observed mass spectral fragmentation, the molecular ion not normally being observed and the M − 1 ion being more intense than the M − 19 ion.[14] $CF_4^+\cdot$ is calculated to be unbound, in agreement with the failure to observe any molecular ion for this species.

B. Relative Energies of Singlets and Triplets. The ground states of CH_2 and NF are well established to be triplets and those of CHF and CF_2 to be singlets, although the singlet-triplet separation of even such a well-studied case as methylene continues to be controversial.[15] The MNDO results (Table IV) predict that the singlet ground state of CF_2 ($^1A_1$) is 34 kcal/mol lower than the triplet $^3B_1$ state, which is qualitatively correct and also in good agreement with the ab initio calculations of Staemmler[16] (34 kcal/mol). However, we incorrectly predict the $^3A''$ state of CHF to be 7 kcal/mol lower than the singlet $^1A'$ state, compared with a separation of 7.4 kcal/mol obtained by Pople using a 3G basis set[17] and 3 kcal/mol obtained by Staemmler using a larger basis set.[16] If allowance for electron correlation is made in the ab initio methods, however, the triplet energy is increased by up to 15 kcal relative to the singlet. Thus the most recent calculations[15] predict a $^3B_1/^1A_1$ separation for methylene itself of about 8-9 kcal/mol, in agreement with photochemical determinations but not with a recent photoelectron value[15] of 19.5 kcal/mol. The MNDO value of 30 kcal/mol[18] is in better agreement with this latter value. The electron affinity, however, is not reproduced very well ($EA_{calcd} - 1.19$ eV, EA_{obsd} 0.21 ± 0.03 eV[15]). The $^3\Sigma^-/^1\Delta$ separation for FN: is calculated by MNDO to be 37.1

Table **V.** Relative Energies of Conformational and Geometrical Isomers

Isomerization reaction	$\Delta(\Delta H)$, kcal mol^{-1}		
	Calcd[a]	Exptl	Ab initio
CH_2FCH_2F (gauche) → CH_2FCH_2F (trans)	0.3	0.6[b]	−1.0[c]
CF_3CF_3 (D_{3d}) → CF_3CF_3 (D_{3h})	2.1	3.9[d]	
CH_2FCH_2OH (gauche) → CH_2FCH_2OH (trans)	0.7	>2.8[e]	0.8[c]
N_2F_4 (C_2) → N_2F_4 (C_{2h})	1.3	−0.9[f]	
B_2F_4 (D_{2d}) → B_2F_4 (D_{2h})	1.1	−0.3[g]	0.3[h]
CHF=CHF (cis) → CHF=CHF (trans)	0.5	0.9[i]	<0[j]
(F,H)C=N–H → (F)C=N(H,H)	2.5		2.0[j]
(F,F)N=N → (F)N=N(F)	4.7	3.0[k]	1.0[l]
CF_3N=NCF_3 (trans) → CF_3N=NCF_3 (cis)	4.0	>0[m,n]	
HNF_2 (C_s) → HNF_2 (C_{2v})	29.6	>18.0[o]	34.4–41.7[p]
FNO$_2$ → O=N(F)O	1.1		
(F)O=N → O=N–O–F	1.3		

[a] Values for ΔH_f are given in Table III. [b] P. Huber-Wälchli and H. H. Günthard, *Chem. Phys. Lett.*, **30**, 347 (1975), who report a value for $\Delta G°$; $\Delta H°$ will be about 700 cal/mol less. [c] L. Radom, W. A. Latham, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **95**, 693 (1973). [d] D. F. Eggers, R. C. Lord, and C. W. Wickstrom, *J. Mol. Spectrosc.*, **59**, 63 (1976). [e] K. Hagen and K. Hedberg, *J. Am. Chem. Soc.*, **95**, 8263 (1973). [f] M. M. Gilbert, G. Gundersen, and K. Hedberg, *J. Chem. Phys.*, **56**, 1691 (1972). The value was obtained from the conformation population as estimated by electron diffraction. [g] D. D. Danielson and K. Hedberg, Sixth Austin Symposium on Gas Phase Molecular Structure, University of Texas at Austin, 1976, p 21. [h] J. M. Howell and J. R. Van Wazer, *J. Am. Chem. Soc.*, **96**, 7902 (1974). [i] N. C. Craig and J. Overend, *J. Chem. Phys.*, **51**, 1127 (1969). [j] J. M. Howell, *J. Am. Chem. Soc.*, **98**, 886 (1976). [k] G. T. Armstrong and S. Marantz, *J. Chem. Phys.*, **38**, 169 (1962). [l] J. M. Howell and L. J. Kirschenbaum, *J. Am. Chem. Soc.*, **98**, 877 (1976). This result was obtained using a 4-31G basis set. The same authors find a barrier to isomerization of 71 kcal/mol with the same basis set. The MNDO value is 63.4 kcal/mol. [m] Infrared and Raman evidence[n] strongly supports the trans configuration in the gas phase. [n] R. A. Hayden, E. C. Tuazon, and W. G. Fateley, *J. Mol. Struct.*, **16**, 35 (1973). [o] The value for an alkyldifluoramine; cf. S. K. Brauman and M. E. Hill, *J. Chem. Soc. B*, 1091 (1969). [p] S. Skaarup, L. L. Griffin, and J. E. Boggs, *J. Am. Chem. Soc.*, **98**, 3140 (1976).

Table **VI.** Proton and Electron Affinities of Fluorine Compounds

Base	Proton affinity,[a] kcal mol^{-1}	Calcd	Error
CH_2CHF	168[b]	166.4	−1.6
CH_2CF_2	177[b]	165.0	−12.0
$CHFCF_2$	167[b]	150.2	−16.8
:CHF		204.5	
:CF$_2$	172[c]	168.4	−3.6

Molecule	Electron affinity,[d] kcal mol^{-1}	Calcd	Error
CF$_3$·	46[e]	42	−4
BF$_2$·	51[f]	41	−10
:CHF		0.5	
:CF$_2$		15.8	

[a] ΔH for the reaction X + H$^+$ → XH$^+$. [b] D. P. Ridge, *J. Am. Chem. Soc.*, **97**, 5670 (1975). [c] J. Vogt and J. L. Beauchamp, *ibid.*, **97**, 6682 (1975). [d] ΔH for the reaction X· + e$^-$ → X$^-$. [e] J. H. Richardson, L. J. Stephenson, and J. I. Brauman, *Chem. Phys. Lett.*, **30**, 17 (1975). [f] R. D. Srivastava, O. M. Uy, and M. Farber, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1033 (1974).

Table **VII.** Mean Absolute Errors in Optimized Bond Lengths and Bond Angles

Geometrical variable	No.	Mean absolute error
All bond lengths	130	0.034[a]
Involving H	23	0.016
BF	5	0.004
CF	37	0.018
NF	9	0.105
OF	3	0.148
FF	1	0.152
BC	1	0.020
CC	32	0.038
CN	8	0.033
CO	4	0.044
BN	1	0.006
BO	1	0.018
NN	5	0.035
All bond angles	75	2.73[b]
Involving F	47	3.07
Not involving F	28	2.14

[a] In angstroms. [b] In degrees.

kcal/mol. MNDO therefore seems to predict the correct singlet–triplet ordering for carbenes, except when the energy difference is small, as is obviously the case for monofluoromethylene. The stability of triplet species may be overestimated, a phenomenon noted previously for doublets (vide supra).

C. Proton and Electron Affinities. Shown in Table VI is a comparison of calculated proton and electron affinities with some recently determined values. The agreement is generally satisfactory.

D. Molecular Geometries.[19] Table VII shows error statistics for geometries calculated by MNDO while Table VIII gives detailed comparisons with experiment. The results are very much superior to those given by MINDO/3,[4c] where totally incorrect geometries were predicted for certain molecules (e.g.,
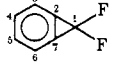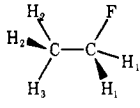
Table VIII. Molecular Geometries
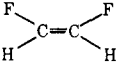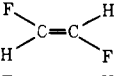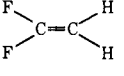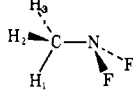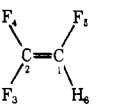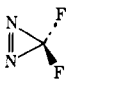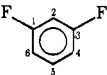
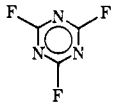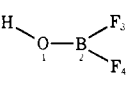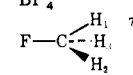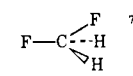| Molecule	Point group	Calcd (obsd) values for geometrical variables[a]	Ref	Molecule	Point group	Calcd (obsd) values for geometrical variables[a]	Ref
HF	$C_{\infty v}$	HF 0.956 (0.917)	b	(phenyl)–F	D_{6h}	CC 1.434 (1.408), CF 1.317 (1.324)	q
CH_3F	C_{3v}	CH 1.118 (1.098),* CF 1.347 (1.382),* HCF 110.6 (108.5)*	c	(bicyclic F₂ structure)	C_{2v}	C^1C^2 1.524 (1.52), C^2C^3 1.364 (1.355), C^3C^4 1.438 (1.423), C^4C^5 1.403 (1.411), C^2C^7 1.420 (1.339), CF 1.338 (1.329), FCF 107.3 (109.4)	r
CH_2F_2	C_{2v}	CH 1.129 (1.093), CF 1.352 (1.358), HCH 108.2 (111.8), FCF 106.8 (108.3)	d	HC≡CF	$C_{\infty v}$	CC 1.192 (1.198), CF 1.277 (1.278)	s
CHF_3	C_{3v}	CH 1.136 (1.098), CF 1.353 (1.332), HCF 111.5 (110.5)	d	HCOF	C_s	CO 1.222 (1.181), CF 1.328 (1.338), OCF 117.9 (122.5)	d
CF_4	T_d	CF 1.347 (1.321)*	e	CH_3COF	C_s	CO 1.226 (1.181), CF 1.332 (1.348), CCO 126.5 (128.3), CCF 117.5 (110.3)	r
(CH₃CHF₂ structure)	C_s	CH 1.108 (1.09), CC 1.547 (1.505), CF 1.352 (1.398), H^1CC 109.3 (112.9), H^3CC 109.3 (110.4), H^2CC 111.6 (109.7)	f	$F_2C{=}O$	C_{2v}	CO 1.219 (1.170),* CF 1.316 (1.317),* FCO 124.1 (126.2)*	u
CF_3CH_3	C_{3v}	CH 1.106 (1.085), CC 1.586 (1.530), CF 1.358 (1.335), HCC 110.0 (108.3), FCC 112.7 (111.0)	e	$(CF_3)_2CO$	C_{2v}	CC 1.607 (1.549), CO 1.208 (1.246), CF 1.351 (1.335), CCC 118.8 (121.3), FCC 111.6 (110.3)	v
CF_3CF_3	D_{3d}	CC 1.674 (1.545), CF 1.346 (1.326), CCF 110.7 (109.8)	h	HOF	C_s	HO 0.964 (0.966), OF 1.277 (1.442), HOF 107.9 (96.8)	w
(difluorocyclopropane)	C_{2v}	CH 1.096 (1.082), C^1C^2 1.528 (1.464), C^2C^3 1.556 (1.553), FCF 107.4 (108.4)	i	F_2O	C_{2v}	OF 1.281 (1.412),* FOF 109.1 (103.2)*	d
(cyclopropenyl F)	D_{3h}	CC 1.607 (1.505), CF 1.329 (1.314), FCF 108.4 (112.2)	j	CF_3OF	C_s	CO 1.443 (1.395), CF 1.342 (1.319), OF 1.274 (1.421), FCF 110.7 (109.4), COF 110.7 (104.8)	x
(cyclobutyl F)	D_{2d}	CC 1.646 (1.566), CF 1.341, 1.333 (1.333), FCF 107.1 (109.9)	k	NF_3	C_{3v}	NF 1.315 (1.365),* FNF 106.1 (102.3)*	y
(vinyl fluoride)	C_s	H^1C 1.099 (1.076),* H^2C 1.087 (1.090), H^3C 1.088 (1.085),* CC 1.350 (1.333),* CF 1.324 (1.348)* H^1CC 123.0 (127.7)*, H^2CC 124.5 (121.4),* H^3CC 120.9 (123.9), CCF 123.3 (121.0)*	l	FNNF	C_{2v}	NN 1.240 (1.214), NF 1.281 (1.410), NNF 121.6 (114.4)	z
CH_2FCH_2F	C_2	CC 1.576 (1.535), CF 1.348 (1.394), HCC 108.5 (108.3), CCF 112.9 (108.3), FCCF 60.6 (74.5)	g	FNNF	C_{2h}	NN 1.261 (1.231), NF 1.277 (1.396), NNF 112.1 (105.5)	z
(cis-difluoroethylene)	C_{2v}	HC 1.097 (1.084), CC 1.367 (1.331), CF 1.320 (1.335), CCH 121.4 (121.6), CCF 123.8 (123.7)	l	F_2NNF_2	C_{2h}	NN 1.519 (1.495), NF 1.302 (1.372), NNF 106.2 (101.4), FNNF 66.5 (64)	aa
(trans-difluoroethylene)	C_{2h}	HC 1.097 (1.080), CC 1.309 (1.329), CF 1.322 (1.344), CCH 124.5 (129.3), CCF 120.9 (119.3)	l	HNF_2	C_s	NF 1.309 (1.400), FNF 107.4 (102.9)	bb
(1,1-difluoroethylene)	C_{2v}	HC 1.086 (1.075), CC 1.359 (1.316), CF 1.325 (1.324), CCH 122.2 (120.4), CCF 125.4 (125.3)	l	(CH₃NF₂ structure)	C_s	CH 1.109 (1.091), CN 1.539 (1.449), NF 1.310 (1.413), CNF 110.5 (104.6), H^1CN 113.9 (110.4), H^2CN 107.1 (106.2), H^1CNF 58.6 (52.9)	cc
(trifluoroethylene)	C_s	HC 1.095 (1.073), CF^5 1.317, CF^4 1.321, CF^3 1.322 (1.336), CC 1.376 (1.309), CCH 122.8 (127.2), CCF^3 123.4 (125.4), CCF^5 121.4 (118.8)	l	(diaziridine structure)	C_{2v}	CN 1.486 (1.426), NN 1.241 (1.293), CF 1.324 (1.315), FCF 112.7 (111.8), NCN 49.4 (54.0)	dd
C_2F_4	D_{2h}	CC 1.381 (1.311),* CF 1.318 (1.319),* CCF 124.2 (123.8)*	l	$CF_3N{=}NCF_3$	C_{2v}	CN 1.531 (1.490), NN 1.191 (1.236), CF 1.343 (1.326), NNC 132.0 (133.0), NCF 109.0 (109.3)	ee
(fluorocyclobutene structure)	C_{2v}	C^1C^2 1.367 (1.348), C^2C^3 1.570 (1.506), C^3C^4 1.674 (1.591), C^3F 1.338 (1.339), C^1F 1.297 (1.312), C^1C^2F 135.3 (136.6), $C^2C^3C^4$ 84.4 (85.4)	m	$F_2N^1{-}CN^2$	C_s	N^1C 1.441 (1.386), CN^2 1.157 (1.158), NF 1.312 (1.399), N^1CN^2 173.5 (173.9), CN^1F 109.6 (105.4)	ff
(allene difluoride structure)	C_{2v}	HC 1.092 (1.083), C^1C^2 1.323 (1.302), C^2C^3 1.301 (1.306), CF 1.325 (1.323), CCH 122.8 (121.2), CCF 125.2 (125.0)	n	FCN	$C_{\infty v}$	CN 1.160 (1.159),* CF 1.273 (1.262)*	s
(fluorobenzene)	C_{2v}	HC 1.09 (1.081), C^1C^2 1.422 (1.383), C^2C^3 1.404 (1.395), C^3C^4 1.406 (1.397), CF 1.326 (1.354), $C^6C^1C^2$ 120.5 (123.4), $C^1C^2C^3$ 119.1 (117.9)	o	CF_3CN	C_{3v}	CC 1.498 (1.461), CN 1.158 (1.153), CF 1.355 (1.335), FCC 111.9 (111.4)	d
(difluorobenzene)	C_{2v}	HC^2 1.090 (1.107), C^1C^2 1.420 (1.383), C^3C^4 1.420 (1.385), C^4C^5 1.404 (1.405)	p	(trifluorotriazine structure)	D_{3h}	CN 1.323 (1.333), CF 1.303 (1.310), CNC 114.0 (113.0)	gg
				FNO	C_s	NO 1.161 (1.136),* NF 1.305 (1.514),* ONF 113.8 (110.1)*	hh
				F_3NO	C_{3v}	NO 1.234 (1.158), NF 1.355 (1.431), ONF 114.2 (119.1)	ii
				BF_3	D_{3h}	BF 1.316 (1.310)*	jj
				B_2F_4	D_{2d}	BB 1.747, BF 1.316, BBF 123.9	
				HBF_2	C_{2v}	BF 1.316 (1.311), FBF 114.8 (118.3)	kk
				$F_2BC{\equiv}CH$	C_{2v}	HC 1.053 (1.058), BC 1.493 (1.513), CC 1.200 (1.206), BF 1.320 (1.323), FBF 114.2 (116.5)	ll

Table VIII (*Continued*)

Molecule	Point group	Calcd (obsd) values for geometrical variables[a]	Ref	Molecule	Point group	Calcd (obsd) values for geometrical variables[a]	Ref
H_2N—BF_2	C_{2v}	HN 0.993 (1.003), BN 1.408 (1.402), BF 1.325 (1.328), FBF 116.8 (117.9), HNH 114.6 (116.9)	mm	$BF_2 \cdot$	C_{2v}	BF 1.291, FBF 125.6	
$H\diagdown O_1$—$B_2\diagup{}^{F_3}_{F_4}$	C_s	HO 0.945 (0.941), BO 1.362 (1.344), BF^3 1.317, BF^4 1.324 (1.323), FBF 118.5 (118.0), OBF 123.0 (122.8)	nn	$CF_2^- \cdot$	C_{2v}	CF 1.342, FCF 106.4	
				CF_3^-	C_{3v}	CF 1.370, FCF 104.5	
				NF_2^-	C_{2v}	NF 1.308, FNF 107.6	
				BF_2^-	C_{2v}	BF 1.359, FBF 105.2	
F_2	$D_{\infty h}$	FF 1.266 (1.418)*	d	BF_4^-	T_d	BF 1.390	
HCF	C_s	HC 1.120 (1.121), CF 1.285 (1.314), HCF 111.1 (101.6)	d	F—$C\diagup^{H_1}_{\diagdown H_3}$ 7+·	C_s	H^1C 1.112, H^2C 1.201, H^2H^3 1.447, CF 1.292, H^1CF 115.8, H^2CF 114.6	
:CF_2	C_{2v}	CF 1.304 (1.304), FCF 108.3 (104.8)	oo	F—$C\diagup^F_{\diagdown H}$ 7+·	C_{2v}	HC 1.207, HH 1.609, CF 1.308, FCF 111.0, HCF 115.0	
$CF_3 \cdot$	C_{3v}	CF 1.312 (1.33), FCF 115.4 (112)	d				
$NF_2 \cdot$	C_{2v}	NF 1.271 (1.350), FNF 109.7 (103.3)	pp	H—CF_3 7+·	C_{3v}	HC 1.380, CF 1.314, HCF 102.8	

[a] Bond length A[i]B[j] (in A), bond angle A[i]B[j]C[k] (in degrees), and dihedral angle A[i]B[j]C[k]D[l] (in degrees) of A-B measured clockwise with respect to C-D. [b] G. A. Knipers, D. F. Smith, and A. N. Nielsen, *J. Chem. Phys.*, 25, 275 (1956). [c] J. L. Duncan, *J. Mol. Struct.*, 6, 447 (1970). [d] D. R. Stull and H. Prophet, "JANAF Thermochemical Tables", 2nd ed, NSRDS-NBS 37, 1971. [e] A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, 3, 117 (1974). [f] S. S. Chen, A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski, *ibid.*, 4, 441 (1975). [g] J. R. Lombardi, W. Klemperer, M. B. Robin, H. Basch, and N. A. Kuebler, *J. Chem. Phys.*, 51, 33 (1969). [h] K. L. Gallaher, A. Yokozeki, and S. H. Bauer, *J. Phys. Chem.*, 78, 2389 (1974). [i] A. T. Perretta and V. W. Laurie, *J. Chem. Phys.*, 62, 2469 (1975). [j] J. F. Chiang and W. A. Bernett, *Tetrahedron*, 27, 975 (1971). [k] C. H. Chang, R. F. Porter, and S. H. Bauer, *J. Mol. Struct.*, 7, 89 (1971). [l] J. L. Carlos, R. R. Karl, and S. H. Bauer, *J. Chem. Soc., Faraday Trans. 2*, 177 (1974). [m] K. L. Gallaher, Y. C. Wang, and S. H. Bauer, *J. Mol. Struct.*, 25, 35 (1975). [n] J. R. Durig, Y. S. Li, C. C. Tong, A. P. Zens, and P. D. Ellis, *J. Am. Chem. Soc.*, 96, 3805 (1974). [o] L. Nygard, I. Bojesen, T. Pedersen, and J. Rastrup-Andersen, *J. Mol. Struct.*, 2, 209 (1968). [p] E. J. H. Van Schaick, H. J. Geise, F. C. Mijlhoff, and G. Renes, *J. Mol. Struct.*, 16, 389 (1973). [q] S. H. Bauer, K. Katada, and K. Kimura in "Structural Chemistry and Molecular Biology", A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, pp 653-670. [r] R. Pozzi, D. R. Ramaprasad, and E. A. C. Lucken, *J. Mol. Struct.*, 28, 111 (1975). [s] J. K. Tyler and J. Sheridan, *Trans.*

Faraday Soc., 59, 2661 (1963). [t] R. W. Davis and M. C. L. Gerry, *J. Mol. Spectrosc.*, 57, 118 (1975). [u] J. H. Carpenter, *ibid.*, 50, 182 (1974). [v] R. L. Hildebrandt, A. L. Andreassen, and S. H. Bauer, *J. Phys. Chem.*, 74, 1586 (1970). [w] M. W. Chase, J. L. Curnutt, H. Prophet, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data*, 4, 1 (1975). [x] F. P. Diodati and L. S. Bartell, *J. Mol. Struct.*, 8, 395 (1971). [y] M. Otake, C. Matsumura, and Y. Morino, *J. Mol. Spectrosc.*, 28, 316 (1968). [z] R. K. Bohn and S. H. Bauer, *Inorg. Chem.*, 6, 309 (1967). [aa] M. M. Gilbert, G. Gundersen, and K. Hedberg, *J. Chem. Phys.*, 56, 1691 (1972). [bb] D. R. Lide, *ibid.*, 38, 456 (1963). [cc] L. Pierce, R. G. Hayes, and J, F. Beecher, *ibid.*, 46, 4352 (1967). [dd] J. L. Hencher and S. H. Bauer, *J. Am. Chem. Soc.*, 89, 5527 (1967). [ee] C. H. Chang, R. F. Porter, and S. H. Bauer, *ibid.*, 92, 5313 (1970). [ff] P. L. Lee, K. Cohn, and R. H. Schwendeman, *Inorg. Chem.*, 11, 1920 (1972). [gg] J. Schlupf and A. Weber, *J. Mol. Spectrosc.*, 54, 10 (1975). [hh] K. S. Buckton, A. C. Legon, and D. J. Millen, *Trans. Faraday Soc.*, 65, 1975 (1969). [ii] V. Plato, W. D. Hartford, and K. Hedberg, *J. Chem. Phys.*, 53, 3488 (1970). [jj] S. G. W. Ginn, J. K. Kenney, and J. Overend, *ibid.*, 48, 1571 (1968). [kk] T. Kasuya, W. J. Lafferty, and D. R. Lide, *ibid.*, 48, 1 (1968). [ll] W. J. Lafferty and J. J. Ritter, *J. Mol. Spectrosc.*, 38, 181 (1971). [mm] F. L. Lovas and D. R. Johnson, *J. Chem. Phys.*, 59, 2347 (1973). [nn] H. Takeo and R. F. Curl, *ibid.*, 56, 4314 (1972). [oo] W. H. Kirchoff, D. R. Lide, and F. X. Powell, *J. Mol. Spectrosc.*, 47, 491 (1973). [pp] R. D. Brown, F. R. Burden, P. G. Godfrey, and I. R. Gillard, *ibid.*, 52, 301 (1974).

NF_3, CF_2, C_2F_4, C_2F_6). All these "problem" molecules are well reproduced by MNDO and the average error in bond angle (2.7°, Table VII) is almost the same as for molecules free from fluorine.[2] Indeed, there are no cases where MNDO predicts geometries that are greatly in error and the rotational

barrier in C_2F_6 is quite well reproduced (Table V).

MNDO also avoids another error of MINDO/3, i.e., its tendency to predict excessive stability for π complex structures with apical fluorine in compounds such as $C_2H_4F^+$, $CF_3CH_2 \cdot$, CH_2FCH_2F, or N_2F_4.[4c] The calculated MNDO geometries

Table IX. First Vertical Ionization Potentials IP_1

| Molecule | IP_1, eV | | | | Molecule | IP_1, eV | | | |
	Obsd	Calcd[a]	Error	Ref		Obsd	Calcd[a]	Error	Ref
HF	16.03	14.82	−1.21	b	$(CF_3)_2CO$	12.09	12.99	0.90	f
CH_3F	13.31	13.05	−0.26	c	NF_3	13.73*	13.93	0.20	m
CH_2F_2	13.17	13.09	−0.08	c	FNNF (trans)	13.4	13.00	−0.40	f
CHF_3	14.67	14.57	−0.10	c	N_2F_4 (gauche)	12.84	13.02	0.18	n
CF_4	16.23*	16.81	0.58	c	N_2F_4 (trans)		12.61		
CH_3CH_2F	12.43	12.61	0.18	d					
CH_3CHF_2	12.8	12.73	−0.07	d	$F_3C\diagdown^{N}_{\diagdown N}$	11.78	12.05	0.27	f
CH_3CF_3	13.8	14.01	0.21	d					
C_2F_6	14.6	14.50	−0.10	d	CF_3NNCF_3 (cis)	11.35	12.27	0.92	f
CH_2=CHF	10.58	10.18	−0.40	e	$(NCF)_3$ (1,3,5)	12.0	12.71	0.71	h
CH_2=CF_2	10.72	10.45	−0.27	e					
CHF=CHF (cis)	10.43	10.18	−0.25	f	$\underset{N}{\bigcirc}$—F	10.27	10.72	0.45	h
CHF=CHF (trans)	10.38	10.19	−0.19	f					
CHF=CF_2	10.53	10.46	−0.07	f	FNO	12.94	12.93	−0.01	o
CF_2=CF_2	10.54*	10.75	0.21	f	FNO_2	13.51	12.99	−0.52	o
C_6H_5F	9.19	9.47	0.28	g	BF_3	15.95	16.22	0.27	p
$C_6H_4F_2$ (1,2)	9.68	9.69	0.01	g	B_2F_4 (D_{2d})	13.26	13.46	0.20	q
$C_6H_4F_2$ (1,3)	9.68	9.73	0.05	g	F_2BNH_2		11.69		
$C_6H_4F_2$ (1,4)	9.15	9.56	0.41	g			(*Continued*)		

Table IX (*Continued*)

Molecule	Obsd	Calcd[a]	Error	Ref	Molecule	Obsd	Calcd[a]	Error	Ref
	IP$_1$, eV					IP$_1$, eV			
C_6F_6	10.12	10.77	0.65	h	F-B$_3$N$_3$F$_2$ ring (FB–N–BF, N–B(F)–N)	10.79	11.43	0.64	f
FC≡CH	11.30	11.07	-0.23	i					
HOF	13.0	12.75	-0.25	j					
CF_3CH_2OH	11.74	12.38	0.64	k					
CF_3OF	13.64	14.23	0.59	k	F_2	15.83	15.25	-0.58	r
OF_2	13.26*	13.52	0.26	f	:CF_2	12.27	12.18	-0.09	s
CH_3COF	11.80	12.21	0.41	l	CF_3·		11.20		t
F_2CO	13.60	13.62	0.02	f	NF_2·	12.10	12.23	0.13	n,t
					OF·		14.11		t

[a] Calculated using Koopmans' theorem. [b] J. Berkowitz, *Chem. Phys. Lett.*, 11, 21 (1971). [c] M. S. Banna, B. E. Mills, D. W. Davis, and D. A. Shirley, *J. Chem. Phys.*, 61, 4780 (1974). [d] P. Sauvageau, J. Doucet, R. Gilbert, and C. Sandorfy, *ibid.*, 61, 391 (1974). [e] R. F. Lake and H. Thompson, *Proc. R. Soc. London, Ser. A*, 315, 323 (1970). [f] C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Am. Chem. Soc.*, 94, 1451 (1972). [g] D. G. Streets and G. P. Caesar, *Mol. Phys.*, 26, 1037 (1973). [h] C. R. Brundle, M. B. Robin, and N. A. Kuebler, *J. Am. Chem. Soc.*, 94, 1466 (1972). [i] E. Heilbronner, K. A. Muszkat, and J. Schäublin *Helv. Chim. Acta*, 54, 58 (1971). [j] J. Berkowitz, E. H. Appleman, and J. L. Dehmer, *Chem. Phys. Lett.*, 19, 334 (1973). [k] M. B. Robin and N. A. Keubler, *J. Electron Spectrosc. Relat. Phenom.*, 1, 13 (1972). [l] D. Chadwick and A. Katrip, *ibid.*, 3, 39 (1974). [m] P. J. Bassett and D. R. Lloyd, *J. Chem. Soc., Dalton Trans.*, 248 (1972). [n] A. B. Cornford, D. C. Frost, F. G. Herring, and C. A. McDowell, *J. Chem. Phys.*, 54, 1872 (1971). [o] D. C. Frost, S. T. Lee, C. A. McDowell, and N. P. C. Westwood, *J. Electron Spectrosc. Relat. Phenom.*, 7, 331 (1975). [p] T. E. H. Walker and J. A. Horsley, *Mol. Phys.*, 21, 939 (1971). [q] N. Lynaugh, D. R. Lloyd, M. F. Guest, M. B. Hall, and I. H. Hillier, *J. Chem. Soc., Faraday Trans. 2*, 68, 2192 (1972). [r] Reference 21. [s] J. M. Dyke, L. Golob, N. Jonathan, A. Morris, and M. Okuda, *J. Chem. Soc., Faraday Trans. 2*, 70, 1828 (1974). [t] Calculated from the energy of the vertical singlet cation.

Table X. Higher Vertical Ionization Potentials IP

Molecule	Orbital[a]	Obsd	Calcd[b]	Ref	Molecule	Orbital[a]	Obsd	Calcd[b]	Ref
		IP, eV					IP, eV		
CH_3F	$2e$	13.31	13.05	c	F_2CO	$7a_1$	19.15	19.54	
	$1e$	16.55	17.17			$1b_2$	19.8	19.68	
	$5a_1$	17.56	17.42			$3b_1$	21.1	20.68	
	$4a_1$	23.48	27.54			$6a_1$	23.4	23.4	
	$3a_1$	38.41	46.24		F_2O	$2b_2$	13.25	13.52 15.4[f]	d
CF_4	$1t_1$	16.33	16.81	c		$6a_1$	16.10	16.14 16.4	
	$4t_2$	17.41	17.12			$4b_1$	16.44	16.62 17.2	
	$1e$	18.43	17.47			$1a_2$	18.50	17.00 18.4	
	$3t_2$	22.14	21.24			$1b_2$	19.55	19.36 20.8	
	$4a_1$	25.11	24.46			$5a_1$		20.01 20.2	
	$2t_2$	40.30	45.52			$3b_1$	20.7	22.09 20.0	
	$3a_1$	43.81	53.70		FNNF (trans)	$7a_g$	13.4	13.00	d
C_2F_4	$2b_{2u}$	10.52	10.74	d		$2a_u$	14.1	13.40	
	$6a_g$	15.95	15.73			$6b_u$		16.51	
	$4b_{1u}$	16.4	16.62[e]			$6a_g$		17.41	
	$4b_{2g}$	16.6	16.64[e]			$1b_g$		17.70	
	$1a_u$	16.9	16.80			$1a_u$	18.7	19.26	
	$1b_{3g}$	17.6	16.86			$5b_u$	19.8	19.54	
	$5b_{3u}$	18.21	17.32			$5a_g$	21.0	21.38	
	$1b_{1g}$		18.38			$4b_u$	22.7	25.01	
	$3b_{2g}$		19.41		FNO	$10a'$	12.94	12.93	g
	$1b_{2u}$		19.58			$2a''$	13.58	15.23	
	$3b_{1u}$	19.46	20.57				to		
	$5a_g$	21.0	20.79			$9a'$	15.59	15.53	
	$4b_{3u}$	22.5	22.54			$1a''$	17.85	18.74	
	$4a_g$		30.32				to		
F_2CO	$5b_1$	13.6	13.61	d		$8a'$		18.75	
	$2b_2$	14.6	14.18			$7a'$	19.61	20.73	
	$8a_1$	16.6	16.46		F_2	$^1\Pi_g$	15.83	15.25	h
	$4b_1$	17.2	16.97			$^1\Pi_u$	18.8	19.22	
	$1a_2$		17.11			$^3\Sigma_g^+$	~21.0	20.9	

[a] The numbering of the MOs refers to a basis set including 1s orbitals for ease of comparison with ab initio calculations. The assignments are identical with those in the literature, with certain exceptions noted below. [b] Calculated using Koopmans' theorem. [c] M. S. Banna, B. E. Mills, D. W. Davis, and D. A. Shirley, *J. Chem. Phys.*, 61, 4780 (1974). [d] C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Am. Chem. Soc.*, 94, 1451 (1972). See also J. A. Pappas, *J. Mol. Struct.*, 22, 69 (1974). [e] Ab initio calculations (see ref d) predict the ordering of these two orbitals to be reversed. See also ref f and text. [f] Orbital energies using Koopmans' theorem from ref d. Note that the MNDO ordering of the $1b_2$ and $3b_1$ orbitals disagrees with ref d, but is in agreement with the ordering reported in ref 22. These latter results were obtained by applying third-order perturbation corrections to Koopmans' theorem eigenvalues. [g] D. C. Frost, S. T. Lee, C. A. McDowell, and N. P. C. Westwood, *J. Electron Spectrosc. Relat. Phenom.*, 7, 331 (1975). [h] Reference 21. See text for further discussion.

Table XI. The "Perfluoro" Effect for Ethylenes

| | Obsd[a] | | MNDO | |
	1st IP, eV	Δ^b	1st IP, eV	Δ^b
C_2H_4	10.51	2.34	10.18	2.66
$H_2C=CHF$	10.58	3.21	10.17	3.23
$H_2C=CF_2$	10.72	4.07	10.45	4.49
FHC=CHF (cis)	10.43	3.54	10.18	3.36
FHC=CHF (trans)	10.38	3.52	10.19	3.23
$F_2C=CHF$	10.53	4.11	10.46	4.04
$F_2C=CF_2$	10.52	5.43	10.74	4.99

[a] C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Am. Chem. Soc.*, **94**, 1451 (1972). [b] Difference (in eV) between the π and the first σ level.

are all qualitatively correct; indeed the bridged form of $C_2H_4F^+$ is 40 kcal higher in energy than the classical isomer.

While qualitatively correct, the MNDO results do show some quantitative failings. As can be seen in Table VII, a regular trend is discernible in the mean errors for the C–F, N–F, O–F, and F–F bond lengths. A similar error was noted previously[2] for O–O and could not be eliminated except at the expense of using bond parameters for the resonance integrals

and core–core repulsions. There is also a quantitative failure in the calculated shrinkage of the C–F bond length on successive fluorination of methane. As noted previously, highly fluorinated compounds also tend to be too unstable.

E. Ionization Energies. The mean absolute error for 43 molecules in the first vertical ionization energy is 0.34 eV, compared with 1.47 eV for MNDO/3[4c] (Table IX). The symmetry of the HOMO, in all cases where it is known, is correct. Both the energies and symmetries of the higher cationic states, as predicted by Koopmans' theorem, agree very well with experiment (Table X).

Probably the most notorious case where Koopmans' theorem has failed to predict the correct orderings of cationic states is for the N_2 and F_2 molecules,[20] and the energies of these states obtained using the Hartree–Fock method have to be corrected using suitable methods.[20] It is therefore interesting that the MNDO orbital energies for F_2 (and also N_2[2]) agree with the experimental assignments for the doublet cationic states[21] (Table X), but not with ab initio RHF eigenvalues.[20] The MNDO values also agree with the calculations of Cederbaum,[20] where corrections for electron correlation and relaxation were made with a perturbation approach using Green's functions. It is significant in this connection that MNDO makes allowance for electron correlation in the neutral ground
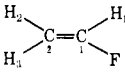
Table XII. Dipole Moments μ

| | μ, D | | | | | μ, D | | | |
Molecule	Obsd[a]	Calcd	Error	Ref	Molecule	Obsd[a]	Calcd	Error	Ref
HF	1.83	1.99	0.16	b	$(CF_3)_2CO$	0.65	0.66	0.01	e
CH_3F	1.86*	1.76	−0.10	c	CF_3CO_2H (trans)	2.28	2.44	0.16	d
CH_2F_2	1.96	2.21	0.25	d	HOF	2.23	1.81	−0.42	m
CHF_3	1.65	2.23	0.58	c	F_2O	0.30	0.33	0.03	d
CH_3CH_2F	1.96	1.87	−0.09	d	CF_3OF	0.33	0.09	−0.24	n
CH_3CHF_2	2.30	2.50	0.20	d	FNNF (cis)	0.16	0.02	−0.14	e
CH_2FCH_2F (gauche)	2.67	2.84	0.17	e	NF_3	0.24*	0.20	−0.04	d
CH_3CF_3	2.32	2.87	0.55	d	HNF_2	1.92	1.89	−0.03	e
⋉F F	2.32	2.72	0.40	f	CH_3NF_2	2.57	2.61	0.03	o
$H_2C=CHF$	1.43*	1.70	0.27	d	N⋉F N F	0.0	0.56	0.56	p
FHC=CHF (cis)	2.42	2.85	0.43	d	F—CN	2.17*	0.89	−1.28	k
$F_2C=CH_2$	1.39	2.03	0.64	c	CF_3CN	1.26	0.35	−0.91	q
$F_2C=CHF$	1.30	1.82	0.52	g					
C_6H_5F	1.66	1.96	0.30	d	⬡-F (N)	0.98	0.59	−0.39	r
$C_6H_4F_2$ (1,2)	2.59	3.36	0.77	h	FNO	1.81	0.60	−1.21	d
$C_6H_4F_2$ (1,4)	1.51	1.93	0.42	h	FNO_2	0.47	0.65	0.18	e
⬡⋉F F	3.57	3.25	−0.32	i	HBF_2	0.97	1.33	0.36	e
=⋉F F	2.07	2.60	0.53	j	CH_3BF_2	1.67	1.98	0.31	s
					⁄BF₂	1.74	2.50	0.76	t
HC≡CF	0.73	1.57	0.84	k	≡—BF₂	1.88	2.49	0.61	e
HC≡CCOF	2.98	3.72	0.75	l	H_2NBF_2	2.60	2.85	0.25	u
HCOF	2.02	2.50	0.48	d	$HOBF_2$	1.86	2.10	0.24	v
CH_3COF	2.96	2.96	0.00	d	$:CF_2$	0.47	0.04	−0.43	w
F_2CO	0.95*	0.81	−0.14	e	NF_2·	0.14	0.01	−0.13	x

[a] All dipole moments, with the exceptions of CF_3CO_2H and $(CF_3)_2CO$, were obtained from measurements of the Stark effect in the microwave spectrum. [b] J. S. Muenter and W. Klemperer, *J. Chem. Phys.*, **52**, 6033 (1970). [c] S. C. Wofsy, J. S. Muenter, and W. Klemperer, *ibid.*, **55**, 2014 (1971). [d] A. L. McClellan, "Tables of Experimental Dipole Moments", Vol. 1, W. H. Freeman, San Francisco, Calif., 1963. [e] *Ibid.*, Vol. 2, 1974. [f] A. T. Perretta and V. W. Laurie, *J. Chem. Phys.*, **62**, 2469 (1975). [g] A. Bhaumik, W. V. F. Brooks, and S. C. Dass, *J. Mol. Struct.*, 16, 29 (1973). [h] L. Nygaard, E. R. Hansen, R. Hansen, J. Rastrup-Andersen, and G. O. Sorensen, *Spectrochim. Acta, Part A*, 23, 2813 (1967). [i] R. Pozzi, D. R. Ramaprasad, and E. A. C. Lucken, *J. Mol. Struct.*, 28, 111 (1975). [j] J. R. Durig, Y. S. Li, C. C. Tong, A. P. Zens, and P. D. Ellis, *J. Am. Chem. Soc.*, 96, 3805 (1974). [k] J. K. Tyler and J. Sheridan, *Trans. Faraday Soc.*, 59, 2661 (1963). [l] R. W. Davis and M. C. L. Gerry, *J. Mol.*

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Table XIII. Net Atomic Charges $q_x{}^a$

Molecule	Atom x	q_x, $|e|$ STO-3G[b]	MNDO
HF	H	0.228	0.287
	F	−0.228	−0.287
CH_3F	H	−0.004	0.005
	C	0.169	0.261
	F	−0.157	−0.246
CF_4	C	0.674	0.815
	F	−0.169	−0.204
	H_1	0.034	0.074
	H_2	0.089	0.057
	H_3	0.090	0.064
	C_1	0.201	0.110
	C_2	−0.302	−0.113
	F	−0.110	−0.192
NF_3	N	0.147	0.424
	F	−0.049	−0.141
	H_2	0.077	0.079
	H_3	0.057	0.066
	H_4	0.049	0.065
	C_1	0.268	0.146
	C_2	−0.166	−0.087
	C_3	−0.025	−0.036
	C_4	−0.064	−0.065
	F	−0.188	−0.181
HC≡CF	H	0.221	0.181
	C_1	0.184	0.037
	C_2	−0.384	−0.136
	F	−0.021	−0.082
F_2CO	C	0.568	0.605
	O	−0.336	−0.274
	F	−0.116	−0.165

^{a} Defined in ref 2. ^{b} Reference 23.

state species via the parameters,[1] although relaxation effects could of course not be allowed for in this manner.

Further examples of this phenomenon are the molecules HOF, CF_2, FNO, and F_2O,[20,22] where again second-and third-order perturbational corrections result in inversion of the ordering of certain σ and π orbitals. The MNDO eigenvectors for HOF and F_2O are in agreement with these calculations, but not for CF_2 and FNO,[22] where the relevant orbitals are found by MNDO to be almost degenerate in energy, with the π orbital lower than the σ.

Another case where MNDO does very well is predicting the so called "perfluoro effect" (Table XI), the π-σ splitting agreeing very well with the photoelectron results.

F. Dipole Moments and Charge Distributions. Table XII lists calculated and observed dipole moments for 46 molecules. The average error in the MNDO values is 0.38 D. In only three cases does the error exceed 0.9 D, namely, FNO (−1.21 D), F_3CCN (−0.91 D), and FCN (−1.28 D). The error in the case of FNO may be related to the error in the predicted FN bond length (1.305 vs. 1.514 Å; Table VIII). It is interesting to note that RH calculations, using the STO-3G or 4-31G basis sets, also underestimate the length of this bond.[17] The errors in the other cases suggest that MNDO, while better than MINDO/3, still fails to deal completely adequately with the CN group. The calculated dipole moment for acetonitrile was also too small (by 1.29 D^2).

The calculated charge distributions (Table XIII) are generally similar to those reported by Pople and Hehre[23] using the STO-3G basis set, although there are significant differences in certain cases (e.g., fluorobenzene). These differences would probably be reduced if a larger basis were used.

Conclusions

The primary objective of the research reported in this series of papers is the development of a theoretical procedure accurate enough, reliable enough, and cheap enough to serve as a

practical tool in the study of chemical phenomena. MINDO/3 has proved useful in this connection[24] but it suffers from a number of obvious shortcomings. In particular, the errors in the calculated energies are too large, there are cases where it breaks down badly, and the use of bond parameters makes difficult its extension to "inorganic" elements, in particular metals. MNDO clearly represents an important advance over MINDO/3 because the results it gives are almost uniformly much better, because there seem to be no situations where it breaks down, and because it contains many fewer parameters (owing to the use of atomic parameters instead of bond parameters) and so should be much more easily extended to additional elements. Since, moreover, the time required for computation is only ca. 25% greater than for MINDO/3, even for calculations involving complete geometry optimization or the location of transition states,[25] MNDO seems destined to prove of major value in the study of chemical phenomena.

Naturally MNDO does not represent the end of the semiempirical SCF MO road but it may prove a rather prolonged stopping point. The NDDO approximation is the simplest version of the RH method that is free from obviously unjustifiable assumptions[1,26] and any attempt to remove the simplifying assumptions made in it, in particular the core approximation or the neglect of diatomic differential overlap, would lead to an enormous increase in computing time. Our uniquely extensive experience with parametrization also suggests that no major improvement in MNDO is likely to be brought about by changes in this respect, except by an increase in the number of parameters (e.g., use of bond parameters instead of atomic ones) which would render its extension to other elements impracticable. The one area where useful progress might be made is in drawing a distinction between the potential energy and the nuclear kinetic energy of molecules. At present both are lumped together, MNDO being parametrized to reproduce heats of formation, not energies of formation. Since it has been shown[27] that MINDO/3 gives good estimates of molecular vibration frequencies and derived thermodynamic properties, and since preliminary studies suggest that MNDO is even better in these respects, it should be possible to parametrize MNDO to reproduce equilibrium energies of molecules, the kinetic terms (zero point energy and specific heat) being calculated and added to the equilibrium energy to give an estimate of the heat content.

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Molecular Orbital Studies of the Radicals of Hydroxybenzenes and Epinephrine

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Abstract: When calculations of proton hyperfine coupling constants of free radicals from hydroxybenzenes (phenol, 1,2- and 1,4-dihydroxybenzene, 1,2,3- and 1,2,4-trihydroxybenzene) and epinephrine were done using the INDO (intermediate neglect of differential overlap) method, experimental data for 1,2-dihydroxybenzene, 1,4-dihydroxybenzene, and 1,2,4-trihydroxybenzene were exactly reproduced. Calculations for the remaining hydroxybenzenes served to explain the experimental data qualitatively. The hyperfine coupling constants of the radical from epinephrine could be assigned from the present calculations. Although past calculations were done to determine structures of a quinol type, we found in the INDO calculations that semiquinone radicals have a quinoidlike structure. In these radicals, the C–O bond lengths are fairly short, the adjacent C–C bond lengths relatively long, and the next C–C bond lengths in the rings relatively short. The proton hyperfine coupling constants of the radical formed by the oxidation of epinephrine in alkaline ethanol media were measured by electron spin resonance absorption spectroscopy and the magnitudes were 1.28, 2.61, and 0.59 G. The splitting constants calculated by means of the INDO method were consistent with the observed values.

Introduction

Most radicals from hydroxybenzenes can be easily produced in alkaline ethanol solution and there are numerous reports[1-11] concerning experimental proton hyperfine coupling constants. Geometries which reproduce the experimental data exactly have apparently not been documented. As stated by Pople,[12] the calculated results in the INDO method for the semiquinones were not supported. The ab initio calculations do not reproduce the observed data. In all these calculations or others,[13-17] the geometries of the semiquinone radicals were considered to be hexagons or a close resemblance and the C–O bond lengths were estimated to be those of a quinol type. The calculated results by Pople also can be reproduced in the geometries of a quinol type.

In the present INDO calculations, we found that these semiquinone anion radicals have a quinoidlike structure, with the rings which are fairly distorted from regular hexagons and the short C–O bond lengths. Lack of success with past calculations may be due to lack of adequate consideration that the molecular geometries of these radicals are distorted as compared to a regular hexagon; i.e., they are of quinoidlike structures. The INDO method has been widely used in studies of radicals and the sigmatropic shifts.[18-25] The INDO calculations in studies of proton hyperfine splitting constants of

semiquinones have not been successful; however, this method may still be used providing that the geometries of quinone type are reinvestigated.

Pyrocatechol, epinephrine, and related compounds are substrates for the COMT (cathechol-O-methyltransferase) and the relationship between their biological activities and chemical structures has not been well determined.

The authors have reported that the diuretic actions of triazine derivatives[26] principally depend upon the force of the charge transfer at their active centers, and that the carbonic anhydrase inhibitory actions of sulfonamide derivatives[27] parallel the formal charge of the sulfonamide groups.

Information on molecular geometries of the radicals from hydroxybenzenes and epinephrine is required to determine the structure selectivity by the COMT or the meta/para ratios of the O-methylated products. In the present work, calculations of the proton hyperfine coupling constants of semiquinone anion radicals and epinephrine anion radical were made using the INDO method as well as the HMO and the McLachlan methods. We measured the ESR spectra of epinephrine radical, calculated its proton hyperfine coupling constants, and made assignments. Molecular geometry which well explains the observed proton hyperfine splitting constants of epinephrine radical was obtained.