Ground States of Molecules. XXVIII.[1] MINDO/3 Calculations for Compounds Containing Carbon, Hydrogen, Fluorine, and Chlorine[2]

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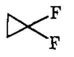
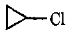
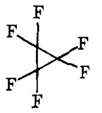
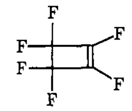
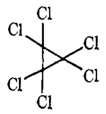
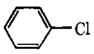
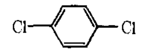
Abstract: MINDO/3 calculations are reported for a number of compounds containing fluorine or chlorine. The calculated heats of formation, geometries, dipole moments, and first ionization potentials are in generally satisfactory agreement with experiment.

Previous papers[1,3,4] of this series have described an improved version[3] (MINDO/3) of the MINDO[5-8] semiempirical SCF-MO method and its application to hydrocarbons[4] and compounds derived from carbon, hydrogen, nitrogen, and oxygen.[1] Here we report analogous calculations for compounds derived from C, H, and Cl or from C, H, O, and F. These were carried out as before[1,3,4] using the parameters listed in part XXV[3] and the CDC 6400/6600 digital computer at The University of Texas Computation Center. The geometry of each molecule was calculated as before[3,4] by minimizing the energy with respect to all geometrical variables, no assumptions whatsoever being made.

Table I. Calculated (MINDO/3) and Observed Heats of Formation (ΔH_f) for Compounds Derived from C, H, F, and Cl

	ΔH_f, kcal/mol (25°)				ΔH_f, kcal/mol (25°)		
Compd	Calcd	Obsd	Error	Compd	Calcd	Obsd	Error
F_2	−2.5	0	−2.5	Cl_2	0.0	0.0	0.0
HF	−64.0	−64.8[a]	0.8	HCl	−21.5	−22.1[b]	0.6
CH_3F	−51.2	−67.0[b]	15.8	CH_3Cl	−15.3	−19.3[b]	4.0
CH_2F_2	−106.0	−107.2[a]	1.2	CH_2Cl_2	−22.3	−22.96 ± 0.35[c]	0.7
CHF_3	−165.8	−165.0[a]	−0.8	$CHCl_3$	−26.0	−24.6 ± 2.0[c]	−1.4
CF_4	−223.8	−222.3 ± 0.4[c]	−1.5	CCl_4	−24.3	−24.6[b]	0.3
$H_2C{=}CHF$	−29.5	−28.0	−1.5	CH_3CH_2Cl	−28.1	−26.1 ± 0.4[c]	−2.0
$H_2C{=}CF_2$	−85.8	−80.5 ± 1.0[c]	−5.3	CH_3CHCl_2	−33.8	−30.65 ± 0.30	−3.1
$HCF{=}CHF$, cis	−69.7			CH_3CCl_3, staggered	−34.7		
Trans	−74.1			Eclipsed	−33.3		
$F_2C{=}CHF$	−120.7	−117.3 ± 2.0[c]	−3.4	Cl_3CCCl_3, staggered	−35.5	−35.3[d]	−0.2
$F_2C{=}CF_2$	−156.3	−155.5[b]	−0.8	Eclipsed	−30.5		
CH_3CH_2F	−67.1			$CH_2{=}CHCl$	9.6	8.1,[d] 10.0[e]	
CH_3CHF_2	−124.0	−121.0	−3.0	$CH_2{=}CCl_2$	3.1	0.61 ± 0.36[c]	2.5
FCH_2CH_2F, gauche	−108.0			$ClCH{=}CHCl$, cis	3.1	1.0 ± 2.1[c]	2.1
H_3CCF_3	−184.2	−178 ± 0.4[c]	−6.2	Trans	1.2	1.2 ± 2.1[c]	0.0
F_3CCF_3	−325.6	−321.3 ± 0.9[c]	−4.3	$Cl_2C{=}CCl_2$	5.7	−2.7 ± 2.0[c]	8.4
$HC{\equiv}CF$	16.1			$HC{\equiv}CCl$	50.0		
$FC{\equiv}CF$	−30.5			$ClC{\equiv}CCl$	43.7		
$(H_3C)_2CHF$	−77.9	−69.4 ± 0.4[c]	−8.5	$(H_3C)_2CHCl$	−34.0	−33.6 ± 2.0	−0.4
$(H_3C)_3CF$	−80.1			$(H_3C)_3CCl$	−31.8	−43.1[b]	11.3
	−92.6			$CH_3C{\equiv}CCH_2Cl$	3.1		
				$ClCH_2C{\equiv}CCH_2Cl$	−4.8		
					1.1		
	−270.9			CCl_2	41.5	66[b]	−24.5
	−249.9				−13.0		
					20.1	12.5[d]	7.6
Perfluorocyclobutane	−384.1						
Fluorobenzene	−21.0	−26.5[b]	5.5		12.8	5.3 ± 0.3	7.5
o-Difluorobenzene	−65.2	−70.26 ± 0.13[c]	5.1				
m-Difluorobenzene	−72.3	−73.96 ± 0.17[c]	1.7	NF_3	−33.0	−29.8[b]	−3.2
p-Difluorobenzene	−69.1	−73.33 ± 0.17[c]	4.2	OF_2	−18.5	−5.2[b]	−12.7
1,3,5-Trifluorobenzene	−123.1			CH_3COF	−120.6	−106.4 ± 0.5[c]	−14.2
Hexafluorobenzene	−72.33	−73.96 ± 0.17[c]	1.7	COF_2	−160.9	−152.95 ± 0.25[c]	−7.9
CF_2	−91.1	−35.0[b]	−56.1	F_3CCOCF_3	−212.7	−218.0[b]	5.3
$CF_3\cdot$	−167.7	−114[b]	−57.7	CH_2FCOOH	−149.9		

[a] “JANAF Thermochemical Tables,” Dow Chemical Co., Midland, Mich., 1965. [b] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, Y. T. Hernon, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser.*, *Nat. Bur. Stand.*, **No. 26** (1969). [c] J. D. Cox and G. Pilcher, “Thermochemistry of Organic and Organometallic Compounds,” Academic Press, London, 1970. [d] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Hargen, H. E. O’Neal, A. S. Rogers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). [e] R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc.*, *Ser. A*, **258**, 459 (1960).

Table II. Calculated and Observed Bond Lengths, Bond Angles, and Dihedral Angles for Compounds Containing Fluorine or Chlorine

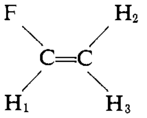
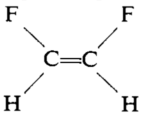
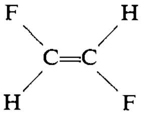
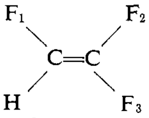
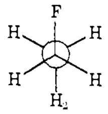
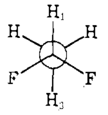
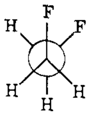
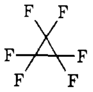
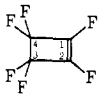
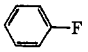
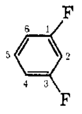
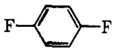
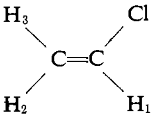
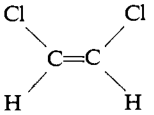
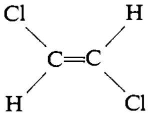
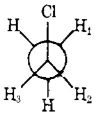
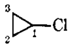
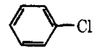
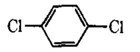
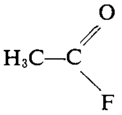
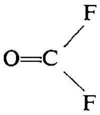
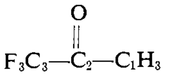
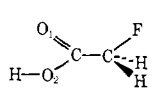
Compd	Ref	Calcd (obsd) bond lengths (ab, Å), bond angles (abc), and dihedral angles (abcd)
F_2	*a*	1.446 (1.418)
HF	*b*	0.913 (0.917)
CH_3F	*c*	CH, 1.102 (1.105); CF, 1.378 (1.385); HCF, 107.3° (109.5°)
CH_2F_2	*d*	CH, 1.100 (1.093); CF, 1.337 (1.360); HCH, 114.4° (112.5°); FCF, 104.8° (1.0.5°)
CHF_3	*e*	CH, 1.099 (1.098); CF, 1.315 (1.332); HCF, 109.3 (104.5°)
CF_4	*f*	CF, 1.303 (1.317)
$HC{\equiv}CF$	*g*	CH, 1.072; CC, 1.199 (1.198); CF, 1.331 (1.278)
	*h*	CF, 1.365 (1.320); CH_1, 1.098 (1.080); CH_2, 1.094 (1.080); CH_3, 1.097 (1.080); CC, 1.309 (1.333); H_1CC, 121.7; CCH_2, 125.1°; CCH_3, 131.2°
$H_2C{=}CF_2$	*i*	CH, 1.090; CC, 1.313 (1.315); CF, 1.325 (1.323); HCC, 122.4° (120.7°); CCF, 131.1° (130.4°)
		CH, 1.097; CC, 1.310; CF, 1.370; FCC, 125.0°; CCH, 127.2°
	*j*	CH, 1.091; CC, 1.306 (1.329); CF, 1.375; HCC, 133.5°; CCF, 115.8°
	*k*	CH, 1.091 (1.08); CF_1, 1.353 (1.33); CF_2, 1.353 (1.32); CF_3, 1.353 (1.32); HCC, 123.0° (121.0°); F_1CC, 124.5° (122.0°); CCF_2, 124.5° (123.6°); CCF_3, 124.5° (123.6°)
$F_2C{=}CF_2$	*l*	CF, 1.293 (1.313); CC, 1.313; CCF, 115.4° (123.0°)
	*a*	CH_1, 1.118 (1.091); CH_2, 1.110 (1.091); CC, 1.456 (1.540); CF, 1.381 (1.375); FCC, 111.0°; HCC, 112.5°
	*m*	CH_1, 1.106; CH_3, 1.109 (1.110); CC, 1.458 (1.540); CF, 1.355 (1.345); CCH_1, 121.3°; CCF, 122.0° (109.4°); CCH_3, 112.3° (109.8°)
	*n*	CH, 1.113 (1.110); CC, 1.469 (1.535); CF, 1.388 (1.394); CCF, 108.7° (108.3°); CCH, 115.2° (108.3°); FCCF, 74.4° (74.5°)
H_3CCF_3	*o*	CH, 1.108; CF, 1.330 (1.335); CC, 1.452 (1.530); FCC, 110.8° (107.3°); CCH, 112.1°
F_3CCF_3	*p*	CF, 1.327 (1.330); CC, 1.475 (1.51); CCF, 107.6° (108.0°); CC, 1.481; CF, 1.409; CCC, 125.3°; HCF, 103.9°
$(H_3C)_3CF$	*a*	CC, 1.498 (1.54); CF, 1.428 (1.38); CCF, 100.0° (108°); HCC, 112.6° (111.5°)
		CC, 1.502; CF, 1.347; FCF, 104.4°
	*q*	C_1F, 1.357 (1.319); C_3F, 1.357 (1.336); C_1C_2, 1.353 (1.342); C_2C_3, 1.493 (1.508); C_3C_4, 1.525 (1.595); FC_1C_2, 136.4° (133.6°); $C_1C_2C_3$, 93.3° (94.8°); FC_3F, 101.7° (108.8)
	*r*	CF, 1.373 (1.354), C_1C_2, 1.407 (1.400); C_2C_3, 1.406 (1.400); C_3C_4, 1.407 (1.400); CH, 1.100 (1.08)
	*s*	C_1C_2, 1.401 (1.384); C_3C_4, 1.400 (1.385); C_4C_5, 1.409 (1.405); CF, 1.371 (1.324); C_2H, 1.098 (1.107); C_4H, 1.099; C_5H, 1.106; $C_1C_2C_3$, 114.4° (120.1°); $C_2C_3C_4$, 122.8° (120.9°); FC_1C_2, 117.2° (119.5°); HC_6C_1, 121.0° (120°)
Hexafluorobenzene	*t*	CF, 1.374 (1.394); CC, 1.403 (1.394)
	*u*	C_1C_2, 1.400 (1.39); C_2C_3, 1.410 (1.39); CF, 1.378 (1.350)
Cl_2	*a*	2.039 (1.988)
HCl	*a*	1.230 (1.274)
$HC{\equiv}CCl$	*a*	CH, 1.068 (1.052); CC, 1.199 (1.211); CCl, 1.693 (1.632)
$ClC{\equiv}CCl$	*a*	CC, 1.201 (1.195); CCl, 1.676 (1.64)
CH_3Cl	*a*	CH, 1.102 (1.096); CCl, 1.751 (1.781); HCCl, 108.8° (108.0°)
CH_2Cl_2	*a*	CH, 1.106 (1.082); CCl, 1.746 (1.772); HCH, 109.8 (113.0°); ClCCl, 114.7° (111.8°)
$CHCl_3$	*v*	CH, 1.100; CCl, 1.744 (1.762); HCCl, 106.8° (108°)
CCl_4	*a*	CCl, 1.752 (1.766)

Table II (*Continued*)

Compd	Ref	Calcd (obsd) bond lengths (ab, Å), bond angles (abc), and dihedral angles (abcd)
	*a*	CH_1, 1.100; CH_2, 1.096; CH_3, 1.094; CC, 1.312 (1.327); CCl, 1.739 (1.740); H_1CC, 127.3°; H_2CC, 122.2°; H_3CC, 124.6°; ClCC, 125.7° (125.0)
$H_2C{=}CCl_2$	*a*	CH, 1.093; CC, 1.311 (1.325); CCl, 1.745 (1.727); CCCl, 125.2° (123.2°); CCH, 123.5°
	*a*	CH, 1.095; CC, 1.313 (1.336); CCl, 1.741 (1.722); CCCl, 128.0° (123.6°); CCH, 124.7°
	*a*	CH, 1.095; CC, 1.308 (1.343); CCl, 1.746 (1.721); CCCl, 123.8° (123.0°); CCH, 127.2°
$Cl_2C{=}CCl_2$	*a*	CC, 1.321 (1.327); CCl, 1.737 (1.724); CCCl, 124.5° (123.4°)
	*a*	CH_1, 1.114 (1.110); CH_2, 1.111 (1.101); CC, 1.475 (1.549); CCl, 1.765 (1.778); CCCl, 113.0° (110.5°); H_1CC, 113.3°; H_2CH_3, 106.7° (110.0°)
H_3CCCl_3	*a*	CH, 1.112; CC, 1.476; CCl, 1.779 (1.775); CCCl, 111.3° (110.0°); HCC, 112.9° (109.5°)
Cl_3CCCl_3	*a*	CC, 1.497 (1.49); CCl, 1.774 (1.763); CCCl, 112.1° (110.7°)
$(H_3C)_2CHCl$	*a*	CC, 1.494 (1.55); CCl, 1.815 (1.76); CCC, 120.4° (109.5); HCCCl, 99.3°
$(H_3C)_3CCl$	*a*	CC, 1.510 (1.55); CCl, 1.842 (1.765); CCCl, 103.1° (109.2°)
CH_3CHCl_2	*a*	CC, 1.471 (1.55); CCl, 1.772 (1.795); CCCl, 112.7° (110°); ClCCl, 124.4°
	*a*	CC, 1.502 (1.513); CCl, 1.772 (1.778); CCCl, 128.8°; $HCCl_1$ (120.9°); HC_1C_2, 127.8°; HC_2C_3, 111.5°; HC_2H_1 (114.6°)
	*a*	C_1C_2, 1.404 (1.404); C_2C_3, 1.408 (1.404); C_3C_4, 1.407 (1.404); CCl, 1.767 (1.706); CH, 1.104
	*a*	C_1C_2, 1.405 (1.37); C_2C_3, 1.409 (1.39); CCl, 1.764 (1.74)
$ClCH_2C{\equiv}CCH_2Cl$	*a*	C_1C_2, 1.430 (1.470); C_2C_3, 1.218 (1.214); CH, 1.110 (1.104); CCl, 1.769 (1.796); CCCl, 113.6° (111.0°); CCH, 113.1° (109.5°)
$H_3CC{\equiv}CCH_2Cl$	*a*	C_1C_2, 1.428 (1.460); C_2C_3, 1.217 (1.207); C_3C_4, 1.436 (1.458); C_1Cl, 1.773 (1.798); C_1H, 1.111 (1.090); C_4H, 1.111 (1.110)
NF_3	*a*	NF, 1.323 (1.370); FNF, 120° (102.1°)
OF_2	*a*	OF, 1.439 (1.413); FOF, 55.2° (103.8°)
	*a*	CC, 1.460 (1.50); CO, 1.174 (1.16); CF, 1.363 (1.370)
	*a*	CO, 1.170 (1.17); CF, 1.320 (1.320)
 $F_3C_3{-}\overset{\overset{O}{\parallel}}{C_2}{-}C_1H_3$	*w*	CO, 1.200 (1.207); C_1C_2, 1.496 (1.481); C_2C_3, 1.502 (1.562); CH, 1.109 (1.089); CF, 1.330 (1.339); CCF, 109.4° (110.7); CCH, 112.3° (105.0°); OC_2C_1, 124.7°; OC_2C_3, 118.9°
	*x*	CC, 1.497 (1.534); CH, 1.112 (1.073); CO_1, 1.209 (1.202); CO_2, 1.336 (1.344); OH, 0.953 (0.953); CF, 1.386 (1.387); O_1CC, 126.1° (126.1°); O_2CC, 103.4° (108.8°); CCF, 109.7° (109.2°); CCH, 115.5°; OH, 118.8° (105.9°)

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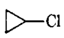
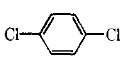
[a] L. E. Sutton, *Chem. Soc.*, *Spec. Publ.*, **No. 11** (1958); **No. 18** (1965). [b] G. A. Knipers, D. F. Smith, and A. N. Nielsen, *J. Chem. Phys.*, **25**, 275 (1956). [c] C. C. Costain, *ibid.*, **29**, 864 (1958). [d] S. P. Porto, *J. Mol. Spectrosc.*, **3**, 248 (1958). [e] S. N. Ghosh, R. Trambarulo, and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952). [f] C. W. W. Hoffman and R. C. Livingston, *ibid.*, **21**, 565 (1953). [g] J. K. Tyler and J. Sheridan, *Trans. Faraday Soc.*, **59**, 2661 (1963). [h] B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *Spectrochim. Acta*, **13**, 120 (1958). [i] V. W. Laurie and D. T. Pence, *J. Chem. Phys.*, **38**, 2693 (1963). [j] J. Carlos, C. H. Chang, and S. H. Bauer, personal communication. [k] A. Bhaumik, W V. F. Brooks, and S. C. Dass, *J. Mol. Struct.*, **16**, 29 (1973). [l] I. L. Karle and J. Karle, *J. Chem. Phys.*, **18**, 963 (1950). [m] N. Solimene and B. P. Dailey, *ibid.*, **22**, 2042 (1954). [n] E. J. M. Van Schaick, H. J. Geise, F. C. Mijlhoff, and G. Renes, *J. Mol. Struct.*, **16**, 23 (1973). [o] W. F. Edgell, G. B. Miller, and J. W. Amy, *J. Amer. Chem. Soc.*, **79**, 2391 (1957). [p] J. L. Brandt and R. L. Livingston, *ibid.*, **76**, 2086 (1954). [q] C. H. Chang, R. F. Porter, and S. H. Bauer, *J. Mol. Struct.*, **7**, 89 (1971). [r] L. Nygaard, I. Bojesen, T. Pederson, and T. Rastrup-Andersen, *ibid.*, **2**, 209 (1968). [s] E. J. H. Van Schaick, H. J. Geise, F. C. Mijlhoff, and G. Renes, *ibid.*, **16**, 389 (1973). [t] A. Almenningen, O. Bastiansen, R. Seip, and H. M. Seip, *Acta Chem. Scand.*, **18**, 2115 (1964). [u] H. Oosaka, *Bull. Chem. Soc. Jap.*, **15**, 31 (1940). [v] P. N. Wolfe, *J. Chem. Phys.*, **25**, 976 (1956). [w] A. L. Andersen and S. H. Bauer, *J. Mol. Struct.*, **12**, 389 (1972). [x] B. B. Van Eijck, G. Van der Plaats, and J. P. Van Roon, *ibid.*, **11**, 67 (1972).

The agreement between the calculated and observed ΔH_f is satisfactory, being about as good for compounds derived from CHON.[1,4] Serious failures occurred in two situations.

The first involves compounds (CF_2, NF_3, OF_2) in which adjacent atoms have lone pairs of electrons in hybrid AOs, according to simple-minded valence theory. As we have already pointed out,[3] MINDO/3 is expected to fail in such cases because it underestimates the corresponding interelec-

Table III. Calculated and Observed Dipole Moments and First Ionization Potentials for Compounds Containing Chlorine or Fluorine

Compd	Dipole moment, D		First ionization potential, eV	
	Calcd	Obsd[a]	Calcd	Obsd
F_2	0	0	13.66	15.83[b]
HF	1.84	1.82	14.80	15.77[c]
CH_3F	1.71	1.85	12.05	12.54[d]
CH_2F_2	2.10	1.97	12.13	12.72[d]
CHF_3	1.65	1.65	12.77	13.8[d]
CF_4	0	0	13.49	15.35[d]
$HC{\equiv}CF$	0.60		10.43	11.26[e]
$H_2C{\equiv}CHF$	1.63	1.43	10.03	10.31[f]
$H_2C{=}CF_2$	1.69	1.38	10.15	
$HFC{=}CF_2$	1.39	1.40	9.87	10.14[g]
$H_3C{-}CH_2F$	1.97	1.94	11.50	
$H_3C{-}CHF_2$	2.87	2.27	11.68	12.68[h]
$H_2C{-}CF_3$	3.20	2.32	12.14	
$F_3C{-}CF_3$	0	0	12.62	
$(CH_3)_2CHF$	2.15		11.12	
$(CH_3)_3CF$	2.22	1.96	10.94	
C_6H_5F	1.74	1.60	8.99	9.20[i]
C_6F_6	0	0	9.93	9.97[g]
Cl_2	0	0	10.83	11.63[j]
HCl	1.71	1.08	12.11	12.8[k]
CH_3Cl	1.62	1.87	11.11	11.26[f]
CH_2Cl_2	1.59	1.60	10.92	11.33[f]
$CHCl_3$	1.14	1.01	11.14	11.50[f]
CCl_4	0	0	11.32	11.47[f]
$CH_2{=}CHCl$	1.61	1.45	9.94	9.99[l]
$CH_2{=}CCl_2$	1.76	1.34	10.06	9.46[m]
$CHCl{=}CHCl$, cis	2.22	1.90	9.69	9.66[n]
Trans	0		9.73	9.95[l]
$CCl_2{=}CCl_2$	0		9.65	
CH_3CH_2Cl	1.90	2.05	10.94	10.97[o]
CH_3CCl_3	2.53	1.78	10.82	
CCl_3CCl_3	0		12.11	
$(CH_3)_2CHCl$	2.23	2.17	11.87	11.2[p]
$(CH_3)_3CCl$	2.24	2.13	11.63	10.61[q]
	1.97		9.99	
C_6H_5Cl	1.96	1.69	9.08	9.07[r]
	0	0	9.04	8.95[g]

[a] "Handbook of Chemistry and Physics," 54th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1973. [b] J. Herron and V. H. Dibeler, *J. Chem. Phys.*, **32,** 1884 (1960). [c] D. C. Frost and C. A. McDowell, *Can. J. Chem.*, **36,** 39 (1958). [d] C. R. Brundle, M. B. Robin, and H. Basch, *J. Chem. Phys.*, **53,** 2196 (1970). [e] H. J. Haink, E. Heilbronner, V. Hornung, and E. Kloster-Jenesen, *Helv. Chem. Acta*, **53,** 1073 (1970). [f] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., 1970. [g] R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc., Ser. A*, **258,** 459 (1960). [h] C. Lifschitz and F. A. Long, *J. Phys. Chem.*, **69,** 3731 (1965). [i] V. J. Hammond, W. C. Price, W. C. Teegen, and A. D. Walsh, *Discuss. Faraday Soc.*, **9,** 53 (1950). [j] D. C. Frost and C. A. McDowell, *Can. J. Chem.*, **38,** 407 (1960). [k] C. R. Brundle and M. B. Robin in "Determination of Organic Structures by Physical Methods," Vol. III, Academic Press, New York, N. Y., 1971. [l] A. D. Walsh, *Trans. Faraday Soc.* **41,** 35 (1945). [m] J. P. Teegan and A. D. Walsh, *ibid.*, **47,** 1 (1951). [n] J. Momigny, *Nature (London)*, **199,** 1179 (1963). [o] K. Watanabe, *J. Chem. Phys.*, **26,** 542 (1957). [p] S. Tsuda and W. H. Hamill, *ibid.*, **41,** 2713 (1964). [q] K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2,** 369 (1962). [r] J. Collin and F. P. Lossing, *J. Amer. Chem. Soc.*, **80,** 1568 (1958).

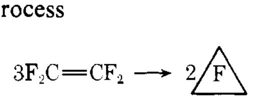
tron repulsions, leading to ΔH_f that are too negative.

The other problem arose only in two specific cases, the eclipsed conformer of hexafluoroethane (F_3CCF_3) and tetrafluoroethylene ($F_2C{=}CF_2$). Each of these molecules collapsed into a ridiculous geometry with very short FF distances and long CC bonds. This is probably a further reflection of our underestimate of lone pair–lone pair repulsions and the same effect was probably responsible for a much-too-small value for the bond angle in OF_2 (see Table III below). The difficulty could undoubtedly be avoided by a modification of the FF core repulsion function to take into account the resulting underestimate of net F–F repulsions. Since the problem has not arisen anywhere else, not even in the case of staggered F_3CCF_3, and since a great deal of time and effort might be needed to find a suitable function, we have not felt the endeavor worthwhile. Unfortunately the problem can be avoided by modification of the normal MINDO/3 parameters for fluorine only at the expense of greatly increased errors elsewhere. The MINDO/3 value of ΔH_f for tetrafluoroethylene in Table I was calculated assuming the CC bond length, the other bond lengths and angles being allowed to vary.

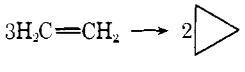
Apart from the general agreement with experiment, the results in Table I also give a good account of various well known features of fluorocarbon and chlorocarbon chemistry. Thus MINDO/3 correctly predicts the nonlinear changes in ΔH_f with successive replacement by fluorine of the hydrogen atoms attached to a given carbon atom, the calculated (observed) increments in ΔH_f (kcal/mol) on successive fluorination of methane being: $CH_4 \rightarrow CH_3F$, $-\delta\Delta H_f$, 44.9 (38.1); $CH_3F \rightarrow CH_2F_2$, $-\delta\Delta H_f$, 54.8 (52.4); $CH_2F_2 \rightarrow CHF_3$, $-\delta\Delta H_f$, 57.4 (58.0); $CHF_3 \rightarrow CF_4$, $-\delta\Delta H_f$, 61.6 (57.0).

The well known stability, and corresponding chemical inertness, of compounds containing geminal fluorine atoms is due to this. The same effect is also seen in the following comparisons: $CH_2{=}CH_2 \rightarrow CH_2{=}CHF$, $-\delta\Delta H_f$, 48.7 (40.5); $CH_2{=}CHF \rightarrow CH_2{=}CF_2$, $-\delta\Delta H_f$, 56.3 (51.5); $CH_3CH_3 \rightarrow CH_3CH_2F$, $-\delta\Delta H_f$, 47.3; $CH_3CH_2F \rightarrow CH_3CHF_2$, $-\delta\Delta H_f$, 56,9; $CH_3CHF_2 \rightarrow CH_3CF_3$, $-\delta\Delta H_f$, 59.8 (57.0). The results in Table I also account for the lack of any such effect in the case of chlorine compounds; *e.g.*, $CH_4 \rightarrow CH_3Cl$, $-\delta\Delta H_f$, 9.0 (1.4); $CH_3Cl \rightarrow CH_2Cl_2$, $-\delta\Delta H_f$, 7.0 (3.7); $CH_2Cl_2 \rightarrow CHCl_3$, $-\delta\Delta H_f$, 3.7 (1.6); $CHCl_3 \rightarrow CCl_4$, $-\delta\Delta H_f$, -1.7 (0.0). Here indeed the increments in ΔH_f tend to *decrease* along the series, accounting for the surprisingly high reactivity of chloroform and carbon tetrachloride.

Another well known peculiarity of fluorine is its ability to stabilize small rings, a tendency also indicated by the results in Table I. Thus the calculated (MINDO/3) heat of reaction for the process

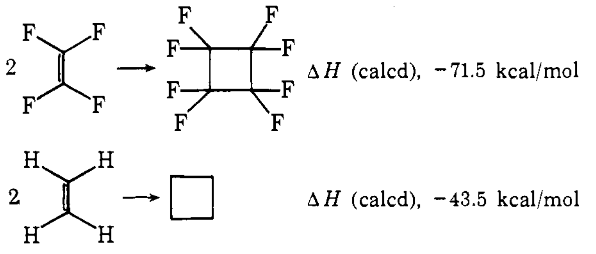

(1)

(−72.9 kcal/mol) is very much more negative than that (−40.5 kcal/mol) for the corresponding conversion of ethylene to cyclopropane.

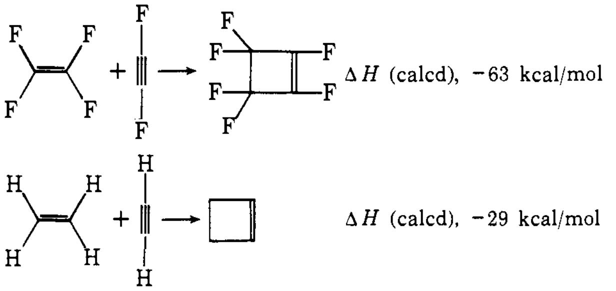

(2)

The strain energy in cyclopropane is thus apparently reduced by *ca.* 16 kcal/mol by perfluorination. The effect of perfluorination is even greater in the case of four-numbered rings as the comparisons shown in eq 3 and 4 indicate. Here the differences are considerably greater than the strain energies of cyclobutane or cyclobutene, respectively. It is therefore easy to see why fluorinated olefines so readily give cyclobutane derivatives by [2 + 2] cycloaddition.

Table II compares calculated and observed geometries for a number of chlorine and fluorine derivatives. The agreement is generally satisfactory, particularly since many of the experimental studies were carried out some time ago and are of uncertain accuracy. Moreover in many of them



difference in ΔH, 28 kcal/mol (3)



difference in ΔH, 34 kcal/mol (4)

assumptions were made concerning bond lengths and bond angles. The only systematic discrepancy occurs in the case of CC single bonds adjacent to fluorine or chlorine. Here the calculated bond lengths seem to be uniformly too small by *ca.* 0.05 Å.

Table III compares calculated and observed dipole moments and first ionization potentials, the latter being estimated by using Koopmans' Theorem.

The agreement between the calculated and observed dipole moments is generally satisfactory, being about as good as for the compounds previously studied[1,4] and at least as good as that given by *ab initio* SCF calculations using moderate basis sets. Note in particular the correct prediction of the order of moment in the series CH_3F, CH_2F, CHF_3, and the difference between this series and the corresponding chlorides.

The agreement between the calculated and observed ionization potentials is also quite reasonable though the scatter is greater than it was in the case of hydrocarbons[4] or compounds containing nitrogen and/or oxygen.[5] The main trends are nevertheless reproduced in a satisfactory manner, *e.g.*, the *decrease* in ionization potential on successive fluorination of ethylene in contrast to the *increase* in the case of benzene.

Thus MINDO/3 seems to be as applicable to compounds containing fluorine or chlorine as to those of the usual "organic" elements, CHON, and it may be expected to give equally satisfactory interpretations and predictions of chemical behavior.

References and Notes

(1) Part XXVII: R. C. Bingham, M. J. S. Dewar, and D. H. Lo, preceding paper of the series.
(2) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and by the Robert A. Welch Foundation through Grant F-126. The calculations were carried out using the CDC 6400/6600 computer at The University of Texas Computation Center.
(3) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, Part XXV of the series
(4) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, Part XXVI of the series, preceding.
(5) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262, 1275 (1969).
(6) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).
(7) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 3854 (1970).
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Ground States of Molecules. XXIX.[1] MINDO/3 Calculations of Compounds Containing Third Row Elements[2]

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Abstract: MINDO/3 calculations are reported for a variety of neutral molecules and positive ions containing the third row elements Si, P, or S. The calculated heats of formation, molecular geometries, and ionization potentials are in satisfactory agreement with experiment. Estimates of the π bond energies of multiple bonds involving silicon, and of the resonance energies of silabenzenes, are reported. Proton affinitives of analogous compounds of second and third row compounds are compared.

Previous papers of this series[1,4] have described MINDO/3 calculations for a wide variety of compounds formed by hydrogen, chlorine, and the second row elements C–F. We now report similar calculations for compounds of the third row elements, Si, P, and S.

The calculations were carried out as before, using the parameters listed in part XXV[4a] and the CDC 6400/6600 computer at The University of Texas Computation Center. Since 3d AOs have not as yet been included in MINDO/3, no attempt was made to extend the calculations to compounds of phosphorus or sulfur in their higher valence states (*e.g.*, phosphates or sulfones). The geometry of each molecule studied was found by minimizing the energy with respect to all geometrical variables, no assumptions of any kind being made. The minimization was carried out by a procedure[5] based on the Davidon–Fletcher–Powell (DFP) method.

The MINDO/3 method gives heats of atomization (ΔH_a); these were as usual[4] converted to heats of formation (ΔH_f) using the experimental values for the heats of formation of gaseous atoms previously listed.[4]

Calculations were also carried out for a number of radicals, using the "half-electron" method.[6] Since the original version of the DFP procedure did not converge satisfactorily