Ground States of Molecules. 53.* MNDO Calculations for Molecules Containing Chlorine

Michael J. S. Dewar[†] and Henry S. Rzepa[‡]

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712
Received 16 October 1982; accepted 25 October 1982

MNDO calculations of heats of formation, dipole moments, ionization potentials, and structures are reported for a wide range of compounds containing chlorine in its characteristic valence state (Cl^I) and one or more of the elements H, B, Be, C, N, O, and F. The calculated errors in the heats of formation and the dipole moments are not significantly greater than those previously reported for compounds containing no chlorine. First vertical ionization potentials were on average 0.95 eV too high. The ordering of higher cationic states was found to be correct, even for species such as Cl_2O, Cl_2, and HOCl, where *ab initio*–Koopmans' theorem calculations predict the incorrect ordering. The calculated energies and geometries of compounds such as ClF_3 are qualitatively incorrect, probably because of the lack of $3d$ atomic orbitals in the orbital basis set.

INTRODUCTION

Previous articles of this series have reported the theoretical background[2] of the MNDO semiempirical SCF–MO method and parameters for the second-period elements H, C, N, and O (ref. 3), B (ref. 4), F (ref. 5), and Be (ref. 6). The MNDO method was found to represent a substantial improvement over the older MINDO/3 method,[7] particularly for the calculation of heats of formation, ionization potentials, molecular geometries, and dipole moments for compounds containing these elements. A significant advantage of MINDO is the use of atomic parameters for the resonance integrals and core repulsion functions.[2] This leads to only five or six additional variables for each element parametrized, whereas the number of bond-pair parameters required in the MINDO/3 approach becomes rapidly prohibitive for the third period elements.[7] In this article, we report results for the MNDO parametrization of chlorine. A preliminary account of the parameters has previously appeared.[8]

Procedure

The theory of the MNDO method has been given elsewhere.[2] In considering the third-period ele-

---

* For part 52, see ref. 1.
† To whom all correspondence should be addressed.
‡ Science Research Council (U.K.) Advanced Postdoctoral Fellow. Present address: Department of Chemistry, Imperial College of Science and Technology, London, SW7 2AY.

ments, we have at present used only a $3s/3p$ orbital basis set, the inner-shell electrons being considered as an unpolarizable core. All previously reported parameters[2,6] were held constant. Initial estimates of the chlorine parameters were refined by fitting the calculated standard enthalpies of formation, the dipole moments, the first vertical ionization potentials, and the geometries of a set of 12 basis molecules to the experimental values. The orbital exponents of the chlorine $3s$ and $3p$ orbitals were at first set equal. Consistently improved results were, however, obtained when the exponents were optimized independently. In the final set of parameters they differ appreciably (Table I).

RESULTS AND DISCUSSION

A. Heats of Formation

Calculated heats of formation, ionization potentials, and dipole moments are presented in Table II, with experimental values where available. The mean error in the heats of formation of 52 compounds is 5.6 kcal/mol, not including the value for ClF_3 (*vide infra*). The energies of all positive ions seem likely to be too high by about 20 kcal/mol, since ionization potentials are calculated to be too positive by an average 0.95 eV (Table II; see also below). The only other compounds for which the heats of formation are in error by more than 20 kcal/mol are ClF (+20.3) and ClF_3 (+116.8). Certainly in the case of the latter, and possibly also the

Table I.   MNDO parameters for chlorine.

| Optimized Parameters	Value	Derived Parameters	Value
U_{ss}/eV	-100.227166	ΔH^A(298K)/kcal mol^{-1}	28.99
U_{pp}/eV	-77.378667	E_{el}/eV	-353.137667
ζ_s/au	3.784645	D_1/Å	0.263889
ζ_p/au	2.036263	D_2/Å	0.434848
β_{sp}/eV	-14.262320	ρ_0/Å	0.478996
α/Å^{-1}	2.542201	ρ_1/Å	0.328218
		ρ_2/Å	0.435988

former, this is a consequence of the absence of $3d$ atomic orbitals (AOs) in the basis set. With these exceptions, the errors are no larger than those previously reported for compounds containing no chlorine,[2-6] which suggests that no major problems should be encountered in extending the MNDO method to other elements with the use of atomic parameters.

Cl—H—Cl⁻   Cl—Cl—H⁻   Cl—H—F⁻   Cl—Cl—Cl⁻
  1   **2**   **3**   **4**
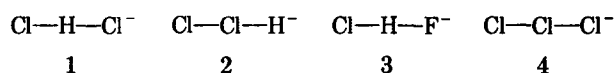
The calculated electron affinity of atomic chlorine (Table II) is very close to the experimental value, in contrast to the MNDO result for fluorine.[9] This suggests that the enthalpies of reactions involving chloride ion should be predicted more reliably than those involving fluoride ion. For example, the heat of reaction of Cl⁻ with HCl to give the symmetrical species (1) is calculated to be −24.9 kcal/mol, a value only slightly less than that predicted by MNDO for the fluorine equivalent,[5] which was indeed too low. Interestingly, an unsymmetrical isomer (2) is predicted by MNDO to be stable, although higher in energy than the symmetrical species by 22.4 kcal/mol (Table II). The mixed halogen species (3) was calculated to be 6.4 kcal/mol lower in energy than HF and Cl⁻, and to be very unsymmetrical with a HF bond length of 0.97 Å and a HCl bond length of 2.22 Å. All these species were calculated to be linear.

The MNDO method predicts for chlorine a marked tendency for catenation. For example, the

species Cl₃⁻ (4) and Cl₅⁻ (5) are calculated to be 47.1 and 64.9 kcal/mol, respectively, lower in energy than isolated Cl₂ and Cl⁻. The calculated electron affinity of Cl₂ itself (2.71 eV) is only slightly greater than the experimental value of 2.35 eV.[10] Trichloride anion is predicted to be linear, whereas
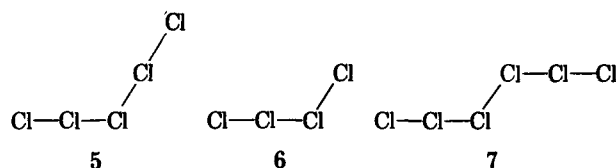
the structure of (5) bears a close qualitative resemblance to that of pentaiodide anion[11] (Fig. 1). These results suggest that the bonding in these polyhalide anions is indeed adequately represented using only a $3s/3p$ basis set. In contrast to these results for the negative ions, neutral chlorine is calculated to be stabilized by dimerization to the extent of only 0.1 kcal/mol, in keeping with the concept of this species as a weak complex only. We also investigated the open-shell species Cl₄⁻ (6) and Cl₆⁻ (7), using a spin unrestricted version of MNDO.[12] Formation of (6) from Cl₂ and Cl₂⁻ was calculated to be exothermic by 26.4 kcal/mol. The optimized geometry had only C_s symmetry, all four atoms being nonequivalent (Fig. 1). Similarly, (7) was calculated to be 42.6 kcal/mol more stable than 2Cl₂ + Cl₂⁻. The optimized structure resembled two Cl₃ units (Fig. 1), with the spin density localized on the two central chlorine atoms.

MINDO/3 rather unreasonably predicted ex-

Table II. Calculated heats of formation, ionization potentials, and dipole moments of molecules containing chlorine.

Compound	ΔH/kcal.mole[1]		IP/eV[a]		Dipole moment/D[b]		Point Group
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	
Cl^-	-54.9	-55.9[c]					
HCl	-15.3	-22.1[c]	13.01		1.48	1.08	$C_{\infty v}$
$(HCl)_2$	-30.9						C_s
$(ClHCl)^-$	-95.1		5.50				$D_{\infty h}$
$(HClCl)^-$	-72.7		4.46				$C_{\infty h}$
$HClF^-$	-126.4		4.42				$C_{\infty v}$
$BeCl_2$	-90.3	-86.1[c]					$D_{\infty h}$
BeClF	-143.5	-140.5[d]					$C_{\infty v}$
BCl_2^+	180.1	161.1[e]	20.0				$D_{\infty h}$
BCl_3	-87.7	-96.3[c]	13.10	11.62[f]			D_{3h}
B_2Cl_4	-116.7	-116.9[c]	11.97				D_{2d}
B_2Cl_4	-110.5						D_{2h}
BOCl	-92.4	-75.6[c]	13.35		1.54		$C_{\infty v}$
$CHCl(^1A')$	80.9	80[c]	10.03		1.61		C_s
$CHCl(^3A'')$	64.9				1.13		C_s
$CCl_2(^1A_1)$	57.4	53.5[g]	10.90		0.09		C_{2v}
$CCl_2(^3B_1)$	55.8				0.92		C_{2v}
CH_2Cl^+	232.5						C_{2v}
CH_3Cl	-22.6	-20.6[h]	12.25	11.3[i]	1.98	1.87	C_{3v}
CH_3ClH^+	208.9	189[j]	19.92				C_s
CH_4Cl^+	256.7		18.13				C_{4v}
CH_4Cl^+	272.3		18.38				C_{3v}
$CHCl_2^+$	226.1	212[k]					C_{2v}
CH_2Cl_2	-28.1	-23.0[h]	12.49	11.4[i]	1.91	1.60	C_{2v}
CH_3ClCl^-	-78.5		4.40				C_{3v}
$ClCH_3Cl^-$	-84.8		4.13				C_{3v}
$ClCH_3Cl^-$	-74.3		5.36				D_{3h}
CCl_3^+	224.3						D_{3h}
CCl_3^-	-29.1		4.08				C_{3v}
$CHCl_3$	-29.1	-24.6[h]	12.92	11.5[i]	1.40	1.01	C_{3v}
CCl_4	-25.6	-25.2[h]	13.25	11.7[i]			T_d
CH_2ClF	-68.1	-63.2[l]	12.54		2.17	1.82	C_s
$CHClF_2$	-114.5	-115.6[l]	13.23		1.96	1.42	C_s
$CHCl_2F$	-69.3	-68.1[l]	12.97		1.68	1.29	C_s
$CClF_3$	-159.7	-169.2[l]	14.14	13.08[m]	0.45	0.50	C_{3v}
CCl_2F_2	-110.3	-117.9[l]	13.36	12.26[m]	0.25	0.51	C_{2v}
CCl_3F	-65.3	-68.1[l]	13.30	11.73[m]	0.10	0.45	C_{3v}
$C_2H_2Cl^+$	269.4						C_s
$HCClCH^+$	278.9						C_{2v}
$ClCCH_2^+$	256.9						C_{2v}
CH_3CHCl^+	211.9						C_s
$ClCH_2CH_2^+$	221.8						C_s
$C_2H_4Cl^+$	216.2						C_{2v}

Table II (*continued*)

Compound	ΔH/kcal.mole[1] Calc.	Obs.	IP/eV[a] Calc.	Obs.	Dipole moment/D[b] Calc.	Obs.	Point Group
C_2H_5Cl	-28.8	-26.1[h]	12.12	11.06[n]	2.10	2.05	C_s
CH_3CHCl_2	-32.7	-30.7[h]	12.41	11.23[n]	2.25	2.06	C_s
CH_2ClCH_2Cl	-35.2		12.29		2.26		C_2
CH_2ClCH_2Cl	-36.5	-30.7[h]	12.42		0.00		C_{2h}
CH_3CCl_3	-31.6	-34.0[h]	12.80	11.25[n]	2.09	1.78	C_{3v}
C_2Cl_6	-27.5	-34.5[h]	13.09	11.22[n]			D_{3d}
C_2Cl_6	-19.4		12.79				D_{3h}
$(CH_3)_2CHCl$	-30.5	-33.6[h]	12.01		2.16		C_s
C_2H_3Cl	4.8	8.6[h]	10.39	10.18[o]	1.71	1.45	C_s
CHClCHCl	-2.8	1.0[h]	10.50	9.83[o]	2.13	1.90	C_{2v}
CHClCHCl	-3.9	1.2[h]	10.56	9.81[o]			C_{2h}
CH_2CCl_2	-0.1	0.6[h]	10.56	9.99[o]	1.86	1.34	C_{2v}
$CHClCCl_2$	-6.6	-2.0[h]	10.65		1.14	0.8	C_s
C_2Cl_4	-8.2	-2.7[h]	10.74		0.00		D_{2h}
CHClCHF(cis)	-42.5		10.34		2.45		C_s
CHClCHF(trans)	-43.2		10.37		0.33		C_s
CH_2CClF	-39.2		10.52	9.97[p]	1.93		C_s
HCCCl	52.0	51.1[c]	10.89		0.79	0.44	$C_{\infty v}$
C_6H_5Cl	13.3	12.2[h]	9.62	9.1[q]	1.86	1.69	C_{2v}
$C_6H_4Cl_2$(o)	8.3	7.1[h]	9.85	9.08[q]	2.85	2.5	C_{2v}
$C_6H_4Cl_2$(m)	8.3	6.1[h]	9.71	9.15[q]	1.57	1.7	C_{2v}
$C_6H_4Cl_2$(p)	6.1	5.3[h]	9.83	9.00[q]			D_{2h}
C_6Cl_6	-2.9	-8.6[h]	10.56	9.20[q]			D_{6h}
NCl_3	44.9		12.12		0.65	0.39[r]	C_{3v}
N_2Cl_4	77.1		12.25		0.79		C_2
N_2Cl_4	80.1		11.60		0.00		C_{2h}
ClNNCl	45.6		12.10		0.00		C_{2h}
ClNNCl	39.5		12.31		0.40		C_{2v}
$Cl_2C{=}N{=}N$ (+ −)	65.5		10.87				C_{2v}
$Cl_2C\underset{N}{\overset{N}{\diagup\vert\vert}}$	61.9		11.85		0.07		C_{2v}
ClCN	32.9	31.6[h]	12.80	12.37[s]	1.99	2.8	C_{2v}
ClNNN	78.7		10.51		1.71		C_s
HCOCl	-48.2		12.04		2.24	1.60[t]	C_s
CH_3COCl	-55.7	-58.4[h]	11.82	11.03[u]	2.83	2.72	C_s
$COCl_2$	-52.9	-52.3[h]	12.70	11.83[v]	0.46	1.17	C_{2v}
COClF	-92.4		13.16		0.92		C_s
$(COCl)_2$	-83.3	-78.0[h]	12.05	11.29[w]	0.09		C_2
p-Chloro phenol	-34.3	-34.9[h]	9.15		1.97	2.11	C_s
p-Chloro Benzoic acid	-72.8	-81.2[h]	10.06		1.24		C_s
HOCl	-15.7	-22.0[c]	12.06	11.22[x]	1.55		C_s
Cl_2O	31.3	21.0[c]	12.30	11.02[x]	0.72		C_{2v}
FOCl	27.4		12.75		0.66		C_s

Table II (*continued*)

Compound	ΔH/kcal.mole[1]		IP/eV[a]		Dipole moment/D[b]		Point Group
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	
$ClOOCl$	41.7	12.66			0.36		C_2
$ClNO$	-4.3	12.4[y]	11.97	11.50[z]	1.69	1.90	C_s
NO_2Cl	17.3	2.9[c]	13.01	12.08[z]	0.50	0.53	C_{2v}
$ONOCl$	2.9						C_s
Cl_3NO	73.7		12.51		1.05		C_{3v}
$ClNCO$	5.5		11.09		1.22		C_s
Cl_2	-10.7	0.00	12.45	11.70[aa]			$D_{\infty h}$
$Cl_3(-)$	-112.7		6.05				$D_{\infty h}$
$Cl_4(-.)$	-110.3						C_s
$Cl_5(-)$	-141.2		7.24				C_{2h}
$Cl_6(-.)$	-137.2						C_{2h}
$Cl_6(-.)$	-134.6						C_{2v}
ClF	8.2	-12.1[c]	13.37	12.86[bb]	1.47	0.89[cc]	$C_{\infty v}$
ClF_3	78.8	-38.0[c]	14.11				D_{3h}

[a] First vertical ionization potential, calculated using Koopmans' theorem.

[b] All experimental dipole moments, with exceptions noted above, were obtained from R. D. Nelson, D. R. Lide, Jr., and A. A. Maryott, *Nat. Stand. Ref. Data Ser. Nat., Bur. Stand. No. 10* (1967).

[c] D. R. Stull and H. Prophet, *JANAF Thermochemical Tables, NSRDS-NBS 37*, 2nd ed., U.S. GPO, Washington, DC, 1971.

[d] M. Farber and R. D. Srivastava, *J. Chem. Soc. Faraday Trans. 1*, 70, 1581 (1974).

[e] M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud, and L. C. Walker, *J. Phys. Chem. Ref. Data*, 3, 311 (1974).

[f] G. H. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *Faraday Discuss. Chem. Soc.*, 54, 70 (1972).

[g] B. A. Levi, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, 99, 8454 (1977).

[h] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic, New York, 1970; J. B. Pedley and J. Rylance, *NPL Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds*, Sussex University, 1977.

[i] F. Hopfgarten and R. Manne, *J. Electron Spectrosc. Relat. Phenom.*, 2, 13 (1972).

[j] Calculated from the experimental cation affinity reported by J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Am. Chem. Soc.*, 94, 2798 (1972).

[k] F. P. Lossing, *Bull. Soc. Chim. Belg.*, 81, 125 (1972).

[l] S. S. Chen, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, 5, 571 (1975).

[m] T. Cvitas, H. Gusten, and L. Klasine, *J. Chem. Phys.*, 67, 2687 (1977).

[n] S. Katsumata and K. Kimura, *J. Electron Spectrosc. Relat. Phenom.*, 6, 309 (1975).

[o] T. Yamazuki and K. Kimura, *Bull. Chem. Soc. Jpn.*, 48, 1602 (1975). See also, K. Wittel and H. Bock, *Chem. Ber.*, 107, 317 (1974).

[p] J. D. Scott and B. R. Russell, *J. Am. Chem. Soc.*, 94, 7634 (1972).

[q] D. G. Streets and G. P. Ceasar, *Mol. Phys.*, 26, 1037 (1973).

[r] G. Cazzoli, P. G. Favero, and A. Dal Borgo, *J. Mol. Spectrosc.*, 50, 82 (1974).

[s] E. Heilbronner, V. Hornung, and K. A. Muszkat, *Helv. Chim. Acta*, 53, 347 (1970).

[t] H. Takeo and C. Matsumura, *J. Chem. Phys.*, 64, 4536 (1976).

[u] D. Chadwick and A. Katrib, *J. Electron Spectrosc. Relat. Phenom.*, 3, 39 (1974).

[v] D. Chadwick, *Can. J. Chem.*, 50, 737 (1972).

[w] D. C. Frost, C. A. McDowell, G. Pouzard, and N. P. C. Westwood, *J. Electron Spectrosc. Relat. Phenom.*, 10, 273 (1977).

[x] D. P. Chong, F. G. Herring, and Y. Takahata, *J. Electron Spectrosc. Relat. Phenom.*, 13, 39 (1978); D. Colbourne, D. C. Frost, C. A. McDowell, and N. P.C. Westwood, *J. Chem. Phys.*, 68, 3574 (1978).

[y] M. W. Chase, J. Curnutt, H. Prophet, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data*, 4, 1 (1975).

[z] D. C. Frost, S. T. Lee, C. A. McDowell, and N. P. C. Westwood, *J. Electron Spectrosc. Relat. Phenom.*, 7, 337 (1975).

[aa] A. B. Cornford, D. C. Frost, C. A. McDowell, J. L. Ragle, and I. A. Stenhouse, *J. Chem. Phys.*, 54, 2651 (1971).

[bb] C. P. Anderson, G. Mamantov, W. E. Bull, F. A. Grimm, J. C. Curver, and T. A. Carlson, *Chem. Phys. Lett.*, 12, 137 (1971).

[cc] J. McGurk, C. L. Norris, H. L. Tigeraar, and W. L. Flygare, *J. Chem. Phys.*, 58, 3118 (1973).
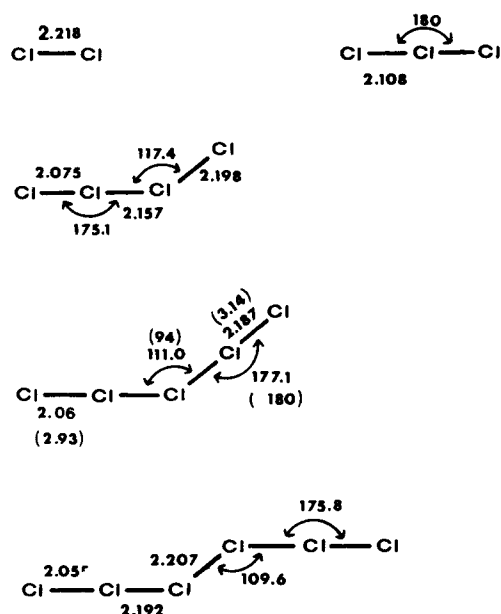
Figure 1. MNDO-calculated geometries (bond lengths in angstroms, angles in degrees) for the polychloride anions Cl_n^- (n = 2–6). The reported[11] values for I_5^- are given in parentheses.

cessive stabilization of hydrogen-bonded structures involving chlorine, i.e., HCl dimer (ΔH, -9 kcal/mol) or CH_4 + HCl (ΔH, -5 kcal/mol).[13] MNDO tends to err slightly on the other side (Table II). For example, the calculated stabilization of HCl dimer was only 0.3 kcal/mol. A similar result was found with HF.[5]

The well-known preference of fluorine compounds for cis or gauche conformations is also found with chlorine. *Cis*-dichloroethene is reported to be about 0.5 kcal/mol more stable than the trans isomer.[14] The MNDO calculations do not reproduce this, the trans isomer being lower in energy by 1.1 kcal/mol. A gauche conformer of 1,2-dichloroethane was also located, although again the trans conformer is the more stable by 1.3 kcal/mol. This is no longer true of tetrachlorohydrazine, where a gauche isomer of C_2 symmetry is favored over the trans form by 3.0 kcal/mol. In the case of dichlorodiimide, the cis configuration is favored by as much as 6.1 kcal/mol. The paucity of accurate experimental data makes comparison with experiment difficult.

B. Energies and Geometries of Chlorocarbenes

Bauschlicher, Schaeffer, and Bagus[15] have recently studied a number of halocarbenes by *ab initio* methods, using double-zeta basis sets with polarization functions on carbon and configuration

interaction. Both chlorocarbene (8) and dichlorocarbene (9) were predicted to have singlet ground states, the triplet states being 1.6 and 9.2 kcal/mol higher in energy. Triplet methylene itself was calculated to be 12.8 kcal/mol lower than the singlet.[15] MNDO predicts both chlorocarbenes to have triplet ground states, by 16.1 and 1.6 kcal/mol, respectively (Table II),* and also predicts the $^3B_1/^1A_1$ separation for methylene to be 30 kcal/mol.[5] The recently determined value for this latter quantity of 19.5 kcal/mol (ref. 16) has been questioned,[17] and a more reasonable estimate of about 10 kcal/mol was suggested. If this smaller value is indeed correct, then MNDO is overestimating the stability of triplet carbenes with respect to the singlet states by about 20 kcal/mol. If the results for the chlorocarbenes are corrected by this amount, they are certainly more in accord with the *ab initio* values.[15] The calculated MNDO geometries of the two chlorocarbenes are also similar to the results obtained by Bauschlicher, Schaefer, and Bagus.[15] In both cases, the calculated CCl bond lengths of singlet (8) and (9) are too long,
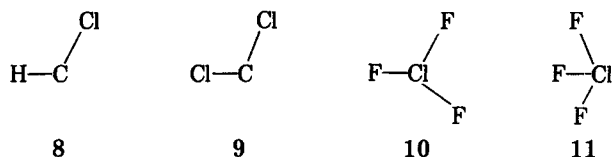
although the MNDO values are closer to experiment than the *ab initio* values (Table III). Both methods concur in predicting a shortening of the CCl bond in the triplet state, although the calculated MNDO contraction for (8) (0.069 Å) is greater than the *ab initio* value (0.027 Å). The greatest divergence between the methods is in the predicted bond angles of the triplet species. Here the MNDO values of about 140° are greater than the *ab initio* ones by about 15°.

C. Molecular Geometries

The calculated geometries of all the species studied here are qualitatively correct as far as they are known (Table III; see also paragraph at end of text regarding supplementary data). The calculated values of 20 CCl bond lengths were on average too long by 0.031 Å, or by 0.028 Å if the value for chlorodifluoromethane is excluded. A correc-

---

* The energies of the singlet carbenes were obtained from single-configuration closed-shell calculations. Inclusion of a 2 × 2 CI (cf. ref. 15) lowers the energies of chlorocarbene and dichlorocarbene by 4.1 and 2.7 kcal/mol, respectively.

Table III.   Calculated (observed) geometrical parameters.

Molecule	Geometrical Variable [a]	Symmetry	Ref.
HCl	HCl 1.348 (1.275)	$C_{\infty v}$	b
$BeCl_2$	BeCl 1.912 (1.77)	$D_{\infty h}$	b
BCl_3	BCl 1.761 (1.75)	D_{3h}	b
$CHCl(^1\underline{A}')$	CCl 1.739 (1.689), HCCl 109.3 (103.4)	C_s	b
$CHCl(^3\underline{A}'')$	CCl 1.670, HCCl 139.2	C_s	
$CCl_2(^1\underline{A}_1)$	CCl 1.748, ClCCl 113.9	C_{2v}	
$CCl_2(^3B_1)$	CCl 1.669, ClCCl 141.4	C_{2v}	
CH_3Cl	CH 1.102 (1.087), CCl 1.795 (1.776), HCH 110.8 (110.3)	C_{3v}	c
CH_2Cl_2	CCl 1.786 (1.772), CH 1.103 (1.068), ClCCl 111.2 (111.8)	C_{2v}	d
$CHCl_3$	CCl 1.782 (1.758), ClCCl 110.3 (11.3), HCCl 108.6 (107.5)	C_{3v}	d
CCl_4	CCl 1.782 (1.760)	T_d	d
CH_2ClF	CCl 1.822 (1.759), CF 1.336 (1.378), ClCF 111.1 (110.0)	C_s	e
$CHClF_2$	CCl 1.839 (1.74), CF 1.341 (1.35), ClCF 110.2 (110.5)	C_s	e
$CClF_3$	ClC 1.837 (1.781)	C_{3v}	f
C_2H_5Cl	CCl 1.806 (1.788), CC 1.523 (1.520), CCCl 112.1 (111.0)	C_s	g
CH_3CHCl_2	CCl 1.798 (1.766), CC 1.527 (1.54)	C_s	g
CH_3CCl_3	CCl 1.795 (1.771), CC 1.535 (1.54), CCCl 111.1 (109.5)	C_{3v}	g
C_2Cl_6	CCl 1.790 (1.769), CC 1.567 (1.54)	D_{3d}	g
C_2H_3Cl	CCl 1.751 (1.73), CC 1.335 (1.36), CCCl 123.0 (121.1)	C_s	h
CHClCHCl	CCl 1.742 (1.718), CC 1.338 (1.354), CCCl 125.5 (123.8)	C_{2v}	i
C_2Cl_4	CCl 1.736 (1.724), CC 1.348 (1.327), ClCCl 112.8 (113.3)	D_{2h}	j
HCCCl	CCl 1.661 (1.637), CH 1.051 (1.055), CC 1.193 (1.204)	$C_{\infty v}$	b
C_6H_5Cl	CCl 1.752 (1.725), c^1c^2 1.408 (1.399), c^2c^3 1.407 (1.389) c^3c^4 1.407 (1.398)	C_{2v}	k
NCl_3	ClN 1.735 (1.754), ClNCl 109.0 (107.7)	C_{3v}	l

Table III (*continued*)

ClCN	ClC 1.660 (1.631), CN 1.159 (1.162)	$C_{\infty v}$	b
ClN$_3$	ClN 1.721 (1.745)	C_s	m
HCOCl	ClC 1.787 (1.760), CO 1.203 (1.188), HCCl 109.7 (110.0)	C_s	n
COCl$_2$	ClC 1.760 (1.746), CO 1.200 (1.166), ClCCl 112.2 (111.3)	C_{2v}	b
ClOH	ClO 1.684 (1.690), HClO 106.4 (102.3)	C_s	o
Cl$_2$O	ClO 1.683 (1.701), ClOCl 112.9 (110.8)	C_{2v}	b
ClNO	ClN 1.783 (1.976), NO 1.136 (1.143), ClNO 117.4 (113.0)	C_s	p
NO$_2$Cl	ClN 1.810 (1.840)	C_{2v}	m
ClNCO	ClN 1.707 (1.703), NC 1.275 (1.218), CO 1.179 (1.165), ClNC 116.6 (119.3), NCO 168.8 (171.3)	C_s	m
Cl$_2$	ClCl 1.996 (1.986)	$D_{\infty h}$	b
ClF	ClF 1.650 (1.628)		

[a] Bond length A^iB^j in angstroms, bond angle $A^iB^jC^k$ in degrees.

[b] Reference c in Table II.

[c] M. Imachi, T. Tanaka, and E. Hirota, *J. Mol. Spectrosc.*, **63**, 265 (1976).

[d] A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **3**, 117 (1974).

[e] S. S. Chen, A. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data* **5**, 571 (1975).

[f] V. Typke and M. Dakkouri, *J. Mol. Struct.*, **44**, 85 (1978).

[g] J. Chao, A. S. Rodgers, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **3**, 141 (1974).

[h] R. C. Ivey and M. I. Davis, *J. Chem. Phys.*, **57**, 1909 (1972).

[i] M. I. Davis and H. P. Hanson, *J. Phys. Chem.*, **69**, 4091 (1965).

[j] A. H. Lowrey, P. D'Antonio, and C. George, *J. Chem. Phys.*, **64**, 2884 (1976).

[k] F. Michel, N. Nery, P. Nosberger, and G. Roussy, *J. Mol. Struct.*, **30**, 409 (1976).

[l] Reference r of Table II.

[m] W. H. Hocking and M. C. L. Gerry, *J. Mol. Spectrosc.*, **42**, 547 (1972).

[n] Reference t of Table II.

[o] A. M. Mirri, F. Scappini, and G. Cazzoli, *J. Mol. Spectrosc.*, **38**, 218 (1971).

[p] Reference y of Table II.

tion of −0.025 Å to each bond reduces the error to only ±0.007 Å. These errors are not significantly greater than previously found for CF bond lengths.[5] The average error for 5 ClN bond lengths was greater (0.054 Å) but fell to 0.018 Å if one compound (ClNO) was excluded. Certainly the ClN bond in nitrosyl chloride is exceptionally long; similar problems were encountered with nitrosyl

fluoride.[5] The errors in bond angles involving chlorine (1.78°) are also no greater than was previously found with fluorine.[5]

MNDO did not reproduce either the energy or the geometry of chlorine trifluoride correctly, predicting a planar molecule with D_{3h} symmetry[9] (**10**), whereas the correct structure[1] (**11**) has only C_{2v} symmetry.[11]

The relative stabilities of the isomers of chloroethylium ion ($C_2H_4Cl^+$) have been investigated by Hehre and Hiberty.[18] Using the STO 4-31G basis set and STO-3G optimized geometries, they found that the energies of 1-chloroethylium ion


12   **13**

14   **15**
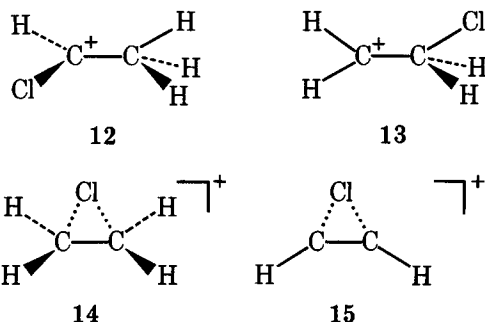
(**12**), 2-chloroethylium ion (**13**), and the bridged halonium ion species (**14**) were all within about 10 kcal/mol of each other. MNDO predicts (**12**) to be most stable, with (**14**) and (**13**) 4.3 and 9.9 kcal/mol higher in energy. Both (**12**) and (**14**) have apparently been detected in solution.[19] In contrast, MNDO predicts that the bridging form of chlorovinyl carbonium ion (**15**) is 9.5 kcal/mol less stable than the 2-chlorovinyl cation (**16**) (Table II). Lucchini, Modean, and Czimadia,[20] using an *ab*

16   **17**   **18**
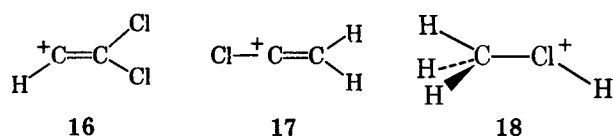
initio method, have similarly calculated (**16**) to be 11 kcal/mol more stable than the bridged halonioum ion (**15**). The most stable isomer according to MNDO is the 1-chlorovinyl cation (**17**), which is 12.5 kcal/mol lower in energy than (**16**).

Only one low-energy isomer (**18**) was found for protonated chloromethane, similar to that previously found by Jorgensen using MINDO/3.[13] It can be described as a complex of CH_3^+ and HCl with a fairly strong carbon chlorine bond. Isomers of C_{3v}

19   **20**
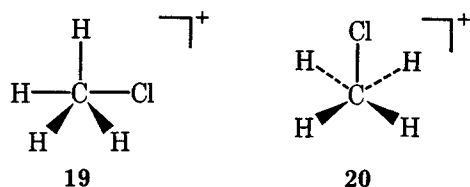
(**19**) and C_{4v} (**20**) symmetry were very much higher in energy (Table II).

D. Ionization Energies

The calculated first-vertical ionization potentials (IPs) of 31 molecules were found to be too high by, on average, 0.95 eV (Table II). This is a rather larger error than found for the second-period elements.[3,5] Attempts to reduce it during parametrization led to unacceptable errors in the calculated dipole moments and charge distributions. One possible explanation may arise from the neglect of the core orbitals. In the case of second-period elements,[3] the calculated energies of orbitals with a high $2s$ character were too negative by 2–6 eV. This was attributed to the neglect of specific $1s/2s$ interactions in the MNDO method. Similar neglect of $2p/3p$ interactions for the third-period elements could well lead to orbitals with considerable $3p$ character, being too low in energy. Applications of Koopmans' theorem would then lead to ionization potentials which would be too high. Certainly, the errors in the first IP of chlorine-substituted ethenes (Table II) are rather less than 0.95 eV and here the HOMO has little chlorine $3p$ character. The same is true of the chlorobenzenes, where the error increases with increasing chlorination of the ring and also with the $3p$ character of the HOMO.

The relative ordering of the higher cationic states seems not to be affected by this error (Table IV). The order of the orbitals agrees in all cases with the literature assignments, including the "problem" molecules HOCl, Cl_2O, Cl_2, FOCl, and ClF.[21] As noted previously for analogous fluorine compounds,[7] the order of the MNDO eigenvalues agrees with that from *ab initio* calculations only if the latter are corrected for the effects of changes in electron correlation and relaxation which accompany ionization.

V. Charge Distribution and Dipole Moments

The mean error in the calculated dipole moments of 29 compounds was found to be 0.32 D, very similar to the errors found for other elements.[3,5] As with all nitriles, the error found for ClCN was larger (−0.81 D).

Charge distributions are shown in Table V. A net positive charge is calculated for chlorine in Cl_2O and ClF. The polarization in ClF is certainly in this sense.[22] Similarly, in dichlorodifluoromethane, the fluorine is calculated to be more negatively charged than the chlorine, as is also true of ClOF. Chlorine has a considerable negative charge in nitrosyl chloride, demonstrating the considerable polarity of this species. One interesting feature is the decrease in the negative charge on the chlorine with increasing chlorination of methane. The charge decreases from $-0.215e$ in chloromethane to $-0.071e$ in tetrachloromethane,

Table IV. Higher vertical ionization energies of molecules containing chlorine.

CH_3Cl	^2E	11.3	12.25	a
	$^2A_1$	14.4	15.02	
	^2E	15.4	15.58	
	$^2A_1$	21.5	24.52	
$CHCl_3$	$^2A_1$	11.5	12.92	a
	$^2A_2$	11.9	12.98	
	^2E	12.0	13.10	
	^2E	12.9	13.83	
	^2E	16.0	17.42	
	$^2A_1$	17.0	17.73	
	$^2A_1$	19.8	24.84	
CCl_4	$^2T_1$	11.7	13.25	a
	$^2T_2$	12.5	13.45	
	^2E	13.4	14.43	
	$^2T_2$	16.6	18.30	
	$^2A_1$	20.0	24.78	
CH_2CCl_2	$^2B_1$	9.99	10.56	b
	$^2B_2$	11.69	12.64	
	$^2A_2$	12.20	13.14	
CH_2CCl_2	$^2A_1$	12.54	13.19	
	$^2B_2$	13.80	14.13	
	$^2B_1$	14.22	14.79	
	$^2A_1$	15.93	16.66	
	$^2B_2$	16.25	17.63	
	$^2A_1$	18.51	22.62	
Cl_2O	$^2B_1$	11.02	12.30	c
	$^2B_2$	12.37	13.15	
	$^2A_1$	12.65	13.39	
	$^2A_2$	12.79	13.66	
	$^2B_1$	15.90	16.52	
	$^2A_1$	16.65	17.11	
	$^2B_2$	17.68	19.23	
Cl_2	$^2\Pi_g$	11.7	12.46	d
	$^2\Pi_u$	14.43	15.32	
	$^2\Sigma_+$	16.10	17.80	

Table IV (*continued*)

ClF	$^2\Pi$	12.86	13.37	e
	$^2\Pi$	17.01	16.99	
	$^2\Sigma$	18.36	18.11	

[a] Reference i of Table II.
[b] J. C. Bunzli, D. C. Frost, F. G. Herring, and C. A. McDowell, *J. Electron Spectrosc. Relat Phenom.*, **xx**, xxx (19xx).
[c] Reference x of Table II.
[d] Reference aa of Table II.
[e] Reference bb of Table II.

and a similar phenomenon is observed with ethene, borane, and ammonia. The decrease in negative charge on chlorine in the former series is reflected by a corresponding decrease in the ^{35}Cl nuclear quadrupole coupling constant (-74.7 to -87.9 MHz, respectively[23]).

CONCLUSIONS

The results reported here suggest that MNDO gives a good description of chlorine compounds in which chlorine is present in its "normal" valence state (Cl^I), even without inclusion of $3d$ AOs. MINDO/3 had also given satisfactory results for compounds containing C, H, and Cl, but its extension to other elements would have required additional parameters. No attempts were made to determine these because of the lack of adequate thermochemical data; this problem is avoided in MNDO by the use of atomic parameters only.

The results for ClF_3 are interesting on this basis

Table V. Calculated charge distributions of compounds containing chlorine.

Molecule	Atom (charge, e)
HCl	Cl (-0.184)
BeCl$_2$	Cl (-0.251)
BCl$_3$	Cl (-0.061)
CH$_3$Cl	Cl (-0.215), C(0.154)
CF$_2$Cl$_2$	Cl (-0.108), F(-0.174), C(0.563)
CCl$_4$	Cl (-0.071)
C$_2$H$_3$Cl	Cl (-0.133)
C$_2$Cl$_4$	Cl (-0.025)
NCl$_3$	Cl (-0.043)
Cl$_2$O	Cl (0.028)
ClOF	Cl (0.020), O(0.042), F(-0.062)
ClNO	Cl (-0.259), N(0.314), O(-0.055)
ClF	Cl (0.149)

since they suggest strongly that the large errors in the calculated heat of formation ($+117$ kcal/mol) and calculated geometry are due to neglect of $3d$ AOs. Similar large errors have indeed been also found in an analogous MNDO treatment[24] of compounds containing sulfur and phosphorus in their higher valence states (S^{IV}, S^{VI}, P^V). Therefore, there should be a good basis in available thermochemical data for the determination of parameters for $3d$ AOs for these elements.

MNDO optimized Cartesian coordinates for the compounds discussed here are available on request.

References

1. M. J. S. Dewar and H. S. Rzepa, *Inorg. Chem.*, submitted for publication.
2. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1977); *Theor. Chim. Acta*, **46**, 89 (1977).
3. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4907 (1977).
4. M. J. S. Dewar and M. L. McKee, *J. Am. Chem. Soc.*, **99**, 5231 (1977).
5. M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **100**, 58 (1978).
6. M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **100**, 777 (1978).
7. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).
8. M. J. S. Dewar, M. L. McKee, and H. S. Rzepa, *J. Am. Chem. Soc.*, **100**, 3607 (1978).
9. M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **100**, 784 (1978).
10. B. M. Hughes, C. Lifshitz, and T. O. Tiernan, *J. Chem. Phys.*, **54**, 3162 (1973).
11. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry: A Comprehensive Text*, 2nd ed., Wiley, New York, 1966.

12. M. J. S. Dewar, S. Olivella, and H. S. Rzepa, *Chem. Phys. Lett.*, **43**, 80 (1977).

13. W. A. Jorgensen, *J. Am. Chem. Soc.*, **99**, 280 (1977).

14. A. M. Rozhnov, S. V. Levanova, G. A. Dvornikova, and S. L. Sadovnikova, *Zh. Prikl. Khim (Leningrad)*, **47**, 661 (1974); *Chem. Abstr.*, **80**, 145155r (1974).

15. C. W. Bauschlicher, Jr., H. F. Schaeffer III, and P. S. Bagus, *J. Am. Chem. Soc.*, **99**, 7106 (1977).

16. P. F. Zittel, G. B. Ellison, S. V. O'Neil, E. Herbst, W. C. Lineberger, and W. P. Reinhardt, *J. Am. Chem. Soc.*, **98**, 3731 (1976).

17. S. K. Shih, S. D. Peyerimhoff, R. J. Buenker, and M. Peric, *Chem. Phys. Lett.*, **55**, 206 (1978); L. B. Harding and W. A. Goddard, *Chem. Phys. Lett.*, **55**, 217 (1978).

18. W. J. Hehre and P. C. Hiberty, *J. Am. Chem. Soc.*, **96**, 2665 (1974).

19. G. A. Olah, D. A. Beal, and P. W. Westerman, *J. Am. Chem. Soc.*, **95**, 3387 (1973); G. A. Olah, Y. K. Mo and Y. Halpern, *J. Org. Chem.*, **37**, 1169 (1972).

20. V. Lucchini, G. Modean, and I. G. Czimadia, *Gazzeta Chim. Ital.*, **105**, 675 (1975).

21. D. P. Chong, F. G. Herring, and Y. Takahuta, *J. Electron Spectrosc. Relat. Phenom.*, **13**, 39 (1978).

22. K. C. Janda, W. Klemperer, and S. E. Novick, *J. Chem. Phys.*, **64**, 2998 (1976).

23. W. J. Considine, *J. Chem. Phys.*, **44**, 4036 (1966).

24. M. J. S. Dewar and M. L. McKee, to be published.