Ab Initio Molecular Orbital Study of the Geometries, Properties, and Protonation of Alkyl Chlorides[1]

William L. Jorgensen

*Contribution from the Department of Chemistry, Purdue University,
West Lafayette, Indiana 47907. Received August 5, 1977*

Abstract: SCF calculations with minimal STO-3G and extended 44-31G basis sets have been performed to examine the geometries and properties, particularly proton affinities, ionization potentials, dipole moments, rotational barriers, and carbonium ion-HCl interaction energies, for the simple alkyl chlorides, HCl to *t*-BuCl. Except for the determination of ionization potentials, the STO-3G approach is superior to 44-31G. The much closer agreement with experiment for STO-3G proton affinities than for 44-31G values is in sharp contrast to the results for first-row bases. Overall, the calculated properties using the STO-3G basis have similar reliability as previously reported MINDO/3 results. Although MINDO/3 is more accurate for dipole moments and ionization potentials, the description of protonated alkyl chlorides is better in the STO-3G framework. An example is the apparently erroneous prediction by MINDO/3 that protonated ethyl chloride is more stable in an eclipsed rather than staggered conformation. However, the excellent correlation between proton affinities and the charge on the ClH fragment in protonated alkyl chlorides, which was reported for the MINDO/3 results, is fully supported by the STO-3G computations. Correlations of PAs with the polar substituent constant, σ^*, and IPs are also reasonable. In addition, the calculated carbonium ion-HCl interaction energy for *t*-BuClH$^+$ indicates that protonated tertiary chlorides are no more than marginally stable in the gas phase. Finally, hydrogen bonded structures for methyl cation and HCl were investigated and found to be bound by ca. 8 kcal/mol at the STO-3G level.

The structure and properties of a wide variety of neutral and protonated alkyl chlorides have been the subjects of a recent series of papers.[2] The conclusions in these studies were based largely on the results of MINDO/3[3] computations which were shown to be in adequate agreement with available experimental data. There is, however, a shortage of experimental information on protonated alkyl chlorides. These species have also been neglected to a large degree in theoretical work using ab initio molecular orbital techniques. This is undoubtedly a consequence of the number of basis functions needed to represent chlorine and is certainly not due to a lack of interest in gas phase basicity.[4]

To test the reliability of the earlier MINDO/3 studies[2] and to help fill the void of more advanced theoretical treatments, ab initio calculations of the geometries and properties of the simple alkyl chlorides (hydrogen, methyl, ethyl, isopropyl, and *tert*-butyl) and their protonated analogues are presented here. The minimal STO-3G[5] basis set has been employed for all the molecules and, in addition, the extended 44-31G[6] basis was applied to the smaller species. Since the STO-3G results were found to be in better agreement with experiment for the most part than the 44-31G results, there was little need to use the extended basis on the larger molecules. The computations were performed with the GAUSSIAN/74[7] program on the CDC/6500 system at the Purdue University Computing Center.

Several important points emerged during the study. (1) The similarity of the STO-3G and MINDO/3 results provides assurance of the fundamental soundness of the earlier work.[2] (2) In contrast to nitrogen, oxygen, and fluorine bases, the calculated proton affinities of chlorides are in better agreement with experiment using the minimal STO-3G basis rather than the 44-31G alternative. (3) The C-Cl bond length in the alkyl chlorides lengthens by ca. 0.1-0.4 Å upon protonation which necessitates some geometry optimization in such studies. (4) The rotational barriers in ethyl chloride and its protonated form are calculated using STO-3G to favor staggered geometries by 3.5 (experimental, 3.7) and 3.0 kcal/mol, respectively. The MINDO/3 method predicts a barrier of only 1 kcal/mol for ethyl chloride and erroneously favors the eclipsed form of the protonated species by 3.5 kcal/mol. (5) The excellent correlation of the MINDO/3 proton affinities with the sum of the charges on the ClH fragment in RClH$^+$

is quantitatively supported by the STO-3G computations. Fair correlations between the proton affinities, Taft's σ^* polar constant, and ionization potentials for the simple alkyl chlorides are also noted. (6) Hydrogen bonding between methyl cation and HCl is found to involve bonding energies of ca. 8 kcal/mol at the STO-3G level. (7) Both the STO-3G and MINDO/3 approaches appear to be viable alternatives for the study of the neutral and positively charged, closed shell chlorine compounds. However, MINDO/3 has a slight tendency to overestimate attractive inter- and intramolecular interactions with chlorine, while the economy of geometry optimization with the STO-3G basis is a drawback.

Geometrical Results

For the smaller molecules in this study, complete geometry optimization was performed at the STO-3G level. The standard procedure of sequential optimization of variables using a quadratic least-squares program was followed.[7] Convergence was usually obtained within two or three cycles. The resulting bond lengths and bond angles are anticipated to be accurate to within ±0.01 Å and ±1°. The structural parameters for the smaller molecules were then used as a guide for assignments and limited optimization of the larger species. The results for the five pairs of alkyl chlorides and protonated analogues are presented individually. Summaries are given in Table I and Figure 1, while the total energies calculated for the molecules in this study are reported in Table II.

HCl and HClH$^+$. The STO-3G energy and bond length for HCl are in perfect agreement with the values recently reported by Pople et al.[8] The 44-31G energy determined by these authors is nominally lower than the present value, since the present 44-31G calculations strictly employ the STO-3G optimized geometries. The STO-3G (1.313 Å) and MINDO/3 (1.230 Å) estimates of the HCl separation bracket the experimental result (1.275 Å). The tendencies of the STO-3G and MINDO/3 methods to make bonds to chlorine too long and too short, respectively, are seen to be a general trend in Table I.

Upon protonation the HCl distance is predicted to lengthen to 1.368 Å according to STO-3G and 1.269 Å for MINDO/3. The increases are more than twice as great as the change in the STO-3G value of 0.956 Å for HF to 0.974 Å in H_2F^+.[9] The

Table I. Calculated and Experimental Geometries[a]

Molecule	Symmetry	Parameter	STO-3G	MINDO/3[e]	Exptl
HCl	$C_{\infty v}$	r (Cl–H)	1.313	1.230	1.275[b]
HClH⁺	C_{2v}	r (Cl–H)	1.368	1.269	
		∠HClH	99.5	93.2	
CH₃Cl	C_{3v}	r (C–Cl)	1.805	1.745	1.781[c]
		r (C–H)	1.088	1.101	1.096
		∠HCCl	108.7	108.7	108.0
H$_a$CH₂ClH⁺	C_s	r (C–Cl)	1.940	1.843	
Staggered		r (Cl–H)	1.351	1.260	
		r (C–H$_a$)	1.097	1.099	
		r (C–H)	1.097	1.096	
		∠CClH	104.2	106.9	
		∠H$_a$CCl	101.7	92.9	
		∠HCCl	104.9	106.5	
		∠H$_a$CH	113.3	116.2	
CH₃CH₂Cl	C_s	r (C–C)	1.544	1.473	1.550[d]
Staggered		r (C–Cl)	1.813	1.775	1.779
		∠CCCl	110.6	113.7	110.5
CH₃CH₂Cl	C_s	r (C–C)	1.559	1.475	
Eclipsed		r (C–CL)	1.810	1.774	
		∠CCCl	111.5	113.9	
CH₃CH₂ClH⁺	C_s	See Figure 1			
(CH₃)₂CHClH⁺	C_1	r (C–Cl)	2.120	1.992	
(CH₃)₃CClH⁺	C_s	r (C–Cl)	2.224	2.096	

[a] Bond lengths in Å; bond angles in degrees. [b] E. W. Kaiser, *J. Chem. Phys.*, **53**, 1686 (1970). [c] S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes, and J. Kraitchman, *ibid.*, **20**, 1112 (1952). [d] R. S. Wagner and B. P. Dailey, *ibid.*, **26**, 1588 (1957). [e] The MINDO/3 calculations were performed with complete geometry optimization. Only the parameters optimized in the STO-3G computations are recorded here.
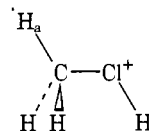
Table II. Calculated Total Energies

Molecule	E_T (STO-3G), au	E_T (44-31G), au
HCl	−455.136 01	−459.563 30
HClH⁺	−455.360 75	−459.749 77
MeCl	−493.723 11	−498.540 46
MeClH⁺	−493.990 27	−498.772 77
Staggered		
CH₃CH₂Cl	−532.305 57	
CH₃CH₂ClH⁺	−532.587 66	
Eclipsed		
CH₃CH₂Cl	−532.300 00	
CH₃CH₂ClH⁺	−532.582 95	
(CH₃)₂CHCl	−570.887 77	
(CH₃)₂CHClH⁺	−571.181 76	
(CH₃)₃CCl	−609.469 73	
(CH₃)₃CClH⁺	−609.778 78	

HXH angle in HClH⁺ is also calculated to be significantly smaller (99.5°) than the corresponding angle in HFH⁺ (112.0°).[9] The prediction is consistent with the simple VSEPR idea that the more diffuse lone pairs of the less electronegative element should pinch to HXH angle to a greater extent.[10] The MINDO/3 value for the HClH angle (93.2°) is in reasonable accord with the STO-3G result.

CH₃Cl and CH₃ClH⁺. The STO-3G energy recorded in Table I for methyl chloride is now slightly lower than Pople's determination[8] since only the C–Cl distance was optimized in the latter study. The 44-31G energies are also similar and substantially lower than Kollman and Rothenberg's result which utilized the experimental geometry.[4a] Pople's assumption[8] of standard bond lengths and angles (1.09 Å and 109.47°)[11] for the methyl group in CH₃Cl is clearly in line with the fully optimized data in Table I.

Protonated methyl chloride was assumed to have a staggered geometry with C_s symmetry as in CH₃FH⁺.[9] This structure is also the MINDO/3 minimum. The geometry was completely optimized with these constraints. The expansion of the C–Cl bond length by 0.135 Å (STO-3G) upon protonation is accompanied by a flattening of the methyl group. These effects reflect a contribution of CH₃⁺···ClH as a resonance structure

and become more pronounced as the stability of the carbonium ion increases. The C–H distances also adopt values interme-

diate between those in CH₃Cl (1.088 Å) and in CH₃⁺ (1.120 Å).[9] The MINDO/3 structure for CH₃ClH⁺ is generally similar to the STO-3G results except for the bonds to chlorine and the 9° smaller H$_a$CCl angle. The short H$_a$···Cl distance (2.193 Å) predicted by MINDO/3 probably results from a tendency to underestimate nonbonded repulsions and/or overestimate nonbonded attractions to chlorine. Other examples are discussed in the following, while it may also be noted that the MINDO/3 value for the HCl dimerization energy (9 kcal/mol) is greater than a variety of ab initio predictions (ca. 2 kcal/mol).[12] The problem may be partly due to the lack of inner shell orbitals on chlorine in the semiempirical calculations.

CH₃CH₂Cl and CH₃CH₂ClH⁺. Staggered and eclipsed structures were considered for ethyl chloride in C_s symmetry. In both cases the only parameters that were optimized at the STO-3G level were the CC and CCl separations and the CCCl angle. The hydrogens were assigned standard bond lengths (1.09 Å) and were assumed to be in a tetrahedral environment. The agreement of the STO-3G and experimental values for the CC length and the CCl angle are excellent (Table I), while the CCl distance is still calculated to be too long by 0.03 Å. The STO-3G result for the rotational barrier about the CC bond (3.5 kcal/mol) is also in impressive accord with experiment (3.7 kcal/mol). The MINDO/3 calculations favor the staggered rotamer by only 1 kcal/mol, another indication of the underestimation of nonbonded repulsions. Furthermore, the CC distance is not well reproduced by MINDO/3. Both methods reasonably predict a lengthening of the CC bond length and widening of the CCCl angle upon rotation to the eclipsed geometry; however, the origin of the slight decrease in the CCl lengths is cryptic. The effects are significantly less
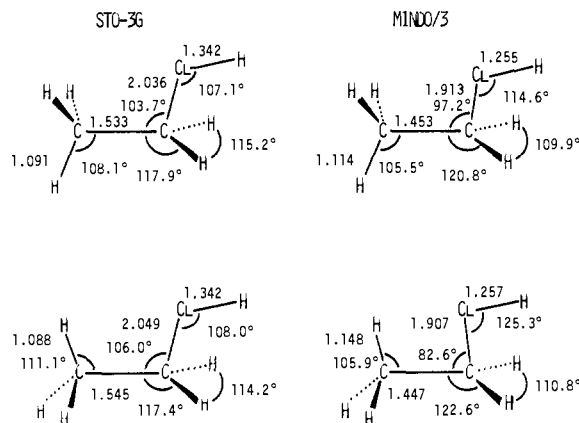
Figure 1. Calculated geometries for staggered and eclipsed, protonated ethyl chloride.

for the MINDO/3 computations consistent with the diminished barrier.

The computed structures for the staggered and eclipsed, protonated ethyl chlorides are presented in Figure 1. Since intuition could not be expected to be as dependable as for the neutral species, nine parameters were optimized in both cases with the STO-3G calculations. The only assumptions other than C_s symmetry were the lengths of the bonds to the equivalent methyl hydrogens (1.09 Å), a tetrahedral CCH angle for these hydrogens, and lengths of 1.097 Å for the CH bonds on C_1 as in CH_3ClH^+. For the STO-3G computations, further lengthening (0.1 Å) of the CCl distance and flattening of the geometry at C_1 as compared to CH_3ClH^+ is observed. This is consistent with the greater stability of $CH_3CH_2^+$ than CH_3^+. The CClH angle is not substantially affected by the change from methyl to ethyl, though the ClH distance is reduced by 0.0i Å. The eclipsed structure is again found to be higher in energy than the staggered by a somewhat smaller margin (3.0 kcal/mol) which is most likely due to the longer CCl distance in the protonated species and lessened eclipsing interactions.

Considering the results for ethyl chloride, the MINDO/3 estimate of the CC distance in the protonated analogues is undoubtedly too short by ca. 0.05–0.1 Å. What is more disturbing, however, is the fact that MINDO/3 favors the eclipsed form of $CH_3CH_2ClH^+$ over the staggered by 3.5 kcal/mol. The preference is accompanied by an unusually small CCCl angle in the eclipsed conformer (82.6°) and the prediction of a substantially attractive bond order (0.35) between the chlorine and the eclipsing hydrogen. It is reasonable to assume that the MINDO/3 prediction is erroneous on the basis of the better agreement of the STO-3G and experimental barriers and geometries for ethyl chloride and the general reliability of ab initio calculations of rotational barriers.[13] It must be said that the MINDO/3 error is not quantitatively egregious.

(CH₃)₂CHCl and (CH₃)₂CHClH⁺. The only parameters optimized by STO-3G calculations for molecules larger than protonated ethyl chloride were the CCl distances in protonated isopropyl and *tert*-butyl chlorides. CH distances of 1.09 Å and staggered, tetrahedral geometries were assumed for all methyl groups. For isopropyl chloride the CC bond lengths were taken as the standard values[11] of 1.54 Å, which also seems reasonable in view of the calculated value of 1.544 Å for ethyl chloride. The CCl distance was assumed to be 1.83 Å, which was arrived at by adding to the calculated value for ethyl chloride roughly the difference between the experimental value for ethyl chloride and the value of the CCl distance in isopropyl chloride estimated by Opaskar and Krimm in their force field study (1.795 Å).[14]

The geometry for the STO-3G computations on protonated isopropyl chloride was obtained by replacing a hydrogen in staggered, protonated ethyl chloride with a methyl group at a CC separation of 1.533 Å. The CCl distance was then reoptimized and determined to be 2.120 Å, an increase of 0.084 Å over $CH_3CH_2ClH^+$. An almost identical increase is predicted by the MINDO/3 calculations.

(CH₃)₃CCl and (CH₃)₃CClH⁺. For the STO-3G calculation, *tert*-butyl chloride was assumed to be staggered with C_{3v} symmetry and all angles tetrahedral. The CC distances were again 1.54 Å and the CCl length was 1.834 Å. The latter quantity was obtained by adding the difference of the experimental values for ethyl chloride (1.779 Å) and *tert*-butyl chloride (1.80 Å) to the calculated value for ethyl chloride (1.813 Å).

The geometry around the quaternary carbon in protonated *tert*-butyl chloride is anticipated to be nearly planar owing to the high t-Bu⁺···ClH nature of the species.[2] Consequently, the CCl angles were taken as 100° and a slightly shorter CC distance (1.53 Å) was employed in the STO-3G calculations. A staggered geometry with C_s symmetry was assumed and the ClH distance and CClH angle were adopted from protonated ethyl chloride as for i-PrClH⁺. The optimized value for the CCl separation was then determined as 2.200 Å. Thus, the CCl distance increases by roughly 0.08–0.10 Å upon each successive methyl substitution in CH_3ClH^+ according to both the STO-3G and MINDO/3 results.

Results for Properties

The properties that were calculated for the alkyl chlorides are compiled in Table III.

The proton affinities determined by the MINDO/3 and STO-3G methods are in adequate agreement with the limited experimental data. As noted previously,[2] MINDO/3 overestimates PAs for alkyl chlorides by ca. 7 kcal/mol. The performance of STO-3G in this regard was surprising in view of its tendency to augment PAs of first-row bases, e.g., the PA of water is computed to be 225 kcal/mol as compared to the experimental number of 169 kcal/mol.[4d] The prediction is improved to 183 kcal/mol using the split 4-31G basis;[15] however, for the alkyl chlorides enhancing the basis to 44-31G yields PAs that are far too low. Correlations involving the PAs are discussed in the next section.

From Table III it is apparent that the strengths of MINDO/3 are its reproduction of ionization potentials and dipole moments. Dipole moments are uniformly overestimated at the STO-3G level. The trend worsens with the 44-31G calculations which are well known to exaggerate the polarity of molecules. On the other hand, ionization potentials are too low using STO-3G and are much improved by the extended basis. The relative STO-3G values reasonably mirror the experimental data.

Finally, the interaction energies, ΔE_s, between the formal carbonium ions and ClH in the protonated chlorides were determined.

$$\Delta E_s \equiv E\ (R^+) + E\ (HCl) - E\ (RClH^+)$$

Published values for the total energies of the carbonium ions were used in the arithmetic.[9,16] The STO-3G results are fine considering the experimental uncertainties. However, the MINDO/3 estimates are again high by about 7 kcal/mol, while the 44-31G basis underestimates the stability of the protonated chlorides. An interesting observation is the small interaction energy for t-BuClH⁺ predicted by STO-3G (4.3 kcal/mol). This suggests that protonated tertiary alkyl chlorides are barely stable complexes and may well eliminate HCl at the elevated temperatures generally employed in mass spectrometry. The origin of the ΔE_s values has been analyzed elsewhere.[2a,2d]

Table III. Calculated and Experimental Properties

Molecule	STO-3G	44-31G	MINDO/3	Exptl
	Proton Affinities, kcal/mol			
HCl	141.1	117.0	148.1	141,[a] 138[h]
CH_3Cl	167.7	145.8	166.3	160[b]
CH_3CH_2Cl	177.1		180.4	172[b,c]
$(CH_3)_2CHCl$	184.5		191.2	
$(CH_3)_3CCl$	194.0		199.1	
	Ionization Potentials, eV			
HCl	11.42	12.75	12.11	12.74[d]
CH_3Cl	10.36	11.70	11.10	11.22
CH_3CH_2Cl	10.18		10.91	10.97
$(CH_3)_2CHCl$	10.00		10.74	10.78
$(CH_3)_3CCl$	9.91		10.51	10.61
	Dipole Moments, D			
HCl	1.76	1.87	1.66	1.08[e]
CH_3Cl	2.33	2.47	1.56	1.87
CH_3CH_2Cl	2.49		1.95	2.05
$(CH_3)_2CHCl$	2.64		2.17	2.17
$(CH_3)_3CCl$	2.72		2.31	2.13
	Rotational Barriers, kcal/mol			
CH_3CH_2Cl	3.5		1.0	3.7[g]
$CH_3CH_2ClH^+$	3.0		−3.5	
	Cation-ClH Interaction Energies, ΔE_s, kcal/mol			
$HClH^+$	141.1	117.0	148.1	141,[a] 138[h]
CH_3ClH^+	46.9	24.0	53.4	51[b,f]
$CH_3CH_2ClH^+$	28.9		33.0	27[b,c,f]
$(CH_3)_2CHClH^+$	11.4		21.0	
$(CH_3)_3CClH^+$	4.3		13.2	

[a] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969). [b] J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Am. Chem. Soc.*, **94**, 2798 (1972). [c] J. L. Beauchamp, private communication. [d] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, and K. Draxl, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **No. 26** (1969). [e] R. D. Nelson, D. R. Lide, and A. Maryott, *Natl. Bur. Stand. (U.S.), Circ.*, **No. 10** (1967). [f] F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970). [g] W. G. Fateley and F. A. Miller, *Spectrochim. Acta*, **19**, 611 (1963). [h] D. H. McDaniel, unpublished drift cell value.

Table IV. Calculated Charges in Protonated Chlorides[a]

| | q_{Cl} | | q_H | |
Molecule	STO-3G	MINDO/3	STO-3G	MINDO/3
$HClH^+$	0.241	0.319	0.379	0.341
CH_3ClH^+	0.147	0.174	0.325	0.297
$CH_3CH_2ClH^+$	0.064	0.096	0.302	0.189
$(CH_3)_2CHClH^+$	0.013	0.022	0.284	0.180
$(CH_3)_3CClH^+$	−0.040	−0.045	0.263	0.181

[a] q_{Cl} is the charge on chlorine and q_H is the charge on hydrogen in $RClH^+$.

Proton Affinity Correlations

An excellent correlation was found previously between proton affinities and the charge on the ClH fragment in $RClH^+$ using MINDO/3 results for 13 acyclic and mono- and bicyclic chlorides.[2d,2f] Analogous correlations have also been reported for alcohols[2d] and primary amines.[2d,4b] The relationship for the MINDO/3 results is given in the equation

$$\Delta PA \ (MINDO/3) = -96.66(q_{Cl} + q_H) + 45.00 \quad (1)$$

expressed relative to the PA of methyl chloride. The STO-3G results for the five compounds in this study yield an almost identical relation:

$$\Delta PA \ (STO-3G) = -105.60(q_{Cl} + q_H) + 48.96 \quad (2)$$

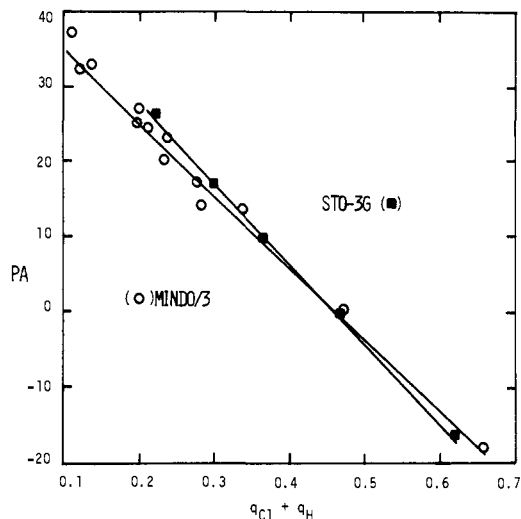**Figure 2.** Correlation of PAs (kcal/mol) for alkyl chlorides relative to methyl chloride with the sum of the charges on the ClH fragment in $RClH^+$.
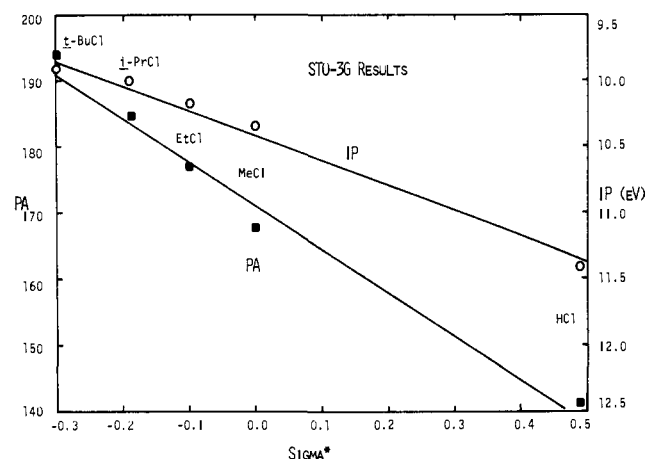

Figure 3. Correlation of calculated proton affinities (kcal/mol) and ionization potentials (eV) for alkyl chlorides and σ^* for the alkyl group.

The fit is, in fact, somewhat better for the STO-3G data: the mean errors are 0.7 and 1.3 kcal/mol for STO-3G and MINDO/3, respectively. If only the five acyclic chlorides are considered, the MINDO/3 mean error is 1.15 kcal/mol. The fits are illustrated in Figure 2 and the STO-3G charges are recorded in Table IV. Although the total charge on the ClH fragment in $RClH^+$ is remarkably similar for the two methods, the hydrogen is significantly more deficient according to STO-3G. As noted in the past,[2] the correlation in Figure 2 is pleasing because it simply implies that the proton affinities of alkyl chlorides are controlled by the ability of the alkyl group to accommodate positive charge. A possible extension of the results would be to define a theoretical polar substituent scale. Furthermore, the relation also led to the discovery of a rough correlation between PAs for alkyl chlorides and solvolysis rates.[2d-f]

Several cruder relations may be noted for the PAs. In Figure 3 the STO-3G results for PAs and IPs are shown to yield nearly linear equations with Taft's σ^* polar constant for the alkyl groups.[17] Similar correlations have been revealed for other bases previously.[2d,4c,18] It has also been mentioned before that MINDO/3 results indicate that the correlation of IPs and σ^* does not carry over to cyclic chlorides.[2d] For the STO-3G calculations, the mean errors for the fits of the proton affinities

to σ^* (eq 3) and the IP's (eq 4) are 3.2 and 4.1 kcal/mol, respectively.

$$\Delta PA \text{ (STO-3G)} = -51.95\sigma^* + 6.14 \qquad (3)$$

$$\Delta PA \text{ (STO-3G)} = -23.33IP \text{ (eV)} + 270.0 \qquad (4)$$

Hydrogen Bonding

Considering the widespread interest in hydrogen bonding,[19] it is odd that there have apparently been no theoretical studies of hydrogen bonding to carbonium ions other than our own.[2] The MINDO/3 work was, however, plaqued by the overestimation of intermolecular interactions with chlorine.[2] Therefore, STO-3G calculations have been executed for hydrogen bonding arrangements of methyl cation and HCl. In each case the optimized geometries of the monomers were held fixed as usual.[19] The lowest energy form has a slightly bent hydrogen bond (1) and a dissociation energy of 8.4 kcal/mol. The amount of electron density transferred from HCl is only 0.037 electron. Two alternatives with C_{2v} symmetry were considered (2 and 3). The hydrogen bond energies were computed to be

1

2   **3**
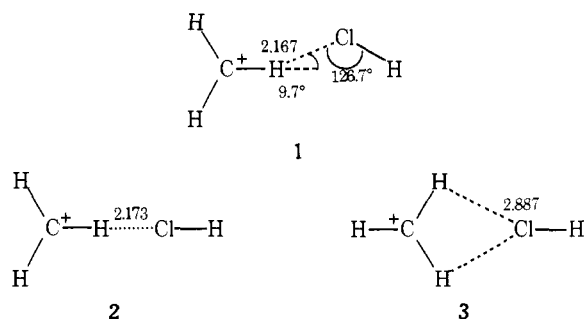
7.0 kcal/mol for **2** and 6.6 kcal/mol for **3**. MINDO/3 calculations predict structures like **1–3** to be roughly isoenergetic with bonding energies of ca. 15 kcal/mol.

The STO-3G results are important owing to the current interest in the solvation of carbonium iors in superacid media.[2] The present data set an upper bound to be expected for hydrogen bonding of carbonium ions to HCl, since the hydrogen bonding ability of a fully solvated carbonium ion would certainly be less than for **1**. Additional studies of hydrogen bonding of carbonium ions to HF are in progress.

Conclusions

In summary, the general agreement between experimental, STO-3G, and MINDO/3 results for alkyl chlorides indicates that both molecular orbital methods are suitable for modeling these compounds. The MINDO/3 geometries could be improved, though the computed properties are not too adversely affected. The difficulty with the STO-3G approach is the expense of geometry optimization. Most of our previous studies could not have been undertaken with this basis set given our moderate resources.[2]

Other significant findings that were covered here included the surprising result that PAs for alkyl chlorides are better reproduced at the STO-3G than 44-31G level; the previously noted correlations of PAs with the charge on the ClH fragment in $RClH^+$, ionization potentials, and σ^* are all upheld by the STO-3G computations; the small ΔE_s for t-BuClH$^+$ indicates that protonated tertiary chlorides will probably prove to be unstable in mass spectrometry experiments; and an upper bound of 8.4 kcal/mol was established for hydrogen bonding interactions between HCl and carbonium ions.

References and Notes

(1) Chemical Consequences of Orbital Interactions. 13. Part 12: ref 2e.
(2) W. L. Jorgensen, *J. Am. Chem. Soc.*, **99**, 280 (1977); (b) W. L. Jorgensen and J. E. Munroe, *Tetrahedron Lett.*, 581 (1977); (c) W. L. Jorgensen, *J. Am. Chem. Soc.*, **99**, 4272 (1977); (d) *ibid.*, preceding paper in this issue; (e) W. L. Jorgensen and J. E. Munroe, *ibid.*, in press; (f) W. L. Jorgensen, *Chem. Phys. Lett.*, in press.
(3) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975), and accompanying papers.
(4) For a recent sampling, see (a) P. A. Kollman and S. Rothenberg, *J. Am. Chem. Soc.*, **99**, 1333 (1977); (b) W. F. Reynolds, P. G. Mezey, W. J. Hehre, R. D. Topsom, and R. W. Taft, *ibid.*, **99**, 5821 (1977); (c) M. Taagepera, W. J. Hehre, R. D. Topsom, and R. W. Taft, *ibid.*, **98**, 7438 (1976); (d) J. E. Del Bene, *ibid.*, **98**, 7526 (1976); (e) K. Morokuma and H. Umeyama, *ibid.*, **98**, 4400 (1976); (f) A. Pullman and P. Brochen, *Chem. Phys. Lett.*, **34**, 7 (1975).
(5) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *ibid.*, **52**, 2769 (1970).
(6) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971); W. J. Hehre and W. A. Lathan, *ibid.*, **56**, 5255 (1972).
(7) GAUSSIAN/74 is a CDC version of GAUSSIAN/70: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, QCPE Program No. 236.
(8) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).
(9) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).
(10) R. J. Gillespie, "Molecular Geometry", Van Nostrand-Reinhold, London, 1972; R. J. Gillespie, *J. Chem. Educ.*, **51**, 367 (1974).
(11) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
(12) P. Kollman, J. McKelvey, A. Johannson, and S. Rothenberg, *J. Am. Chem. Soc.*, **97**, 955 (1975); P. Kollman, A. Johannson, and S. Rothenberg, *Chem. Phys. Lett.*, **24**, 199 (1974).
(13) A. Veillard in "Quantum Mechanics of Molecular Conformations", B. Pullman, Ed., Wiley-Interscience, New York, N.Y., 1976, p 1.
(14) C. G. Opaskar and S. Krimm, *Spectrochim. Acta, Part A*, **23**, 2261 (1967).
(15) M. D. Newton and S. Ehrenson, *J. Am. Chem. Soc.*, **93**, 4971 (1971).
(16) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 311 (1972); L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, **94**, 5935 (1972).
(17) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, p 619.
(18) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971); D. W. Davis and J. W. Rabalais, *J. Am. Chem. Soc.*, **96**, 5305 (1974); D. W. Davis and D. A. Shirley, *ibid.*, **98**, 7898 (1976); D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94**, 4726 (1972); R. Yamdagni, T. B. McMahon, and P. Kebarle, *ibid.*, **96**, 4035 (1974); Y. K. Lau and P. Kebarle, *ibid.*, **98**, 7452 (1976); J. M. McKelvey, S. Alexandratos, A. Streltwieser, Jr., J. M. Abboud, and W. J. Hehre, *ibid.*, **98**, 244 (1976).
(19) For recent summaries, see (a) P. Kollman, J. McKelvey, A. Johannson, and S. Rothenberg, *J. Am. Chem. Soc.*, **97**, 955 (1975); (b) L. C. Allen, *ibid.*, **97**, 6921 (1975).