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An *ab initio* Energy Surface for the Trichloride Ion, Cl_3^-

A Comparison of CNDO and *ab initio* Results for a Model Trihalide Ion

E. F. Riedel and Roger D. Willett

Chemical Physics Program, Washington State University, Pullman,
Washington 99163, USA

A partial energy surface for the trichloride ion has been calculated via an *ab initio* SCF molecular orbital method. The significant feature of the surface is the existence of a single minimum, indicating the isolated Cl_3^- ion exists in a symmetrical ($D_{\infty h}$) configuration. The calculated Cl-Cl bond length is 0.26 Å longer than the Cl-Cl bond length calculated for the Cl_2 molecule. The calculated change distribution is in excellent agreement with that deduced from NQR data. Standard CNDO calculations gave a very poor description of the bonding in the trichloride ion. However, by reparameterizing β to give the correct bond distance for the Cl_2 molecule and excluding *d* orbitals, excellent agreement between the CNDO and *ab initio* results was obtained.

Key words: Trichloride ion, energy surface of ~

1. Introduction

An *ab initio* calculation of the electronic structure of the trichloride ion was undertaken with three purposes in mind. First to ascertain if there existed a feature on the potential energy surface of the isolated ion which might account for the existence in the solid state of both symmetrical and asymmetrical trihalide ions of the form XYX^-. Second an accurate estimate of the bond lengths and energies for the trichloride ion was desired. Third we wanted a quantitative description of the binding in Cl_3^- which could be used for a comparison with qualitative and semiemperical MO calculations.

The existence of the trihalogen ions has long been known [1] and much structural data is available. All of the known trihalides are essentially linear, having bond angles between 171° and 180° in the solid state. For trihalides of the form XYX^-, the central atom may be in the middle or it may be found greatly shifted to one side. Bond lengths for X_3^- ions normally have been found to be 5–25% longer than those found for the corresponding X_2 molecule.

There are several qualitative descriptions of the binding in X_3^- [2, 3]. One of the early attempts to understand the trihalides is due to Slater [4]. He concluded that the trihalide ions prefer to be asymmetrical but packing forces in the solid state may be strong enough to force them into a symmetrical environment. Valence bond descriptions of the bonding have generally made use of the outer *d* orbitals on the central atom [5] while simple MO descriptions have utilized a three-centre four-electron picture [6]. This is illustrated by

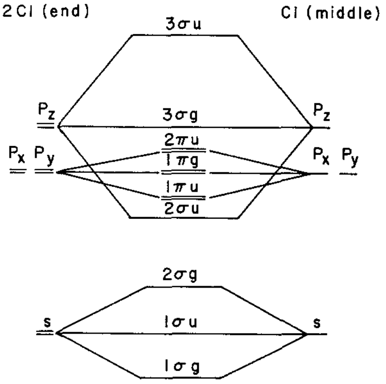

Fig. 1. Molecular orbitals for Cl_3^-. All orbitals are fully occupied except the highest, $3\sigma_\mu$

the MO correlation diagram for the symmetrical trichloride ion shown in Fig. 1. Of importance here in this representation is the existence of the occupied non-bonding σ orbital, $3\sigma_g$.

2. *Ab initio* Calculations

The *ab initio* method used here for the molecular wave function and its properties is the conventional Hartree-Fock-Roothaan SCF-LCGTO-MO method in which all integrals are evaluated analytically [7]. The calculations were carried out using the program IBMOL [8] which calculates the wave function as well as other properties for molecular and atomic systems using Gaussian-type orbitals. All the calculations were done on the IBM System 360 Model 67 computer of the Washington State University Computing Center.

A canonical Gaussian basis set which had been optimized for chlorine and published by Clementi [9] consisting of eleven *s*-type and twenty-one *p*-type (seven in each direction)

Table 1. Uncontracted Gaussian set for Cl_3^-

Type	Label			Orbital Exponents
s	β_1			14554.4
s	β_2			2192.81
s	β_3			505.97
s	β_4			151.57
s	β_5			56.630
s	β_6			23.7847
s	β_7			6.6443
s	β_8			2.6949
s	β_9			0.93360
s	β_{10}			0.45890
s	β_{11}			0.17790
x, y, z	β_{12}	β_{19}	β_{26}	227.265
x, y, z	β_{13}	β_{20}	β_{27}	54.7353
x, y, z	β_{14}	β_{21}	β_{28}	17.9135
x, y, z	β_{15}	β_{22}	β_{29}	6.52914
x, y, z	β_{16}	β_{23}	β_{30}	2.50257
x, y, z	β_{17}	β_{24}	β_{31}	0.709073
x, y, z	β_{18}	β_{25}	β_{32}	0.207862

Table 2. Contracted Gaussian set for Cl_3^- (unnormalized)

Contracted Gaussian[a]	Type
$\gamma_1 = 0.00361\beta_1 + 0.02715\beta_2 + 0.12300\beta_3$	s; $1s$
$\gamma_2 = 0.32288\beta_4 + 0.41715\beta_5 + 0.23860\beta_6$	s; $1s'$
$\gamma_3 = 0.49478\beta_7 + 0.59062\beta_8$	s; $2s$
$\gamma_4 = 0.06465\beta_9 + 0.66304\beta_{10}$	s; $3s$
$\gamma_5 = \beta_{11}$	s; $3s'$
$\gamma_6 = 0.01427\beta_{12} + 0.09045\beta_{13} + 0.28702\beta_{14} + 0.47772\beta_{15}$	x; $2p_x$
$\gamma_7 = \beta_{16}$	x; $2p'_x$
$\gamma_8 = \beta_{17}$	x; $3p_x$
$\gamma_9 = \beta_{18}$	x; $3p'_x$
$\gamma_{10} = 0.01427\beta_{19} + 0.09045\beta_{20} + 0.28702\beta_{21} + 0.47773\beta_{22}$	y; $2p_y$
$\gamma_{11} = \beta_{23}$	y; $2p'_y$
$\gamma_{12} = \beta_{24}$	y; $3p_y$
$\gamma_{13} = \beta_{25}$	y; $3p'_y$
$\gamma_{14} = 0.01427\beta_{26} + 0.09045\beta_{27} + 0.28702\beta_{28} + 0.47773\beta_{29}$	z; $2p_z$
$\gamma_{15} = \beta_{30}$	z; $2p'_z$
$\gamma_{16} = \beta_{31}$	z; $3p_z$
$\gamma_{17} = \beta_{32}$	z; $3p'_z$

[a] The β_i are defined in Table 1.

Gaussian functions was used. The ninety-six functions so chosen were then formed into a supra-atomic set of fifty-one contracted functions. The contracted set consists of five *s*-type and twelve *p*-type (four in each direction) functions. The contracted functions were then symmetry adapted to two sets of functions, one of which spanned $D_{\infty h}$ and the others spanning $C_{\infty v}$. Once this was done no further optimization or changes were made on the basis set. The orbital exponents of the contraction coefficients and the symmetry adapted functions for the atoms are given in Tables 1-4.[1]

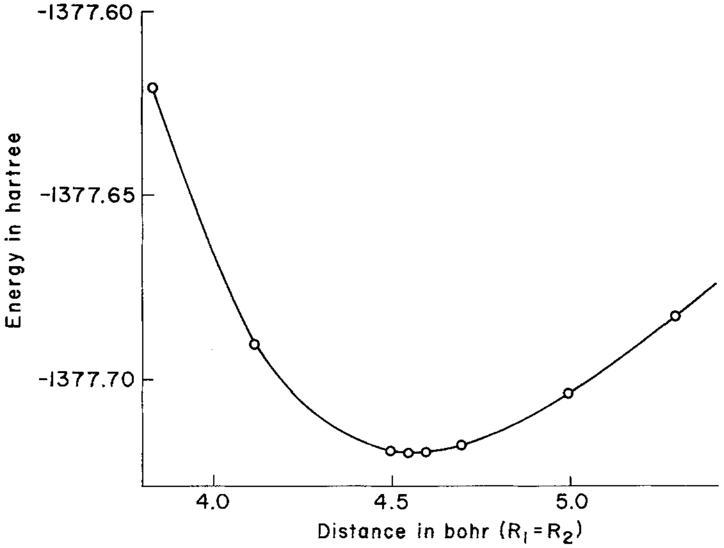

Fig. 2. Plot of energy versus distance in the linear symmetrical Cl_3^- ion ($D_{\infty h}$)

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[1] Tables 4–9 are not reproduced in the paper. Copies are available from the authors.

Table 3. Total contracted basis set for Cl_3^-

Center			
Cl1	Cl2	Cl3	Contracted Function[a]
α_1	$= \alpha_6$	$= \alpha_{11}$	$= \gamma_1$
α_2	$= \alpha_7$	$= \alpha_{12}$	$= \gamma_2$
α_3	$= \alpha_8$	$= \alpha_{13}$	$= \gamma_3$
α_4	$= \alpha_9$	$= \alpha_{14}$	$= \gamma_4$
α_5	$= \alpha_{10}$	$= \alpha_{15}$	$= \gamma_5$
α_{16}	$= \alpha_{20}$	$= \alpha_{24}$	$= \gamma_6$
α_{17}	$= \alpha_{21}$	$= \alpha_{25}$	$= \gamma_7$
α_{18}	$= \alpha_{22}$	$= \alpha_{26}$	$= \gamma_8$
α_{19}	$= \alpha_{23}$	$= \alpha_{27}$	$= \gamma_9$
α_{28}	$= \alpha_{32}$	$= \alpha_{36}$	$= \gamma_{10}$
α_{29}	$= \alpha_{33}$	$= \alpha_{37}$	$= \gamma_{11}$
α_{30}	$= \alpha_{34}$	$= \alpha_{38}$	$= \gamma_{12}$
α_{31}	$= \alpha_{35}$	$= \alpha_{39}$	$= \gamma_{13}$
α_{40}	$= \alpha_{44}$	$= \alpha_{48}$	$= \gamma_{14}$
α_{41}	$= \alpha_{45}$	$= \alpha_{49}$	$= \gamma_{15}$
α_{42}	$= \alpha_{46}$	$= \alpha_{50}$	$= \gamma_{16}$
α_{43}	$= \alpha_{47}$	$= \alpha_{51}$	$= \gamma_{17}$

[a] The γ_i are defined in Table 2.

Due to the structural and spectral data available it was assumed that the ion was linear. In all, nineteen data points were used to calculate the energy and define the energy surface. Each point on the surface required approximately 2.2 hours of CPU time for convergence. A total of nine points were calculated under the restriction of $D_{\infty h}$ symmetry ($R_1 = R_2$). In addition, in order to obtain a better estimate of the binding energy and also a better estimate for the equilibrium distance for the ion, a partial surface was calculated for the chlorine molecule. The energy for the chloride ion was also calculated.

The expansion coefficients and the orbital energies are listed in Tables 5–8. Table 9 lists the occupancy (population) of the basis functions for each of the MO's. Table 10 lists the orbital type and location of the various molecular orbitals. The ordering and the symmetry type of the occupied molecular orbitals are in Table 11. The ordering of the valence orbitals shown in Table 11 and Fig. 1 shows remarkable equality in a qualitative sense.

Fig. 2 is a plot of the energy for $R_1 = R_2$. The bottom four data points have been fit to the parabola $E = 0.1167(R\text{-}4.56)^2 - 1377.7208$. Fig. 3 shows the entire surface which was calculated. It is immediately apparent that there is no evidence for any subsidiary minimum. This is in contrast to Slater's earlier conclusion that the occurrence of the symmetrical ions must be due to the influence of the packing forces in the solid state.

Table 12 lists the distances and energies calculated for the chlorine molecule. The equilibrium bond distance is seen to be approximately 10% longer than the accepted value (2.175 vs. 1.987). If, as seems reasonable, the calculated equilibrium bond distance of 2.43 Å for the trichloride ion also is overestimated by 10%, the predicted value would be 2.22 Å. It should be noted here that on the basis of the observed bond lengthening on going from iodine to triiodide and from bromine to tribromide, one would predict a bond distance for the Cl_3^- ion of 2.17–2.25 Å.

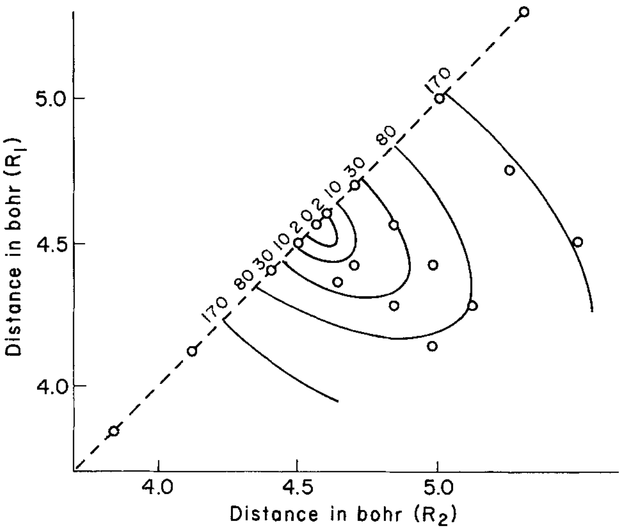

Fig. 3. Energy surface for the linear Cl_3^-. The values of the contours are in 10^4 Hartree relative to E_{min} (1377.7208) = 0

Table 10. Type and location of molecular orbitals

Molecular Orbital ($_i$)	End Atoms	Orbital Type	Middle Atom	Orbital Type
1	0.0	–	1.999992	s
2	0.999993	s	0.0	–
3	0.0	–	1.99453	s
4	0.999858	s	0.0	–
5	0.999966	p_z	0.0	–
6	0.194455	s	1.58076	s
	0.015368	p_z	0.0	–
7	0.805856	s	0.385564	s
	0.0014	p_z	0.0	–
8	0.980653	p_z	0.040496	s
9	1.000007	s	0.0	–
10	0.999682	s	0.0	–
11	0.0	–	1.999895	p_z
12	0.999965	p_z	0.0	–
13	0.966162	s	0.062489	p_z
	0.0026	p_z	0.0	–
14	0.548163	p_z	0.854568	p_z
	0.024562	s	0.0	–
15	0.0	–	1.99998	p_x
16	1.000001	p_x	0.0	–
17	0.137332	p_x	1.72532	p_x
18	0.86211	p_x	0.275754	p_x
19	0.0	–	1.99998	p_y
20	1.000001	p_y	0.0	–
21	0.137332	p_y	1.72532	p_y
22	0.862110	p_y	0.275754	p_y
23	1.000002	p_x	0.0	–
24	0.999999	p_x	0.0	–
25	1.000002	p_y	0.0	–
26	0.999999	p_y	0.0	–

Table 11. Ordering of SCF molecular orbitals

Inner Shells		Valence Shell	
Orbital[a]	(–) Energy (a.u.)	Orbital[a, b]	(–) Energy (a.u.)
$1\sigma_g$	104.53611	$6\sigma_g$ ($1\sigma_g$)	0.92221841
$9\sigma_u$	104.41154	$13\sigma_u$ ($2\sigma_u$)	0.81961709
$2\sigma_g$	104.41153	$7\sigma_g$ ($2\sigma_g$)	0.77797968
$3\sigma_g$	10.364164	$14\sigma_u$ ($2\sigma_u$)	0.34751877
$10\sigma_g$	10.242562	$17, 21\pi_u$ ($1\pi_u$)	0.33544378
$4\sigma_g$	10.242499	$24, 26\pi_g$ ($1\pi_g$)	0.24353555
$11\sigma_u$	7.8735055	$18, 22\pi_u$ ($2\pi_u$)	0.22537663
$15, 19\pi_u$	7.8701156	$8\sigma_g$ ($3\sigma_g$)	0.17531589
$12\sigma_u$	7.7539835		
$5\sigma_g$	7.7539830		
$16, 20\pi_u$	7.7519767		
$23, 25\pi_g$	7.7519758		

[a] Numbers refer to i in Ψ_i in Tables 5–8.

[b] Figures in parentheses refer to orbital labels in Fig. 1.

Table 13 lists the energy for the chloride ion as well as the binding energy for the trichloride ion. As can be seen the reaction is highly exothermic. An earlier semiempirical calculation by Wiebinga and Kracht [10] predicted a binding energy of about 6 kcal. The value of 32.6 kcal may be also compared to the result of CNDO which is 240 kcal.

Particularly satisfying is the agreement with the calculated charge distribution deduced from the NQR studies [11]. The *ab initio* results give a charge of +0.07 on the central atom and –0.54 on each terminal atom. This compares with the NQR values of +0.07 and –0.50 respectively. Since *d* orbitals were not used in the IBMOL calculations, this gives credulance to the three-center four-electron type of MO description of the bonding in the trihalide ion.

3. CNDO Calculations

For the semiempirical CNDO calculations the computer program CNINDO [12] was used. This method considers only the valence shell electrons. Overlap integrals are neglected and other one-electron integrals are calculated empirically. The zero differential overlap approximation is used for electron repulsion integrals and the other two-electron integrals are replaced by average values dependent upon centers and not the orbital.

Table 12. Energy calculated for the chlorine molecule

R (a.u.)	E (a.u.)
3.754958	–918.39154
3.854958	–918.39971
3.954958	–918.40472
4.054958	–918.40709
4.154958	–918.40727
4.254958	–918.40563

Bottom 4 points fit to $E = +0.10025\,(R\text{-}4.114)^2 - 918.4072$

Table 13. Binding energy for Cl_3^-

	R_{eq} (a.u.)	E (a.u.)
Cl_3^-	4.56	−1377.7208
Cl_2	4.114	−918.4072
Cl^-	–	−459.26106
$(Cl_2 + Cl^-) - Cl_3^-$	–	0.524 = 32.63 kcal/mole

In Table 14 are listed some of the results obtained with the CNDO method. As can be seen the basic method sees the trichloride ion as a double chlorine molecule with the charge of – 1/3 on every atom along with bond distances of those found in the chlorine molecule (by CNDO). Physically these results make absolutely no sense. For this reason, it was decided to see if some slight modification in the basic CNDO approach would yield more tractable results. In this light, two areas which had been subject to previous manipulation namely the exclusion of *d* functions and the adjustment of the β parameter, were examined.

The fundamental approximation in the CNDO method of Pople [13] involves the approximation of the off-diagonal elements in the Hartree-Fock matrix by

$$F_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} - 1/2 P_{\mu\nu}\gamma_{AB} \qquad (\mu \neq \nu) \tag{1}$$

where $P_{\mu\nu}$ is the usual charge-density matrix and bond-order matrix, γ_{AB} is an average Coulomb repulsion between an electron in any valence orbital centered on atom A and atom B (normally an *s* orbital), β^0_{AB} is an empirically chosen parameter, and $S_{\mu\nu}$ is the overlap integral. The parameter β^0_{AB} was originally chosen via the expression

$$\beta^0_{AB} = 1/2(\beta^0_A + \beta^0_B) \tag{2}$$

where the β^0_A are determined empirically so that the CNDO calculations give the best overall fit with accurate LCAO-SCF calculations on diatomics. In principal these were done by comparison with calculations on the hydrides. For our purposes, it seemed more reasonable to choose β^0_{AB} so as to obtain the proper equilibrium distance for the chlorine molecule. As can be seen in Table 14 once this is done the distances and charges in the tri-

Table 14. Charge distributions and bond lengths for various modifications of CNDO

	Bond Distance (Å)		Charge	
Method	Cl_2	Cl_3^-	Middle Atom	End Atom
Unmodified	1.75	1.79	−0.26	−0.37
With β optimization	1.99	2.07	−0.029	−0.485
β optimization with charge consistency	1.99	2.08	−0.045	−0.478
No *d* functions	1.89	2.08	+0.078	−0.539
No *d* functions with β optimization	2.04	2.18	+0.071	−0.535
IBMOL	2.17	2.43 (2.23)[a]	+0.074	−0.537
NQR[b]	–	–	−0.16	−0.50

[a] Corrected to Cl_2 = 1.987 [b] Ref.

Table 15. Ordering of valence shell molecular orbitals obtained from modifications of CNDO (in Hartree)

Standard		β Optimization		β Optimization with Charge Consistency		No d Functions with β Optimization		No d Functions		IBMOL	
$1\sigma_g$[a, b]	1.037	$1\sigma_g$	0.8834	$1\sigma_g$	0.8902	$1\sigma_g$	0.9167	$1\sigma_g$	1.0593	$1\sigma_g$	0.9222
$1\sigma_u$	0.8440	$1\sigma_u$	0.7543	$1\sigma_u$	0.7569	$1\sigma_u$	0.7622	$1\sigma_u$	0.8775	$1\sigma_u$	0.8196
$2\sigma_g$	0.5964	$2\sigma_g$	0.6824	$2\sigma_g$	0.6766	$2\sigma_g$	0.6732	$2\sigma_g$	0.6014	$2\sigma_g$	0.7780
$2\sigma_u$[a]	0.4135	$1\pi_u$	0.3484	$1\pi_u$	0.3480	$1\pi_u$	0.3798	$2\sigma_u$	0.4461	$2\sigma_u$	0.3475
$1\pi_u$[a]	0.3801	$2\sigma_u$	0.3374	$2\sigma_u$[a]	0.3439	$2\sigma_u$	0.3657	$1\pi_u$	0.4171	$1\pi_u$	0.3354
$1\pi_g$[d]	0.3143	$1\pi_g$[b]	0.2660	$1\pi_g$[b]	0.2679	$1\pi_g$	0.2541	$1\pi_g$	0.2477	$1\pi_g$	0.2435
$3\sigma_g$[d]	0.1565	$2\pi_u$	0.2359	$2\pi_u$	0.2305	$2\pi_u$	0.2372	$2\pi_u$	0.2747	$2\pi_u$	0.2254
$2\pi_u$[a]	0.1228	$3\sigma_g$[b]	0.1787	$3\sigma_g$[b]	0.1831	$3\sigma_g$	0.1358	$3\sigma_g$	0.0440	$3\sigma_g$	0.1753
Lowest Unoccupied Molecular Orbital											
$3\sigma_u$[c][d]	−0.3596	$3\sigma_u$[a]	−0.2101	$3\sigma_u$[a]	−0.2207	$3\sigma_u$	−0.2159	$3\sigma_u$	−0.4539	$3\sigma_u$	−0.1793

[a] A *d*-orbital coefficient greater than 0.1 on the end atom.
[b] A *d*-orbital coefficient greater than 0.1 on the middle atom.
[c] A *d*-orbital coefficient greater than 0.25 on the end atom.
[d] A *d*-orbital coefficient greater than 0.25 on the middle atom.

chloride ion are greatly improved. Nevertheless, insufficient bond lengthening in the trichloride is predicted and the charges do not agree with the *ab initio* and NQR results. Also, excellent agreement with the orbital energies calculated by IBMOL was obtained (see Table 15).

Table 16. Force constants

Cl_3^-		Cl_2	
Method	Value (mdyne/Å)	Method	Value (mdyne/Å)
Experimental[a]		IBMOL	2.84
symmetrical	1.51	Experimental[b]	3.56
asymmetrical	1.23		
IBMOL			
symmetrical	3.68		
asymmetrical	1.77		
CNDO			
standard	29.2		
with β optimization	9.8		
β optimization with charge consistency	11.7		
no *d* functions	9.62		
with β optimization (no *d* functions)	7.83		

[a] Evans, J. C., Lo, G. Y.-S.: J. Chem. Phys. **44**, 3638 (1966).
[b] Herzberg, G.: Spectra of diatomic molecules. New York: Van Nostrand 1951, reprint.

Santry and Segal [14] and Santry [15] have discussed at length the importance of the *d*-orbital contribution in CNDO. However, they examined only geometries with fixed bond lengths and so only looked at a part of the whole energy surface. Upon exclusion of *d* orbitals from the CNDO calculation, considerable improvement in the relative bond lengths of the chlorine molecule and the trichloride ion occurred, as well as in the charge distribution within the trichloride ion. However, as can be seen by examination of Table 15, the orbital energies are in very poor agreement with the *ab initio* results. This is remedied by both excluding the *d* orbitals and using the optimized value of β^0_{AB}. In this manner, distances, charges, and orbital energy levels are all in reasonable agreement with the *ab initio* calculations.

One last idea was also tried, namely, that of charge consistency as used by Brown [16]. The charges used to calculate the orbital exponents were required to be within 10% of those which were calculated at the end of the run. No substantial improvement was obtained over the β optimization procedure by itself.

Listed in Table 16 are the force constants which were calculated by the various methods. The IBMOL results are marginally satisfactory, while the CNDO values are in very poor agreement with experimental values. Nevertheless, the combination of β optimization with exclusion of *d* orbitals gives the most reasonable force constant.

4. Conclusions

There have recently been a number of semiempirical and *ab initio* calculations [17–19] reported on the interhalogen compounds. It is hoped that the *ab initio* results reported herein may serve as a standard of comparison for such calculations. These calculations confirm that the most stable configuration for the isolated trihalide ion is the symmetrical conformation. The *ab initio* calculations also were able to accurately reproduce the experimental charge distributions without inclusion of *d* orbitals.

The results from the CNDO calculations are mildly encouraging. Reparameterizing CNDO in a very "honest" fashion greatly improved the calculations. In addition it has been demonstrated that the exclusion of the *d* functions is necessary in order to obtain an accurate quantitative description of the bonding in these compounds from the CNDO calculations.

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