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QUANTUM CHEMICAL CALCULATIONS ON THE STRUCTURE OF (Cl₂F)⁺
AND RELATED MOLECULES

ROGER L. DEKOCK*, CRAIG P. JASPERSE

Department of Chemistry, Calvin College, Grand Rapids, Michigan 49506
(USA)

DANIEL T. DAO, JAMES H. BIEDA and JOEL F. LIEBMAN*

Department of Chemistry, University of Maryland Baltimore County
Catonsville, Maryland 21228 (USA)

SUMMARY

Molecular orbital calculations using the MNDO method have been completed on several diatomic and triatomic molecules and cations. The predicted most stable triatomic isomers are: (ClClF)⁺, (FClF)⁺, HOCl, HOF, ClOCl, FOF, ClOF, and (HFCl)⁺. For the first six, these calculated isomers are in agreement with the experimentally observed most stable structures. The most stable isomers of the last two are not yet known experimentally. Calculated heats of formation, structures, charge distributions, and Wiberg bond indices are reported. Comparison with ab initio calculations at the 4-31G level is also made.

INTRODUCTION

In 1969 Christe and Sawodny [1] observed the formation of 2:1 adducts of ClF with AsF₅ and BF₃ to produce the salts (Cl₂F)⁺(AsF₆)⁻ and (Cl₂F)⁺(BF₄)⁻. They were unable to determine experimentally the structure of the cation: (ClClF)⁺ or (ClFCl)⁺. However, based on electrostatic considerations they concluded that a 'Cl⁺' species would attack the negative end of the Cl^{δ+} F^{δ-} dipole to form (ClFCl)⁺. Gillespie and Morton [2] reported the Raman spectra of these 2:1 adducts in 1970 and concluded that the cation must be unsymmetrical, i.e.,

*To whom all correspondence should be addressed.

(ClClF)⁺. In 1975 one of us rationalized this unsymmetrical structure on the basis of the frontier orbital theory [3]. Since the highest occupied molecular orbital (HOMO) of ClF is predominantly chlorine, the electrophilic "Cl⁺" species should attack the chlorine end of ClF to produce the experimentally verified structure of (ClClF)⁺. Implicit in the application of frontier orbital theory to this reaction (Cl⁺ + ClF) is the assumption that charge transfer terms will be more important than electrostatic terms in determining the most stable structure.

Ab initio calculations on (ClClF)⁺, (ClFC1)⁺ (HFC1)⁺, and (HClF)⁺ at the STO-3G and 4-31G basis set level were reported by Joshi and Morokuma in 1979 [4]. For protonated ClF they found the most stable structure to be (HFC1)⁺; the cation of interest, (Cl₂F)⁺, was favored to be (ClClF)⁺ by 7.6 kcal/mol for the STO-3G calculation whereas the (ClFC1)⁺ structures was calculated to be more stable by 9.5 kcal/mol in the larger basis set 4-31G calculation. The result of the 4-31G calculation was adopted as the more stable structure: (ClFC1)⁺. An energy decomposition analysis was performed for all the calculations and the interaction energy between the electrophile (H⁺ or Cl⁺) and ClF was broken down into five terms: electrostatic, charge transfer, polarization, exchange repulsion, and a coupling term. The analysis of these terms showed that the calculated structure could not be predicted on the basis of any one term.

In this work we set out to perform MNDO calculations [5] on the four cations mentioned heretofore and several other molecules: F₂, Cl₂, HF, HCl, ClF, F₂O, Cl₂O, ClF₂⁺, HOF, HOCl, and ClOF. Our purpose was to ascertain the applicability of the MNDO method to these compounds by comparing experimentally observed structures and heats of formation with those calculated. We were especially interested in the results obtained for (Cl₂F)⁺. We hoped to provide some further rationale for its unsymmetrical structure, particularly in view of our interest to describe a set of simple 'topological rules' [6].

The MNDO method was chosen for this study because it has been extensively utilized by the chemical community to calculate relative energies of a wide variety of molecular systems. Since the MNDO method utilizes extensive parameterization to mimic nature, it can be argued that correlation energy already is taken into account [7]. Studies where correlation energy has been explicitly included (MNDOC) have shown that for closed-shell ground state molecules there is a negligible difference between MNDO and MNDOC [8].

TABLE 1
Heats of formation (kcal/mol)

Molecule	Calculated	Experimental ^c	Error
(ClClF) ⁺	290.9	----	---
(ClFCl) ⁺	313.3	----	---
(FClF) ⁺	321.1	----	---
(FFCl) ⁺	347.2	----	---
(HClF) ⁺	276.2	----	---
(HFCl) ⁺	233.4	----	---
HOF	-18.7 ^a	-22.8	4.1
HFO	47.4	----	---
HOCl	-15.7	-17.8	2.1
HClO	76.3	----	---
ClOF	27.3	----	---
OClF	95.0	----	---
FOF	18.2 ^a	5.9	12.2
FFO	125.8	----	---
ClOCl	31.3	19.5	11.8
ClClO	73.2	----	---
ClF	8.2	-12.1	20.3
HF	-59.8 ^a	-65.1	5.3
HCl	-15.3	-22.1	6.8
F ₂	7.3 ^a	0	7.3
Cl ₂	-10.7	0	-10.7
H ₂ O	-60.9 ^b	-57.8	- 3.1

^aSee ref. 10. ^bSee ref. 9. ^cSee ref. 16.

RESULTS AND DISCUSSION

Heats of formation

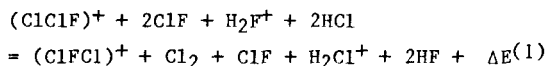
In Table 1 we present the MNDO calculated heats of formation and compare these to the experimental values. The mean error in the heats of formation is 8.4 kcal/mol which compares favorably with that found in other, more extensive studies utilizing MNDO [9,10]. Our results for F₂, HF, HOF, and F₂O agree with those reported by Dewar and Rzepa [10].

The calculated heats of formation indicate the more stable triatomic isomers to be $(\text{ClClF})^+$, $(\text{FClF})^+$, HOCl , HOF , ClOCl , FOF , ClOF , and $(\text{HFCl})^+$. These results are in agreement with experimental observations on the first six molecules [11]. For the latter two there is no experimental information available. The experimental results for $(\text{FClF})^+$ do not preclude the existence of a more stable $(\text{FFCl})^+$ isomer since the chemical reaction resulted from a 1:1 adduct of ClF_3 with SbF_5 or AsF_5 [12].

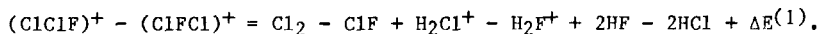
The difference in the calculated heats of formation for $(\text{ClClF})^+$ and $(\text{ClFCl})^+$ is 22.4 kcal/mol. These MNDO results predict $(\text{ClClF})^+$ to be more stable, in agreement with experiment [2] and with the *ab initio* STO-3G results but in disagreement with the *ab initio* 4-31G results of Joshi and Morokuma [4]. This probably represents a case where a larger basis set results in poorer agreement with experiment. There are other instances where it is known that the quality of the calculated result does not improve uniformly as the size of the basis set is increased [13]. As pointed out by Joshi and Morokuma, they have included neither d orbitals nor configuration interaction in their calculations.

In order to further compare the MNDO and 4-31G *ab initio* calculations on Cl_2F^+ we have carried out an extensive comparison of reaction heats involving several of the molecules listed in Table 1. The reactions that we have investigated are shown in Table 2. Following general theoretical chemical custom, the *ab initio* results have not been corrected for the comparatively small zero point energy differences between reactants and products. The mean error for MNDO is 17 kcal/mol whereas that for the 4-31G *ab initio* calculations is only 5.6 kcal/mol. Even with this small mean error in reaction heats, the *ab initio* calculations are not more definitive since the energy difference between $(\text{ClFCl})^+$ and $(\text{ClClF})^+$ is calculated to be small.

Further insight into the structure of Cl_2F^+ can be obtained by examining the isodesmic [14] reaction with $\Delta E_{\text{reaction}} = \Delta E^{(1)}$ explicitly included



This approach tends to cancel errors due to inadequate parametrization in the case of MNDO or due to basis set deficiencies and lack of explicit electron correlation in the case of *ab initio* calculations. This reaction can be rearranged as



Adding in $(\text{H}^+ - \text{H}^+)$ and rearranging terms leads to $(\text{ClClF})^+ - (\text{ClFCl})^+ = \text{Cl}_2 + \text{HF} - \text{HCl} - \text{ClF} + (\text{H}_2\text{Cl}^+ - \text{HCl} - \text{H}^+) - (\text{H}_2\text{F}^+ - \text{HF} - \text{H}^+) + \Delta E^{(1)}$.

From the definition of proton affinities (PA), $(\text{ClClF})^+ - (\text{ClFCl})^+ = (\text{Cl}_2 + \text{HF} - \text{HCl} - \text{ClF}) - \text{PA}(\text{HCl}) + \text{PA}(\text{HF}) + \Delta E^{(1)}$.

Now, using the 4-31G ab initio results we obtain (in kcal/mol)

$$+ 9 = -31 - 118 + 124 + \Delta E_G^{(1)} = 34; \Delta E_G^{(1)} = 36$$

and from the MNDO results

$$-22 = -63 - 122 + 156 + \Delta E_M^{(1)}; \Delta E_M^{(1)} = 7.$$

From experiment, the equation is written as

$$E(\text{ClClF}^+ - \text{ClFCl}^+) = -31 - 136 + 112 + \Delta E^{(1)} = 55 + \Delta E^{(1)}.$$

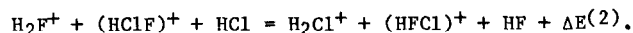
Equivalently, whether we use $\Delta E_G^{(1)}$ or $\Delta E_M^{(1)}$ in place of $\Delta E^{(1)}$ the result is

$$-55 + \Delta E_i^{(1)} < 0;$$

$(\text{ClClF})^+$ is the more stable isomer.

Notice that each of the three energy terms on the right hand side of the equation for MNDO are significantly in error when compared to experiment. Yet by a cancellation of these errors we obtain $\Delta E_M^{(1)} = 7$ kcal/mol. The PA values of the 4-31G ab initio calculation are also in error. Nevertheless, it is interesting to note that in the isodesmic reaction analysis the $(\text{ClClF})^+$ isomer is predicted to be more stable than $(\text{ClFCl})^+$, by either the 4-31G ab initio or MNDO results.

Next we turn our attention to the $(\text{HFCl})^+$ versus $(\text{HClF})^+$ isomers. On a simple relative energy basis, both calculations predict $(\text{HFCl})^+$ to be more stable. To gain further insight we can write an isodesmic reaction



This can be rearranged as before so that

$$E(\text{HClF}^+ - \text{HFCl}^+) = -\text{PA}(\text{HCl}) + \text{PA}(\text{HF}) + \Delta E^{(2)}$$

$$4-31\text{G} : + 36 = -118 + 124 + \Delta E_G^{(2)}; \Delta E_G^{(2)} = +30$$

$$\text{MNDO} : + 43 = -122 + 156 + \Delta E_M^{(2)}; \Delta E_M^{(2)} = + 9$$

$$\text{Expt.} : E(\text{HClF}^+ - \text{HFCl}^+) = -136 + 112 + \Delta E^{(2)} = -24 + \Delta E^{(2)}.$$

It is quite satisfying that

$$\Delta E_M^{(1)} < \Delta E_G^{(1)} \quad \text{and} \quad \Delta E_M^{(2)} < \Delta E_G^{(2)}$$

and

$$\Delta E_M^{(1)} - \Delta E_G^{(1)} \cong \Delta E_M^{(2)} - \Delta E_G^{(2)}.$$

However, in this case the isodesmic reaction does not allow us to predict the relative stability of $(\text{HClF})^+$ versus $(\text{HFCl})^+$ because $-24 + \Delta E_M^{(2)}$ and $-24 + \Delta E_G^{(2)}$ are of opposite sign. The large error in $\text{PA}(\text{HF})$ for MNDO is not offset by cancelling errors for the second isodesmic reaction as it was for the first. Consequently, we favor the isomer predicted by the calculated relative energies and by $\Delta E_G^{(2)}$: $(\text{HFCl})^+$.

TABLE 2

Heats of reaction (kcal/mol)

Reaction	MNDO	4-31G ^a	Experiment	$\Delta\text{ZPE}^{\text{d}}$
$\text{F}_2 + \text{Cl}_2 \rightarrow 2\text{ClF}$	+20	-19	-24	0
$\text{HF} + \text{Cl}_2 \rightarrow \text{HCl} + \text{ClF}$	+63	+31	+31	+3
$\text{HF} + \text{ClF} \rightarrow \text{HCl} + \text{F}_2$	+44	+50	+55	+3
$\text{H}_2\text{O} + \text{OF}_2 \rightarrow 2\text{HOF}$	+ 5	+ 3	+6	-2
$\text{H}_2\text{O} + \text{OCl}_2 \rightarrow 2\text{HOCl}$	- 2	- 2	- 3	-2
$\text{H}_2\text{O} + \text{Cl}_2 \rightarrow \text{HOCl} + \text{HCl}$	+41	+23	+18	+3
$\text{H}_2\text{O} + \text{ClF} \rightarrow \text{HOF} + \text{HCl}$	+19	+26	+25	+3
$\text{H}_2\text{O} + \text{ClF} \rightarrow \text{HOCl} + \text{HF}$	-23	- 8	-13	+3
$\text{H}_2\text{O} + \text{F}_2 \rightarrow \text{HOF} + \text{HF}$	-25	-24	-30	0
$\text{H}_2\text{F}^+ \rightarrow \text{HF} + \text{H}^+$	+156 ^b	+125 ^c	+112 ^c	--
$\text{H}_2\text{Cl}^+ \rightarrow \text{HCl} + \text{H}^+$	+122 ^b	+118 ^c	+136 ^c	--

^aSee ref. 17

^bThe MNDO proton affinities were obtained by using the experimental heat of formation of H^+ (365.7 kcal/mol) along with the calculated heats of formation of the neutral and protonated molecules.

^cSee P. J. Desmeules and L. C. Allen, *J. Chem. Phys.*, **72** (1980) 4731 for ab initio results and leading references to the experimental results.

^dThese are zero point energies determined from experimental spectroscopic studies, $\text{ZPE} = 1/2 \sum_i h \nu_i$, where we sum over all of the vibrational frequencies of the species of interest. The values of the desired frequencies for HOF and HOCl were taken from T. Shimanouchi, *J. Phys. Chem. Ref. Data*, **6** (1977) 993 while for the other neutrals reference 16 was used. We know of no ZPE data for H_2F^+ , H_2Cl^+ , or of any other of the cations of interest. For completeness, we list the ZPE values for the neutral species in this paper: F_2 , 2.6; Cl_2 , 1.6; ClF , 2.2; HF , 11.8; HCl , 8.5; H_2O , 25.7; OF_2 , 6.3; H_2O , 25.7; OF_2 , 6.3; HOF , 16.6; OCl_2 , 4.7; HOCl , 15.9 kcal/mol.

TABLE 3

Calculated MNDO Properties

Molecule	Calculated Properties ^a		Bond Angle
(ClClF) ⁺	(0.272)	$\frac{2.040}{0.957} \text{ (0.729)} \quad \frac{1.682}{0.977} \text{ (-0.001)}$	102.96°
(ClFCl) ⁺	(0.499)	$\frac{1.690}{0.724} \text{ (0.002)} \quad \frac{1.690}{0.724} \text{ (0.499)}$	134.36°
(FClF) ⁺	(0.015)	$\frac{1.676}{1.000} \text{ (0.970)} \quad \frac{1.676}{1.000} \text{ (0.015)}$	97.94°
(HClF) ⁺	(0.362)	$\frac{1.430}{0.856} \text{ (0.633)} \quad \frac{1.678}{1.006} \text{ (0.005)}$	97.50°
(HFCl) ⁺	(0.486)	$\frac{0.987}{0.738} \text{ (0.004)} \quad \frac{1.681}{0.718} \text{ (0.510)}$	137.57°
HO ₂ F	(0.190)	$\frac{0.964}{0.953} \text{ (-0.094)} \quad \frac{1.277}{0.994} \text{ (-0.096)}$	107.88°
FO ₂ F	(-0.073)	$\frac{1.281}{0.992} \text{ (0.147)} \quad \frac{1.281}{0.992} \text{ (-0.073)}$	109.06°
HOCl	(0.184)	$\frac{0.949}{0.963} \text{ (-0.170)} \quad \frac{1.684}{1.001} \text{ (-0.014)}$	106.44°
ClOCl	(0.028)	$\frac{1.683}{0.999} \text{ (-0.056)} \quad \frac{1.683}{0.999} \text{ (0.028)}$	112.94°
ClOF	(0.020)	$\frac{1.709}{0.975} \text{ (0.042)} \quad \frac{1.267}{1.013} \text{ (-0.062)}$	112.99°
HF	(0.287)	$\frac{0.956}{0.918} \text{ (-0.287)}$	
HCl	(0.184)	$\frac{1.348}{0.966} \text{ (-0.184)}$	
ClF	(0.149)	$\frac{1.650}{0.978} \text{ (0.149)}$	
ClCl	(0.00)	$\frac{2.000}{1.000} \text{ (0.00)}$	

^aThe numbers in parentheses refer to the atomic charges on the appropriate atom. The numbers above the horizontal lines refer to the bond length (Å), and beneath the horizontal lines to the Wiberg bond index.

TABLE 4

Comparison of experimental and calculated (MNDO) geometries^a

Molecule	Calculated (observed) ^b geometrical variables
(FClF) ⁺	FCl 1.676 (1.54-1.57), FClF 97.9 (96-103)
HOF	HO 0.964 (0.966), OF 1.277 (1.442), HOF 107.9 (96.78)
HOCl	HO 0.949 (0.96), OCl 1.684 (1.72), HOCl 106.4 (104)
FOF	FO 1.281 (1.409), FOF 109.1 (103.3)
ClOCl	ClO 1.683 (1.701), ClOCl 112.9 (110.8)
HF	HF 0.956 (0.917)
HCl	HCl 1.348 (1.275)
Cl ₂	ClCl 2.000 (1.986)
ClF	ClF 1.650 (1.628)

^aBond lengths in Å, angles in degrees.^bObserved structures taken from JANAF Thermochemical Tables, ref. 16.Structures, atomic charges, and Wiberg bond indices

These calculated MNDO properties are presented in Table 3 for the diatomic molecules and the most stable isomers of the triatomic species. Also presented are the results for (ClFCl)⁺ and (HClF)⁺.

The experimental bond lengths and bond angles are shown in Table 4 for the species for which they are accurately known. The MNDO method agrees reasonably well with experiment.

The computed charge on the fluorine atom is close to zero in all of the molecules, no matter whether the fluorine atom is central or terminal. The chlorine atom has a relatively large positive charge if it is centrally located in the cationic species. Taken at face value, these results indicate that there would be little electrostatic stabilization in (HFC1)⁺ and (ClFC1)⁺, and that there would be electrostatic destabilization for (HClF)⁺ and (ClClF)⁺.

Since the MNDO method is a zero-overlap approximation, one cannot calculate Mulliken overlap populations. Wiberg [15] has shown that in such cases the square of the bond order serves as an appropriate 'bond index.' We define the bond order between two AOs i and j in the usual way: $P_{ij} = \sum n_k c_{ik} c_{jk}$ where n_k is the electron occupation of the kth MO and c_{ik} is the coefficient of the ith AO in the kth MO. These values are shown also in Table 4 and illustrate that, for the cationic species, the Wiberg bond index is always larger for molecules with the chlorine atom centrally located. If one associates the Wiberg bond index with covalent bond strength, one can say that the greater covalent bonding in the case of $(ClClF)^+$ compared to $(ClFCl)^+$ is sufficient to overcome the electrostatic repulsion effect in the former.

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- 17h HOF, see reference 17a.
- 17i OCl₂, this study, geometry optimized E_{total} = -992.58265 a.u..
- 17j H₂F⁺, see reference 17d.
- 17k H₂Cl⁺, see reference 17d.