

CNDO/2 calculations on the structure and properties of chlorine difluoride

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Abstract. According to the open-shell CNDO/2 calculations on ClF_2 , performed by using the computer programme developed by Pople, Beveridge and Dobosh, the molecule is linear and stable, with equilibrium bond length 1.507\AA and binding energy -173.7 kcal/mole. The molecule has a tendency to dimerise and to disproportionate into ClF_3 and ClF . The net d -orbital population in the monomer is 0.88. Bonding characteristics and other molecular properties are also discussed.

Keywords. Chlorine difluoride; CNDO/2 calculations; open-shell calculations; molecular structure and properties.

1. Introduction

In recent years although there have been several semi-empirical and *ab initio* calculations (Deb and Coulson 1971, Spurling and Snook 1973, Guest *et al* 1973, Sannigrahi and Noor Mohammad 1973, Sichel and Whitehead 1968) on the bonding, geometry and properties of known interhalogen molecules, of formula XX'_n where n is odd, little attempt has been made (Gregory 1974) to study the molecules with n =even. In this paper we report all-valence-electron CNDO/2 calculations on chlorine difluoride, an open-shell molecule. Our object is to find out (a) whether the molecule is stable, (b) if stable, what are its equilibrium geometry and certain common properties, and (c) whether the molecule tends to dimerise into Cl_2F_4 , or disproportionate to give ClF and ClF_3 . Experimentally ClF_2 has been characterised by Mamantov *et al* (1971) by the photolysis of $\text{F}_2 + \text{ClF}$, and of ClF_3 . They interpreted the observed vibrational frequencies in terms of a bent symmetric ClF_2 molecule of bond angle $140 \pm 19^\circ$. This result offers an interesting contrast to the spectroscopic studies on the related 21-valence-electron Cl_3 molecule by Nelson and Pimentel (1968) who concluded that Cl_3 is linear.

Calculations were performed with the CNDO/2 programme written by Pople *et al* (Pople and Beveridge 1970) and set up on the Soviet EC-1030 computer at the Indian Institute of Technology, Bombay. The programme deals with open-shell systems by an unrestricted Hartree-Fock-type method that calculates single-determinantal wavefunctions in the framework of CNDO/2 approximations. Such wavefunctions are, in general, spin-contaminated. Details of the method and the programme may be found in Pople and Beveridge (1970). For fluorine atoms the basis functions are valence s and p AO's, whereas for chlorine the basis also includes d orbitals, all AO's being of Slater-type.

2. Results and discussion

2.1. Geometry and stability

According to the models of Walsh (1953) and Deb *et al* (Deb 1974, 1975; Deb *et al* 1974, 1976), ClF_2 should be linear. Calculations with bond angles of 170° , 175° and 180° , using an assumed bond length of 1.641 \AA (this is the arithmetic mean of experimental bond lengths in ClF and ClF_3), showed that the molecule is stable, and the total energy is indeed a minimum in the linear configuration. Taking the linear configuration, the equilibrium Cl-F bond length was found to be 1.507 \AA by least-squares fit of a quadratic function in the bond length range 1.30 to 1.641 \AA . Figure 1 depicts the corresponding potential energy curve for bond length variation. The calculated bond length for ClF_2 may be compared with the observed values 1.58 \AA

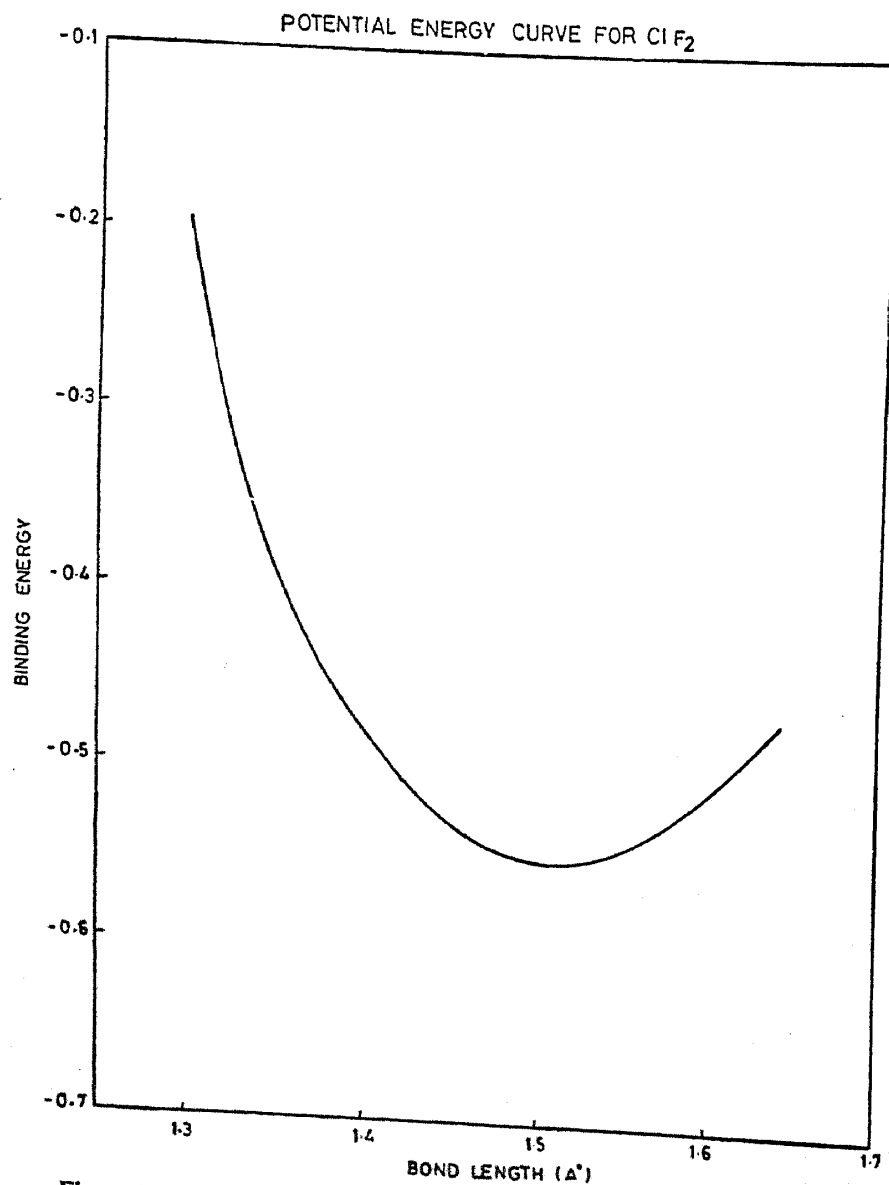


Figure 1. Variation of the binding energy (a.u.) of chlorine difluoride with bond length (Å). Bond angle = 180° .

(Edwards and Sills 1970) and 1.541 Å (Lynton and Passmore 1971) for ClF_2^+ . Using the equilibrium bond length, we have then covered the bond angle range 120–180°. We observed only one energy minimum at 180°. Thus, the present calculations do not agree (see conclusion) with the conclusions of Mamantov *et al* (1971).

Figure 2 gives a plot of orbital energies vs. the bond angle. The HOMO energy shows a minimum at 180°. This is in accord with the HOMO postulate (Deb 1974) according to which the HOMO would be shape-determining in situations like this. Figure 3 shows a schematic diagram of the HOMO (the HOMO energy level is two-fold degenerate in the linear configuration) of the bent molecule. This is an a_1 mild antibonding MO that becomes a π antibonding MO in the linear molecule. Figure 4 depicts the orbital energy variations with respect to bond length. Assuming that one can place some reliance on the CNDO/2 virtual orbital energies, we find from figure 2 that the molecule will retain its linear shape on electronic excitation to the

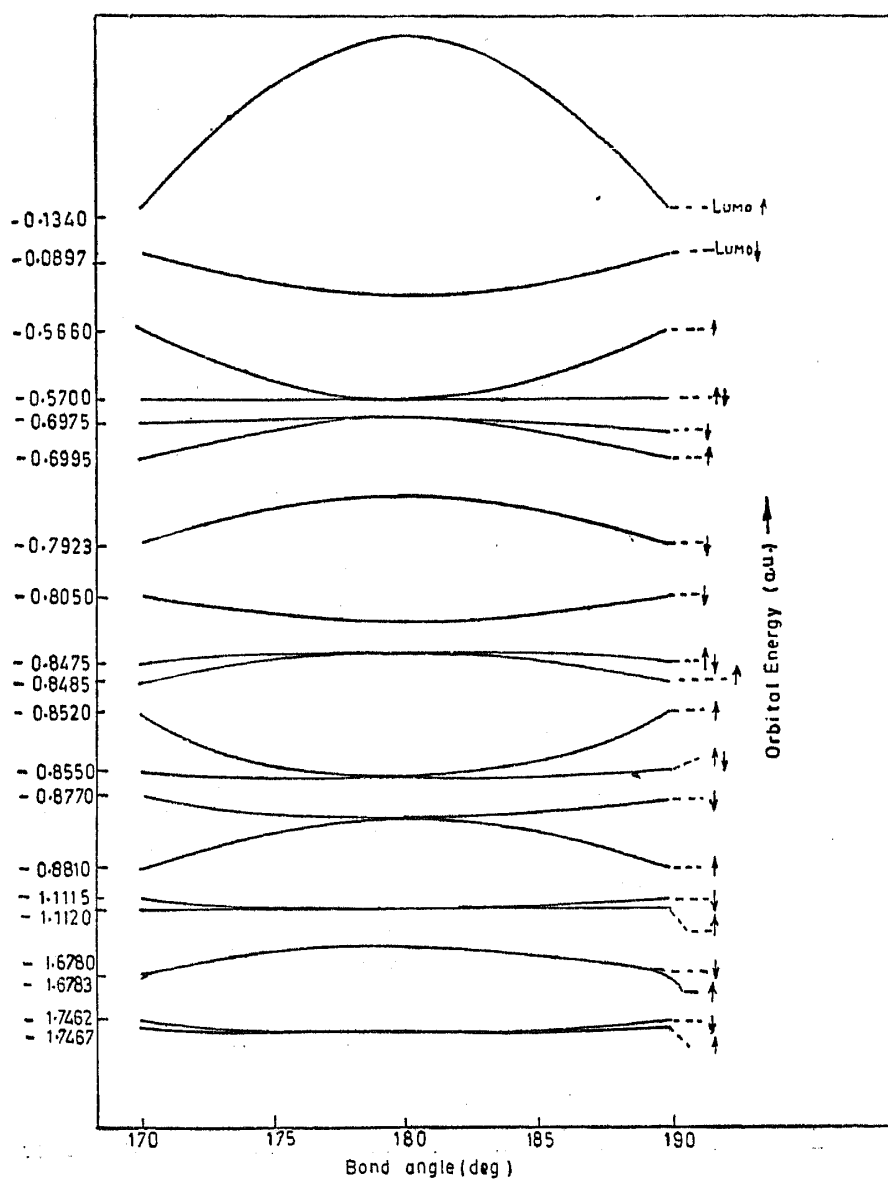


Figure 2. Variation of the MO energies of chlorine difluoride with bond angle (bond length = 1.507 Å). An upward arrow denotes α -spin, a downward arrow denotes β -spin.

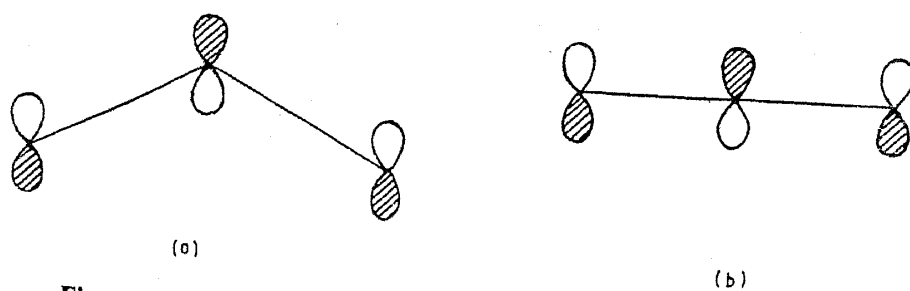


Figure 3. Schematic diagram of the anti-bonding HOMO (α -spin) of (a) bent, and (b) linear chlorine difluoride. The p orbitals are in the plane of the paper.

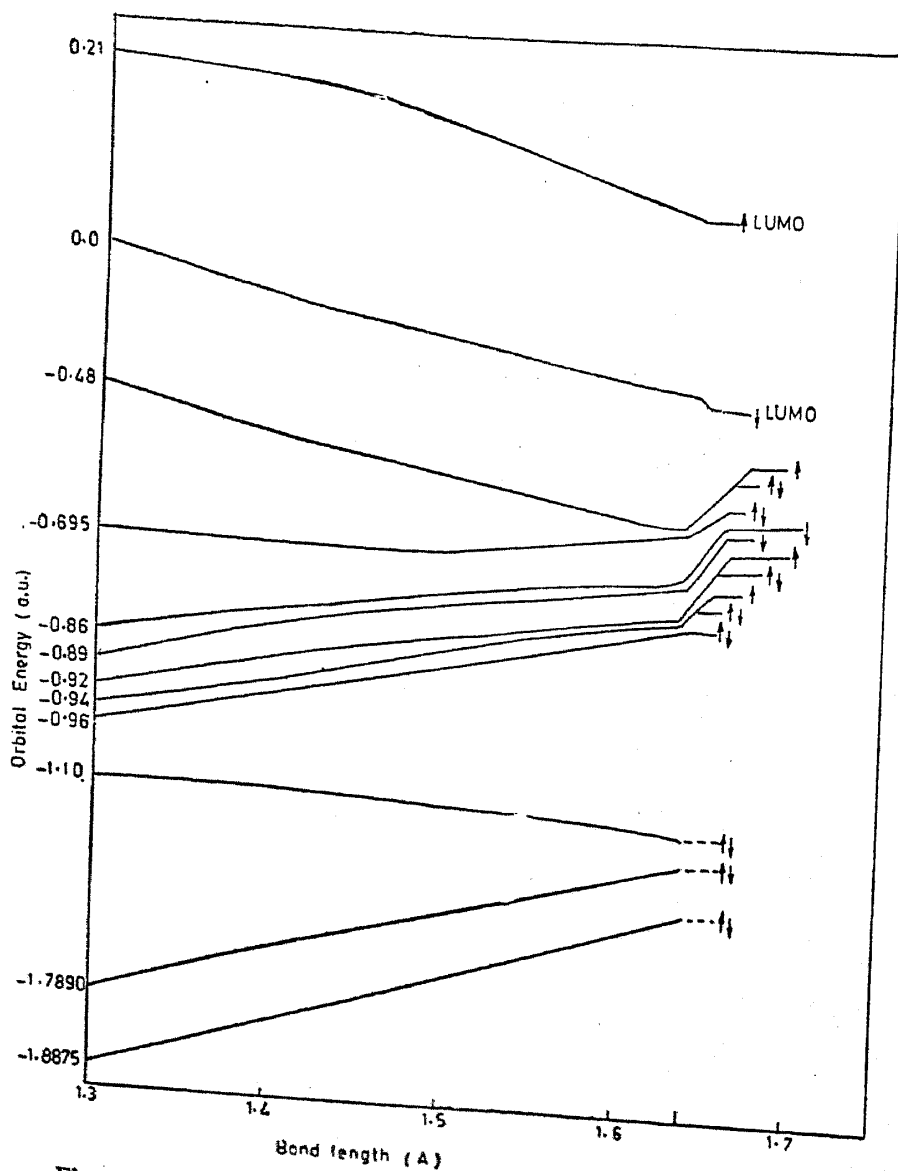


Figure 4. Variation of the MO energies of linear chlorine difluoride with bond length.

LUMO (β -spin) although the bond length is expected to increase; excitation to the LUMO (α -spin) will, however, bend the molecule (Deb 1974).

2.2. Bonding characteristics

The binding energy of ClF_2 (equilibrium configuration) is -0.5536 a.u., i.e. -0.2768 a.u. (-173.7 kcal/mole) per Cl—F bond. This may be compared with the calculated binding energy, -0.2688 a.u. (-168.7 kcal/mole), for the ClF molecule with the experimental bond length (1.628 Å). The observed bond energy for ClF is 59.5 kcal/mole, while for ClF_3 it is 41.2 kcal/mole per Cl—F bond. It is well known (Pople and Beveridge 1970) that, in general, CNDO/2 highly exaggerates binding energy, a factor of 3 being quite common. Tables 1 and 2 give the orbital and total atomic densities with regard to bond angle variation (taking 1.507 Å as the bond length), and bond length variation respectively (taking bond angle as 180°).

For the equilibrium configuration, there is a substantial π bonding, in addition to σ bonding, between the chlorine and the fluorine atoms. Both chlorine and fluorine π orbitals have greater population than the σ orbitals. The calculations also reveal that chlorine d orbitals have a population of 0.88 ; this is ~ 4 per cent of the total number of valence electrons and ~ 12.6 per cent of the chlorine valence electrons. This d -population may be compared with the corresponding CNDO/2 values of 0.15 (H_2S), 0.66 (SF_2), 1.40 (SF_4) and the value 0.66 for PF_3 (all values quoted in Coulson 1972). Thus the value of 0.88 for ClF_2 may be regarded as indicating significant d participation in bonding.

As the molecule bends from linearity, increasing charge is accumulated in the atomic orbitals perpendicular to the molecular plane while the overall charge in orbitals in the molecular plane decreases. The chlorine d -participation in bonding decreases

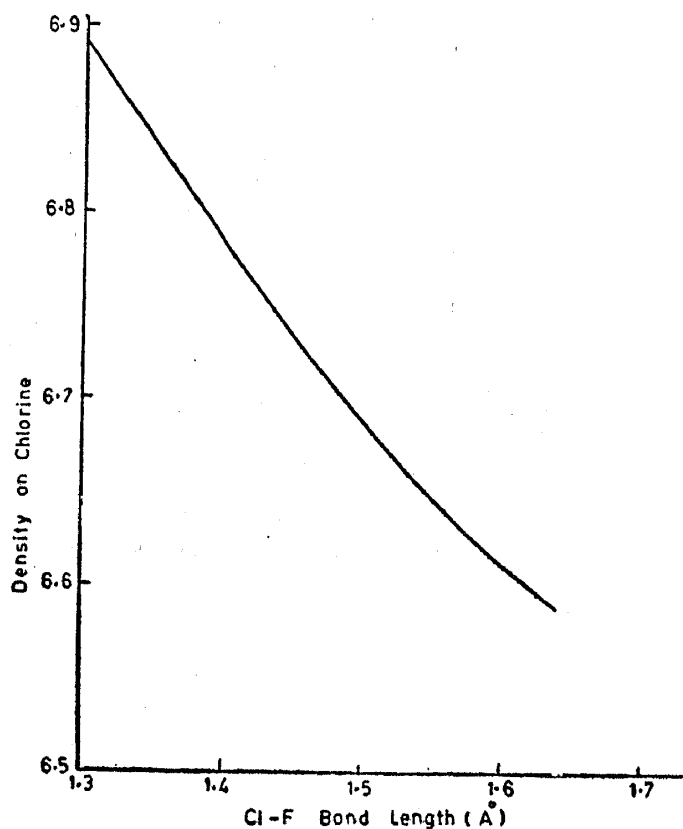


Figure 5. Variation of the valence electron density (a.u.) on chlorine with Cl—F bond length.

Table 1. Variation in molecular properties of ClF_3 with a change in bond angle. The Cl-F bond length is 1.507 Å (equilibrium value).

Bond angle (deg.)	Binding energy (a.u.)	Electronic energy (a.u.)	Total energy (a.u.)	HOMO energy (a-spin) (a.u.)	Dipole moment (D)	<i>s</i> spin density		Hyperfine coupling constant				Densities for Cl			Densities for F		
						Cl	F	Cl	F	Cl	F	π	d	σ	π	σ	π
170	-0.5526	-114.7450	-71.6975	-0.5662	0.0403	0.0024	0.0002	0.0	0.0	4.5052	2.1779	0.8765	5.2475	1.9110			
175	-0.5534	-114.7211	-71.6983	-0.5690	0.0180	0.0006	0.0001	0.0	0.0	4.5035	2.1774	0.8794	5.2483	1.9113			
180	-0.5536	-114.7132	-71.6986	-0.5699	0.0	0.0	0.0	0.0	0.0	3.1765	3.5036	0.8804	3.4118	3.7482			

Table 2. Variation in molecular properties of ClF_3 with a change in bond length (bond angle = 180°). The HOMO energy is doubly degenerate.

Bond length (Å)	Binding energy (a.u.)	Electronic energy (a.u.)	Total energy (a.u.)	HOMO energy (a.u.)	Energy of MO below HOMO (a.u.)	Densities for Cl				Densities for F			
						σ	π	d	Total	σ	π	σ	Total
1.42	-0.5047	-117.2996	-71.6496	-0.5359	-0.7034	3.1315	3.6296	0.9795	6.7611	3.4343	3.6851	7.1194	
1.44	-0.5260	-116.6869	-71.6709	-0.5440	-0.7030	3.1415	3.5997	0.9562	6.7412	3.4293	3.7001	7.1294	
1.507	-0.5536	-114.7132	-71.6986	-0.5699	-0.6973	3.1765	3.5036	0.8804	6.6801	3.4118	3.7481	7.1599	
1.52	-0.5525	-114.3442	-71.6975	-0.5747	-0.6955	3.1838	3.4855	0.8662	6.6693	3.4081	3.7573	7.1654	
1.54	-0.5475	-113.7853	-71.6924	-0.5818	-0.6922	3.1951	3.4583	0.8445	6.6534	3.4025	3.7708	7.1733	

slightly as a result of this bending. That the molecule would be more stable in the linear form is also indicated by the increased polarity of the Cl—F bond in the linear molecule.

From table 2 several features can be observed. First, as the bond length increases the charge on the chlorine atom decreases (figure 5) while that on the fluorine atom increases. This artificial tendency of a molecule to dissociate into ions is a well-known drawback of MO wavefunctions. Next, with increasing bond length the σ density on chlorine increases while the π density decreases; the reverse is true for fluorine σ and π densities. The π densities on chlorine and fluorine suffer more variations than the corresponding σ densities, again indicating the relative significance of π bonding in the molecule. With increasing bond length chlorine d -participation also decreases.

Tables 3 and 4 list a number of properties of the molecule at the theoretical equilibri-

Table 3. Orbital energies of ClF_2 for α -spin and β -spin electrons in the equilibrium configuration. The highest occupied MO energy level is doubly degenerate.

Orbital energies for α -spin (11 α -electrons) (a.u.)	Orbital energies for β -spin (10 β -electrons) (a.u.)
+0.1435	
	−0.0921
−0.5699	
−0.5699	−0.5699
−0.6973	−0.6973
	−0.7896
	−0.8063
−0.8469	
−0.8469	−0.8469
−0.8558	
−0.8558	−0.8558
−0.8782	−0.8782
−1.1121	−1.1121
−1.6765	−1.6765
−1.7470	−1.7470

Table 4. Predicted molecular properties^(a) of ClF_2 in the equilibrium configuration

Stretching force constant (a.u.)	Bending force constant (a.u.)	Quadrupole coupling constant for ^{35}Cl (MHz)
3.643	0.0361	−93.54 ^(b)

(a) For other molecular properties refer to table 1 for bond angle 180°

(b) The quadrupole coupling constant (C) is obtained by using the relation $C = C_0 [P_{zz} - (P_{xx} + P_{yy})/2]$, where P_{zz} is the p_z population for Cl, and C_0 for $^{35}\text{Cl} = 109.746$ MHz. The z -axis is along the molecular axis (Sichel and Whitehead 1968).

um configuration. The highest occupied energy level is doubly degenerate. This is expected to result in the Renner effect which, however, will not be discussed in this paper. From table 3 we also see that three α energy levels are doubly degenerate whereas there is no degeneracy among the β MO's. Further, the stretching force constant for the molecule seems highly exaggerated (table 4).

2.3. Dimerisation and disproportionation

In spite of its predicted stability the fact remains that chlorine difluoride has rarely been observed. Therefore, we carried out a limited study of possible dimerisation and disproportionation of the molecule. We consider two ClF_2 molecules in five different configurations involving essentially two modes of approach (figure 6). Finding the equilibrium configuration of each of these 'dimers' was not possible because of limitations on computer time.

Table 5 makes a comparison between the energy values, atomic densities, etc., of the five 'dimers'. Assuming that the total binding energy $= 2 \times (\text{binding energy of } \text{ClF}_2) + (\text{Cl}-\text{Cl binding energy})$, the Cl-Cl binding energy (-0.3345 a.u.) in configuration I seems much too high, in view of the fact that the dimer seems to be

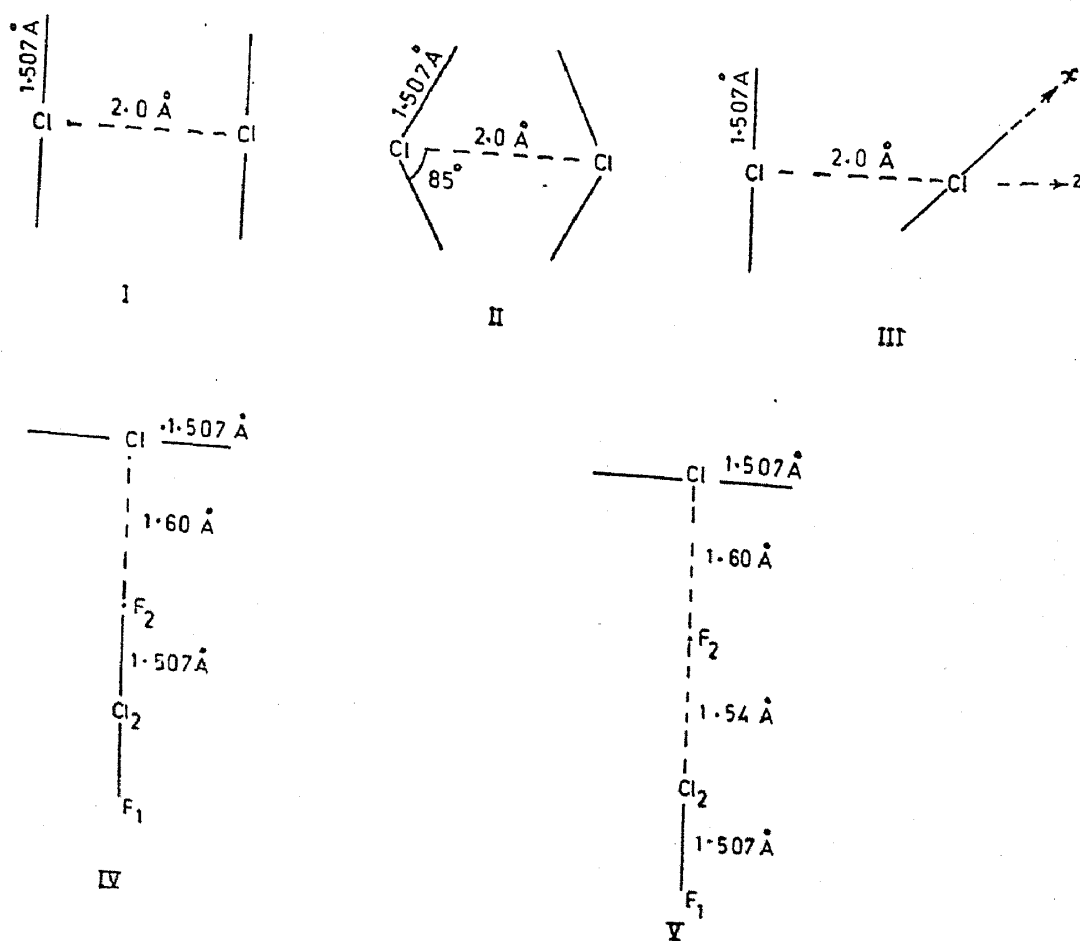


Figure 6. Five relative orientations of two ClF_2 fragments. Except the Cl_2-F_1 distance in V, all other Cl-F bond lengths are equal to 1.507 \AA .

Table 5. Relative comparison of five non-equilibrium configurations for the 'dimer' Cl_2F_4 (see figure 6).

Property	Configuration				
	I	II	III	IV	V
Electronic energy (a.u.)	-324.4082	-327.4366	-319.6351	-309.0105	-308.2364
Total energy (a.u.)	-143.7317	-143.7257	-143.7376	-143.5153	-143.5274
Binding energy (a.u.)	-1.4418	-1.4358	-1.4477	-1.2253	-1.2375
Dipole moment (D)	0.0	0.0	0.0	6.2167	5.9524
Atomic densities					
Cl ₁	6.6824	6.6816	6.6707	6.4228	6.4260
Cl ₂	6.6824	6.6816	6.6707	7.1463	7.1288
F ₁	7.1588	7.1592	7.1646	7.1907	7.1873
F ₂	7.1588	7.1592	7.1646	6.9947	7.0085
F ₃	7.1588	7.1592	7.1646	7.1227	7.1247
F ₄	7.1588	7.1592	7.1646	7.1227	7.1247
d-orbital densities					
Cl ₁	1.0652	1.0535	1.0615	1.1522	1.1553
Cl ₂	1.0652	1.0535	1.0615	0.6183	0.6001
HOMO energy (a.u.)	-0.5429	-0.5433	-0.5765	-0.4530	-0.4593
LUMO energy (a.u.)	-0.0475	-0.0450	-0.0543	-0.1371	-0.1330
Lowest eigenvalue (a.u.)	-1.8224	-1.8414	-1.7929	-1.9192	-1.9075

unknown. In order to test whether this causes some bonding between the fluorine atoms (F_1, F_3) and (F_2, F_4), the bond angle in each ClF_2 fragment was decreased by 5° (configuration II). This caused a substantial decrease in the electronic energy indicating bonding between the two pairs of fluorine atoms, as a consequence of which one should expect the fluorine atomic densities to increase somewhat due to this bending. This is indeed the case. Clearly, the CNDO/2 method, by virtue of its neglect of a significant number of electron repulsion integrals, tends to concentrate more charge between two neighbouring atoms. Between the configurations I, II and III, all having the same Cl-Cl distance, the last i.e. staggered conformation is the most stable. All these three configurations are more stable than IV and V. Since V has less energy, and thus a greater magnitude in binding energy than IV, we may say that when two ClF_2 molecules approach each other in this manner they do tend to disproportionate into ClF_3 (*T*-shaped) and ClF .

2.4. A disturbing feature

It was observed that in all linear configurations of ClF_2 , with z axis along the internuclear axis, the populations of px and py atomic orbitals are not identical. For example, with bond length = 1.507 \AA , the populations are: $(px)_\text{F} = 1.8856$, $(py)_\text{F} = 1.8626$, $(px)_\text{Cl} = 1.7009$, $(py)_\text{Cl} = 1.4341$. This non-equivalence of the two π orbitals arises from the population-bond-order matrix for β electrons; the matrix for α electrons shows equivalence of px and py . Going further backwards, the elements of the Hartree-Fock energy matrix for β -spin are unequal for px and py orbitals, while the corresponding matrix elements for α -spin are identical. This non-equivalence implies that CNDO/2 calculations on open-shell systems should be regarded with caution.

3. Conclusion

After this work had been communicated for publication, we came across the *ab initio* single-configurational calculations of Ungemach and Schaefer (1976) on ClF_2 , ClF_2^+ , ClF_2^- , ClF_4 , ClF_4^+ and ClF_4^- , employing minimum, double-zeta and, in case of ClF_2 , extended basis sets. We describe here briefly only those of their results which are of immediate interest to us: ClF_2 is unstable relative to the separated atoms. Its ground state prefers a bond angle near 148° and bond length 1.72 \AA . However, their minimum basis set calculations predict the ground state of ClF_2 to be linear with bond length 1.83 \AA . The bond length in ClF_2^+ is calculated to be $\sim 1.7 \text{ \AA}$ in contrast to the observed values of 1.541 and 1.58 \AA . The first excited state of ClF_2 is predicted to be linear.

There is thus a clear conflict between our calculations and the calculations of Ungemach and Schaefer (1976) which seem to agree with the experimental findings of Mamantov *et al* (1971) as far as the bond angle in the ground state of ClF_2 is concerned. However, we feel that in view of the well-known ability of CNDO/2 and INDO methods to correctly predict the bond angles in small molecules (a case in point is the previous highly controversial structure of the CH_2 ground triplet), it would be unwise to dismiss the present CNDO/2 calculations lightly. We would venture to suggest that these conflicting results strongly indicate the necessity for more detailed theoretical and experimental studies on the ClF_2 molecule. Further examination of the CNDO/2 method may also be necessary, especially in view of the non-equivalence of px and py AO's in a linear configuration of ClF_2 .

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