

Study on the Electronic and Molecular Structures of Fluorocyclopropyl Derivatives

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CNDO/2 calculation was carried out on hexafluorocyclopropane, tetrafluorocyclopropene, 1,2-dichlorodifluorocyclopropene and 1-lithio-2-chlorodifluorocyclopropene. A partial geometry optimization was carried out on 1-lithio-2-chlorodifluorocyclopropene.

Introduction

The chemistry of small ring systems has been the focus of scientific interest for a long time and, despite the efforts of experimentalists and theoreticians, many questions still remain unanswered. Widespread interest in the unsaturated character and structural peculiarities of the cyclopropane ring has recently been reawakened by a number of new experimental observations. The system is well suited for theoretical studies because of their small size. Over 30 years ago it was shown by Bastiansen and Hassel¹ that the HCH angle in cyclopropane itself is 118°, a value which was later rationalized by Walsh² on assumption of sp² hybridization at the carbon atoms with the three sp² orbitals directed toward the two hydrogen atoms and the center of the ring. The qualitative characteristics of the Walsh model and other similar proposals^{3,4} have been used with great success in interpreting the conformation of a very large number of cyclopropyl derivatives. More recent interest has centered around changes induced in the cyclopropyl ring by interaction with substituent groups. These effects have been studied for 1,1-difluorocyclopropane, 1,1-dichlorocyclopropane and *etc.*⁵⁻⁸

We here report the results of CNDO/2 calculations about electronic and molecular structure of hexafluorocyclopropane, tetrafluorocyclopropene, 1,2-dichlorodifluorocyclopropene and 1-lithio-2-chlorodifluorocyclopropene. The electronic and molecular structures of these compounds are important since this knowledge can assist in understanding the organic reaction. To gain deeper understanding of the reaction site for these intermediates to obtain their derivatives, the electronic structure of these compounds were discussed and explained qualitatively in terms of inductive and mesomeric effects. The geometry for 1-lithio-2-chlorodifluorocyclopropene was obtained by variational method. The total energy were minimized by searching the optimum geometry. For efficient execution of these search, the Fletcher-Powell method of optimization was employed.

The Calculation Method for the Electronic and Molecular Structure

The calculations were carried out using the computer program CNINDO which has been obtained from QCPE.

The C1-C2, C2-C3 and C1-C3 distances in 1-lithio-2-

chlorodifluorocyclopropene were found by optimizing the energy. For other parameters, we used the standard values⁵⁻⁸. The distances of carbon atoms in 1-lithio-2-chlorodifluorocyclopropene adjust itself to minimize the total energy. To implement geometry optimization for numerical calculation, the above CNINDO program was combined with the Fletcher-Powell optimization method.¹⁰ The algorithm for the geometry optimization method is;

(1) Start from the approximate geometry and compute the total energy.

(2) The path of the steepest descent was found by computing the gradient for small changes in one parameter.

(3) The optimized geometry is searched along this gradient until a minimum is located.

Since these methods are susceptible to the false local minimum, these optimization were carried out from two different starting geometries.

Result and Discussion

Labelling of the atom and gross atomic charges computed are shown in Figure 1.

The molecular structure of hexafluorocyclopropane was based on a recent analysis of electron diffraction data¹¹ C-C=1.505 Å, C-F=1.314 Å, and $\angle FCF=112.2^\circ$. The coordinates of hexafluorocyclopropane as the input data are listed in Table 1.

The effect of fluorine upon the electronic structure has been investigated in some detail by considering the electron population analysis. Tables 2, 3 show the electron population for each atoms. The values for the total electron population clearly demonstrate the fact that the fluorine atoms act as electron acceptors. The electron flow must be of the inductive

TABLE 1: Coordinates of Hexafluorocyclopropane

Atom	X	Y	Z
C1	0.7526	0.0000	0.0000
C2	-0.7526	0.0000	0.0000
C3	0.0000	1.3036	0.0000
F4	1.3873	-0.3664	1.0906
F5	1.3973	-0.3664	-1.0906
F6	-1.3873	-0.3664	1.0906
F7	-1.3873	-0.3664	-1.0906
F8	0.0000	2.0365	1.0906
F9	0.0000	2.0365	-1.0906

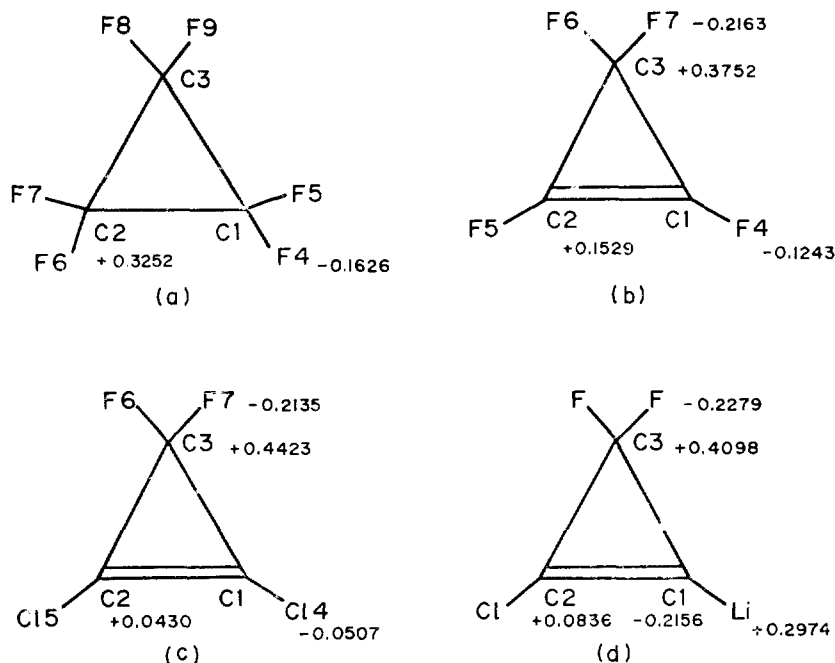


Figure 1. Labelling of the atoms and computed gross atomic charges. (a) Hexafluorocyclopropene, (b) tetrafluorocyclopropene, (c) 1,2-dichlorodifluorocyclopropene, (d) 1-lithio-2-chlorodifluorocyclopropene.

TABLE 2: Electron Population of Hexafluorocyclopropene

C	3.6748	F	7.1626
C2s	0.9271	F2 _s	1.8229
C2p _x	0.7642	F2p _x	1.5698
C2p _y	0.7888	F2p _y	1.7913
C2p _z	1.1947	F2p _z	1.9786

TABLE 3: Electron Population of Tetrafluorocyclopropene

C1	3.8471	F4	7.1243
2s	0.9340	2s	1.7981
2p _x	0.8515	2p _x	1.5289
2p _y	1.0437	2p _y	1.8594
2p _z	1.0178	2p _z	1.9380
C3	3.6248	F6	7.2163
2s	0.8851	2s	1.8276
2p _x	0.7485	2p _x	1.5883
2p _y	0.7685	2p _y	1.8213
2p _z	1.2226	2p _z	1.9791

TABLE 4: Electron Population of 1, 2-Dichlorodifluorocyclopropene

Cl 3.9570	Cl	7.0507	C3 3.5577	F	7.2135
	3s	1.8930		2s	1.8272
	3p _x	1.2042		2p _x	1.5918
	3p _y	1.7974		2p _y	1.8196
	3p _z	1.9559		2p _z	1.9750
	3d _{z²}	0.0203			
	3d _{xx}	0.0413			
	3d _{yz}	0.0095			
	3d _{x²-y²}	0.0652			
	3d _{xy}	0.0638			

type. To a certain extent this might be counter-balanced by donation from the fluorine lone pairs. In order to estimate the possible magnitude of this effect, the contributions to the total populations on the fluorine atoms from the s,p_x,

p_y and p_z orbitals have been calculated. Some insight into the calculated charge alternation may be obtained by breaking down the electron distribution into σ and π parts relative to the C-F bonds. The s, p_x and p_y orbitals contribute σ part and the p_z orbital is π part. The population of 2p_z atomic orbital on carbon and fluorine in hexafluorocyclopropane are

$$\begin{array}{cc} 1.1947 & 1.9786 \\ \text{C} & - \text{F} \end{array}$$

The fact that the fluorine figure is less than 2 implies a "back-donation" effect by the fluorine lone pairs. Although there is a π -system in cyclopropane, vinylic fluorine in cyclopropene is more effective π -electron donor than the fluorine in cyclopropane.

Table 4 shows the electron population of 1,2-dichlorodifluorocyclopropene. For 1,2-dichlorodifluorocyclopropene, total charge on chlorine is practically negligible. In order to investigate the populations of the

orbitals, a splitting of the total charge into its different spatial directions was performed. The inclusion of d orbitals is seen to have a rather large effect on the chlorine charge as 0.20 electron populate the d orbitals.

For 1-lithio-2-chlorodifluorocyclopropene, the electron flow is much larger. As expected, lithium is a powerful electron donor. Inspections of the orbital populations reveal that the Li p_z orbital (perpendicular to the ring) is populated by 0.1 electrons. (see Table 5). This is an indication that there is a two-way flow of electrons in this system. The two features responsible for this are the highly electropositive character of lithium and vacant p orbitals on lithium as contrasted to lone pairs in fluorocompounds. This result makes clear the necessity of providing p orbitals in the basis set for lithium in calculations of this sort.

Hoffmann has predicted¹² that electrons should be drawn from the highest occupied ring orbital into substituents capable of acting as π -electron acceptors, leading to a shortening of the C-C bond opposite the substituent and to a lengthening of the adjacent bond. If the substituent is

TABLE 5: Electron Population of 1-Lithio-2-chlorodifluorocyclopropene

Cl 4.2156	Li	0.7026	C2 3.9164	Cl	7.1195
	2s	0.2385		3s	1.8919
	2p _x	0.2313		3p _x	1.2741
	2p _y	0.1316		3p _y	1.7915
	2p _z	0.1012		3p _z	1.9606
				3d _{z²}	0.0196
C3 3.5902	F	7.2279		3d _{xx}	0.0402
	2s	1.8261		3d _{yz}	0.0101
	2p _x	1.6025		3d _{x²-y²}	0.0684
	2p _y	1.8214		3d _{xy}	0.0632
	2p _z	1.9779			

TABLE 6: Optimized Ring Distances of 1-Lithio-2-chlorodifluoro-Cyclopropene

C1-C2	1.29 Å
C1-C3	1.54
C2-C3	1.45

a π -electron donor, he suggested that electron density should be fed into the lowest unoccupied molecular orbital of the ring and showed that this should lead to lengthening of all of the ring C-C bonds. As is seen Table 6, rather dramatic changes occur in the ring distances when one of chlorine atom is replaced by lithium. In 1-lithio-2-chlorodifluorocyclopropene, lithium is a π -electron acceptor, and the removal of electrons from the ring causes a lengthening of the bond adjacent to lithium and shortening of opposite bond. As a result of these considerations, it was concluded that the computed geometries were in accord with the rationalization of Hoffmann's suggestion.

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References

- (1) O. Bastiansen and O. Hassel, *Tids. Kjemi, Bergves, Metall.*, **6**, 71 (1946).
- (2) D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).
- (3) Coulson, C. A., and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).
- (4) L. L. Ingrahm, "Steric Effects in Organic Chemistry", (Editor, Newman, M. S.), p. 479, John Wiley and Sons, Inc., New York, 1956.
- (5) A. Skancke, E. Flood and J. E. Boggs, *J. Mol. Struct.*, **42**, 235 (1977).
- (6) A. Skancke, E. Flood and J. E. Boggs, *J. Mol. Struct.*, **40**, 263 (1977).
- (7) A. Skancke, J. E. Boggs, *J. Mol. Struct.*, **50**, 173 (1978).
- (8) A. Skancke, *J. Mol. Struct.*, **30**, 95 (1976).
- (9) Card copies of this program has been obtained from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind. 47401.
- (10) J. Kuester and J. Mija, "Optimization Techniques with Fortran", p. 355, McGraw Hill, 1973.
- (11) J. F. Chiang and W. A. Bennett, *Tetrahedron*, **27**, 975 (1971).
- (12) R. Hoffmann, *Tetrahedron Lett.*, **33**, 2907 (1970).

Calculation of the Dipole Moments for Transition Metal Complexes

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A new approach in calculating the dipole moments for transition metal complexes has been proposed and the calculated results are tabulated with the experimental values. The calculated dipole moments are applied to the theoretical prediction or confirmation of the geometric structure for the transition metal complexes.

1. Introduction

For a few decades, a great deal of interest has been focussed on the measurement of the dipole moments of transition metal complexes in inert solvent solutions.¹ On the basis of the measured dipole moments, their geometric structures in liquid solutions have been predicted.

Only a few theoretical calculations of the dipole moments for transition metal complexes² have been performed, adopting the vector model of Wilcox and Gilmann³ and a semiempirical method.⁴

A model for theoretical calculation of the dipole moments for transition metal complexes is developed in this work and the calculated results are listed with the experimental values. The calculated dipole moments were applied to the theoretical prediction or confirmation of

the geometri structure for the transition metal complexes involved in the dipole moments calculation.

The required dipole moment matrix elements and overlap integrals were evaluated using the general translation method⁵.

2. The Theoretical Model For Calculation of the Dipole Moments for Transition Metal Complexes

Since the octahedral, tetrahedral and square planar complexes which are formed by bonding with n equal ligands belong to O_h , T_d and D_{4h} point groups ($n=6$ or 4), they should not have permanent dipole moments.⁶ When three or two ligands in octahedral and tetrahedral or square planar complexes are replaced to form cis complexes by the ligands of different nature, their group theoretical nature is also changed, and these complexes belong to one