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# Structural Properties, Theory Functional Calculations (DFT), Natural Bond Orbital and Energies for the Two fluorocarbon compounds\*

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**Abstract:** B3LYP/6-311 calculation results indicated that some selected bond length and bond angles values for the C<sub>2</sub>Cl<sub>3</sub>H and C<sub>2</sub>Cl<sub>3</sub>F. In this paper, the optimized geometries and frequencies of the stationary point and the minimum-energy paths of two new compounds with C<sub>2</sub>Cl<sub>3</sub>H and C<sub>2</sub>Cl<sub>3</sub>F chemical formula are calculated by using the DFT methods with 6-311 basis set. The detail group points of two compounds are C<sub>1</sub>.

**Keywords:** Electronic structure, Fluorocarbon compounds, DFT Calculations, Vibrational analysis, B3LYP level.

## Introduction

Fluoroalkanes can serve as oil-repellent/water-repellent fluoropolymers, solvents, liquid breathing research agents, and powerful greenhouse gases. Fluorocarbon liquids are colorless. They have high density, up to over twice that of water, due to their high molecular weight. Low intermolecular forces give the liquids low viscosities when compared to liquids of similar boiling points. Fluorocarbons, sometimes referred to as semi perfluorocarbons, are organofluorine compounds that contain only carbon and fluorine bonded together in strong carbon-fluorine bonds. Fluoroalkanes that contain only single bonds are more chemically and thermally stable than alkanes. However, fluorocarbons with double bonds (fluoroalkenes) and especially triple bonds (fluoroalkynes) are more reactive than their corresponding hydrocarbons. However, other fluorocarbon based molecules that are not technically fluorocarbons are commonly referred to as fluorocarbons, because of similar structures and identical properties.

Also, low surface tension, heats of vaporization, and refractive indices are notable. They are not miscible with most organic solvents (e.g., ethanol, acetone, ethyl acetate and chloroform), but are miscible with some hydrocarbons (e.g., hexane in some cases). They have very low solubility in water, and water has a very low solubility in them (on the order of 10 ppm). The number of carbon atoms in a fluorocarbon molecule largely determines most physical properties. The greater the number of carbon atoms, the higher the boiling point, density, viscosity, surface tension, critical properties, vapor pressure and refractive index. Gas solubility decreases as carbon atoms increase, while melting point is determined by other factors as well and is thus not readily predicted [1-6].

Fluorocarbons with only single bonds are very stable because of the strength and nature of the carbon-fluorine bond. It is called the strongest bond in organic chemistry. Its strength is a result of the electronegativity of fluorine imparting partial ionic character through partial charges on the carbon and fluorine atoms. The partial charges shorten and strengthen the bond through favorable coulombic interactions. Additionally, multiple carbon-fluorine bonds increase the strength and stability of other nearby carbon-fluorine bonds on the same geminal carbon, as the carbon has a higher positive partial charge. Furthermore, multiple carbon-fluorine bonds also strengthen the "skeletal" carbon-carbon bonds from the inductive effect. Therefore, saturated fluorocarbons are more chemically and thermally stable than their corresponding hydrocarbon counterparts. However, fluoroalkanes are not inert. They are susceptible to reduction through the Birch reduction.

In continuation of our interest to fluorine chemistry, we investigated the structures and properties of the  $C_2Cl_3H$  and  $C_2Cl_3F$  fluorocompounds.[6-13] The structure of the compound has been optimized by using the DFT (B3LYP) method with the 6-311 basis sets, using the Gaussian 09w program. Density functional theory methods were employed to determine the optimized structures of  $C_2Cl_3H$  and  $C_2Cl_3F$ . Initial calculations were performed at the DFT level and split – valence plus polarization 6-311 basis sets were used. Local minima were obtained by full geometrical optimization have all positive frequencies.

## Experimental

### Chemicals and reagents

The optimized structural parameters were used in the vibrational frequency calculations at the DFT level to characterize all stationary points as minima. All computational are carried out using Gaussian 09w program. Harmonic vibrational frequencies ( $\nu$ ) in  $cm^{-1}$  and infrared intensities (int) in Kilometer per mole of all compounds were performed at the same level on the respective fully optimized geometries. Energy minimum molecular geometries were located by minimizing energy, with respect to all geometrical coordinates without imposing any symmetrical constraints.

### NBO (Natural Bond Orbital) study on structures

NBO Calculated Hybridizations are significant parameters for our investigation. The structure of the compound has been optimized by using the DFT (B3LYP) method with the 6-311basis sets, using the Gaussian 09w program. Density functional theory methods were employed to determine the optimized structures of  $C_2Cl_3H$  and  $C_2Cl_3F$ (Table 1, Figure 1).

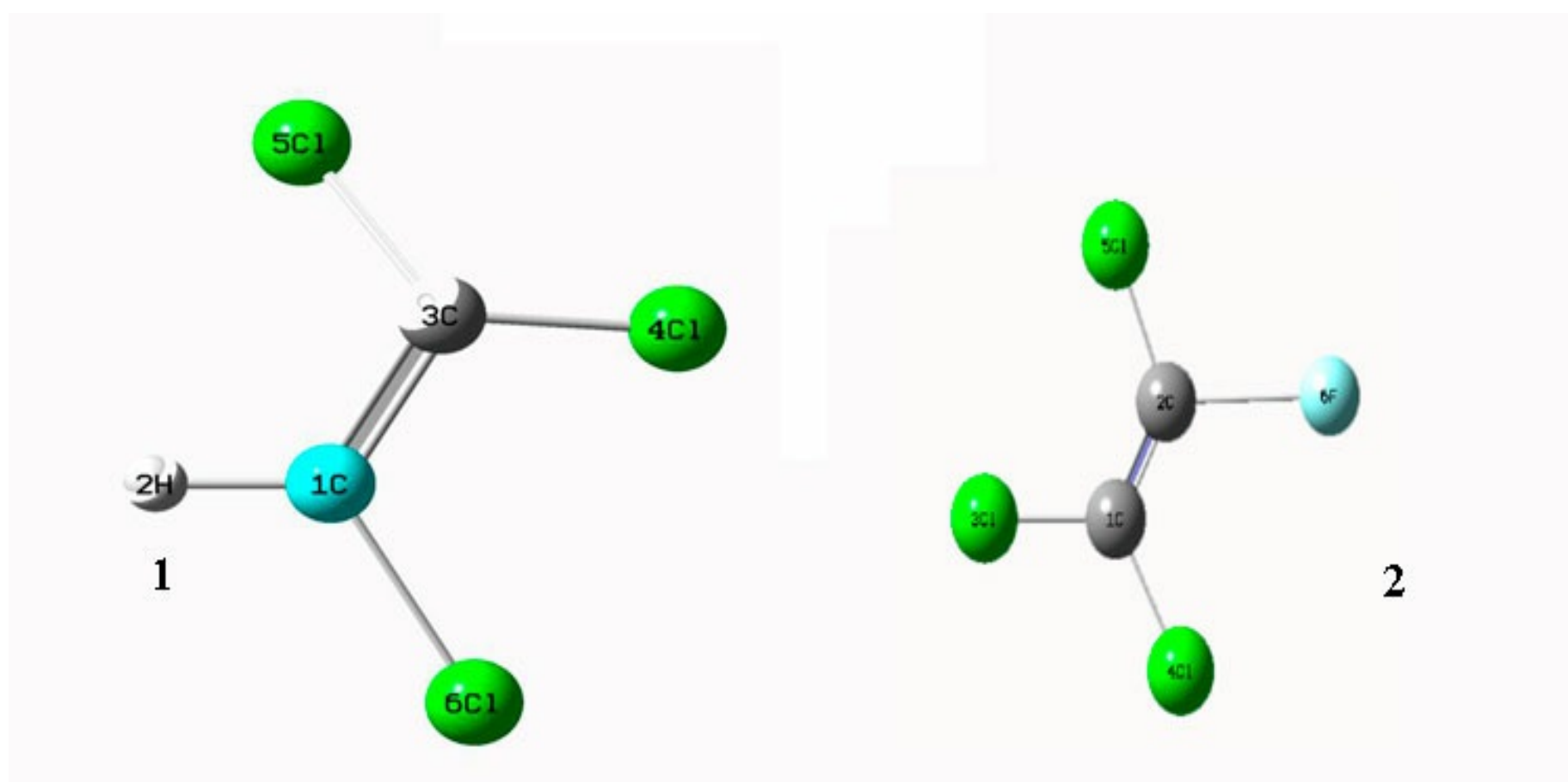


Figure 1. Optimized geometries of (1) $C_2Cl_3H$ , (2)  $C_2Cl_3F$  at B3LYP/6-311level of theory.

Table 1. Geometrical parameters optimized for (1) $C_2Cl_3H$ , (2) $C_2Cl_3F$  some selected bond lengths (Å) and angles (°).

B3LYP/6-311		Method	
(1)C <sub>2</sub> Cl <sub>3</sub> H		(2) C <sub>2</sub> Cl <sub>3</sub> F	
Bond lengths (Å)		Bond lengths (Å)	
C <sub>1</sub> -H	1.07	C <sub>1</sub> -C <sub>2</sub>	1.3552
C <sub>1</sub> -C <sub>2</sub>	1.3552	C <sub>1</sub> -Cl <sub>3</sub>	1.76
C <sub>1</sub> -Cl <sub>6</sub>	1.76	C <sub>1</sub> -Cl <sub>4</sub>	1.76
C <sub>2</sub> -Cl <sub>4</sub>	1.467	C <sub>2</sub> -Cl <sub>5</sub>	1.76
C <sub>2</sub> -Cl <sub>5</sub>	1.5841	C <sub>2</sub> -F <sub>6</sub>	1.35
Bond angles (°)		Bond angles (°)	
H-C <sub>1</sub> -C <sub>2</sub>	119.8865	C <sub>2</sub> -C <sub>1</sub> -Cl <sub>3</sub>	119.8865
H-C <sub>1</sub> -Cl <sub>6</sub>	119.8865	C <sub>2</sub> -C <sub>1</sub> -Cl <sub>4</sub>	120.2269
C <sub>2</sub> -C <sub>1</sub> -Cl <sub>6</sub>	120.2269	Cl <sub>3</sub> -C <sub>1</sub> -Cl <sub>4</sub>	119.8865
C <sub>1</sub> -C <sub>2</sub> -Cl <sub>4</sub>	115.6142	C <sub>1</sub> -C <sub>2</sub> -F <sub>6</sub>	122.0279

Natural Bond Orbital's (NBOs) are localized few-center orbital's that describe the Lewis-like molecular bonding pattern of electron pairs in optimally compact form. More precisely, NBOs are an orthonormal set of localized "maximum occupancy" orbital's whose leading N/2 members (or N members in the open-shell case) give the most accurate possible Lewis-like description of the total N-electron density. This analysis is carried out by examining all possible interactions between "filled" (donor) Lewis-type NBOs and "empty" (acceptor) non-Lewis NBOs, and estimating their energetic importance by 2nd-order perturbation theory. Since these interactions lead to donation of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals (and thus, to departures from the idealized Lewis structure description), they are referred to as "delocalization" corrections to the zeroth-order natural Lewis structure.

Natural charges have been computed using natural bond orbital (NBO) module implemented in Gaussian 09w. The. These quantities are derived from the NBO population analysis. The former provides an orbital picture that is closer to the classical Lewis structure. The NBO analysis involving hybridizations of selected bonds are calculated at B3LYP methods and 6-311 level of theory (Tables 2, 3).

Table2. The NBO Calculated Hybridizations for (1)C<sub>2</sub>Cl<sub>3</sub>H, (2) C<sub>2</sub>Cl<sub>3</sub>Fat the B3LYP/6-311.

(1) C <sub>2</sub> Cl <sub>3</sub> H			(2) C <sub>2</sub> Cl <sub>3</sub> F		
Bond	Atom	B3LYP	Bond	Atom	B3LYP
C-C	C <sub>1</sub> -C <sub>2</sub>	S <sup>1</sup> P <sup>1.23</sup>	C-C	C <sub>1</sub> -C <sub>2</sub>	S <sup>1</sup> P <sup>1.22</sup>
C-C	C <sub>1</sub> -C <sub>2</sub>	S <sup>1</sup> P <sup>1</sup>	C-C	C <sub>1</sub> -C <sub>2</sub>	S <sup>1</sup> P <sup>1</sup>
C-Cl	C <sub>1</sub> -Cl <sub>3</sub>	S <sup>1</sup> P <sup>2.65</sup>	C-Cl	C <sub>1</sub> -Cl <sub>3</sub>	S <sup>1</sup> P <sup>2.67</sup>
C-Cl	C <sub>1</sub> -Cl <sub>4</sub>	S <sup>1</sup> P <sup>2.57</sup>	C-Cl	C <sub>1</sub> -Cl <sub>4</sub>	S <sup>1</sup> P <sup>2.60</sup>

Table 3 Second order perturbation theory analysis of Fock matrix in NBO basis for (1)C<sub>2</sub>Cl<sub>3</sub>H, (2) C<sub>2</sub>Cl<sub>3</sub>F E(2)a means energy of hyper conjugative interaction (stabilization energy); b Energy difference between donor and acceptor i and j NBO orbital's; c F(i, j) is the Fock matrix element between i and j NBO orbital's.

Donor (i)	Typ e	ED/e	Acceptor (j)	Type	ED/e	E(2) <sup>a</sup> (KJ/mol)	E(j)-E(i) <sup>b</sup> (a.u)	F(i,j) <sup>c</sup> (a.u)
C <sub>2</sub> Cl <sub>3</sub> H (1)								
C <sub>1</sub> C <sub>2</sub>	σ	1.98887	C <sub>1</sub> Cl <sub>5</sub>	σ*	1.98983	0.59	1.21	0.024
C <sub>1</sub> C <sub>2</sub>	σ	1.99119	C <sub>2</sub> Cl <sub>4</sub>	σ*	1.99117	0.75	0.86	0.023
C <sub>1</sub> C <sub>2</sub>	σ	1.92956	C <sub>2</sub> Cl <sub>5</sub>	σ*	1.99768	1.10	1.13	0.032
C <sub>1</sub> Cl <sub>3</sub>	σ	1.79180	C <sub>1</sub> F <sub>6</sub>	σ*	1.98887	1.07	1.75	0.039
C <sub>2</sub> Cl <sub>3</sub> F (2)								
C <sub>1</sub> H	σ	1.97964	C <sub>1</sub> C <sub>2</sub>	σ*	1.98076	2.39	1.12	0.046
C <sub>1</sub> H	σ	1.99181	C <sub>2</sub> Cl <sub>4</sub>	σ*	1.99092	10.49	0.62	0.073
C <sub>1</sub> C <sub>2</sub>	σ	1.93516	C <sub>1</sub> H	σ*	1.97964	1.99	1.27	0.045
C <sub>2</sub> Cl <sub>5</sub>	σ	1.72110	C <sub>1</sub> C <sub>2</sub>	σ*	1.98076	0.75	1.31	0.028

These data shows the hyper conjugation of electrons between ligand atoms with central metal atom. These conjugations stand on the base of p-d π-bonding. The NBO calculated hybridization for C<sub>2</sub>Cl<sub>3</sub>H and C<sub>2</sub>Cl<sub>3</sub>F shows that all of compounds have SP<sup>X</sup> hybridization and non planar configurations. The total hybridization of these molecules are SP<sup>X</sup> that confirmed by structural. The amount of bond hybridization showed the in equality between central atoms angles (Table 2) shown distortion from normal VSEPR structures and confirmed deviation from VSEPR structures. (Figure 2).

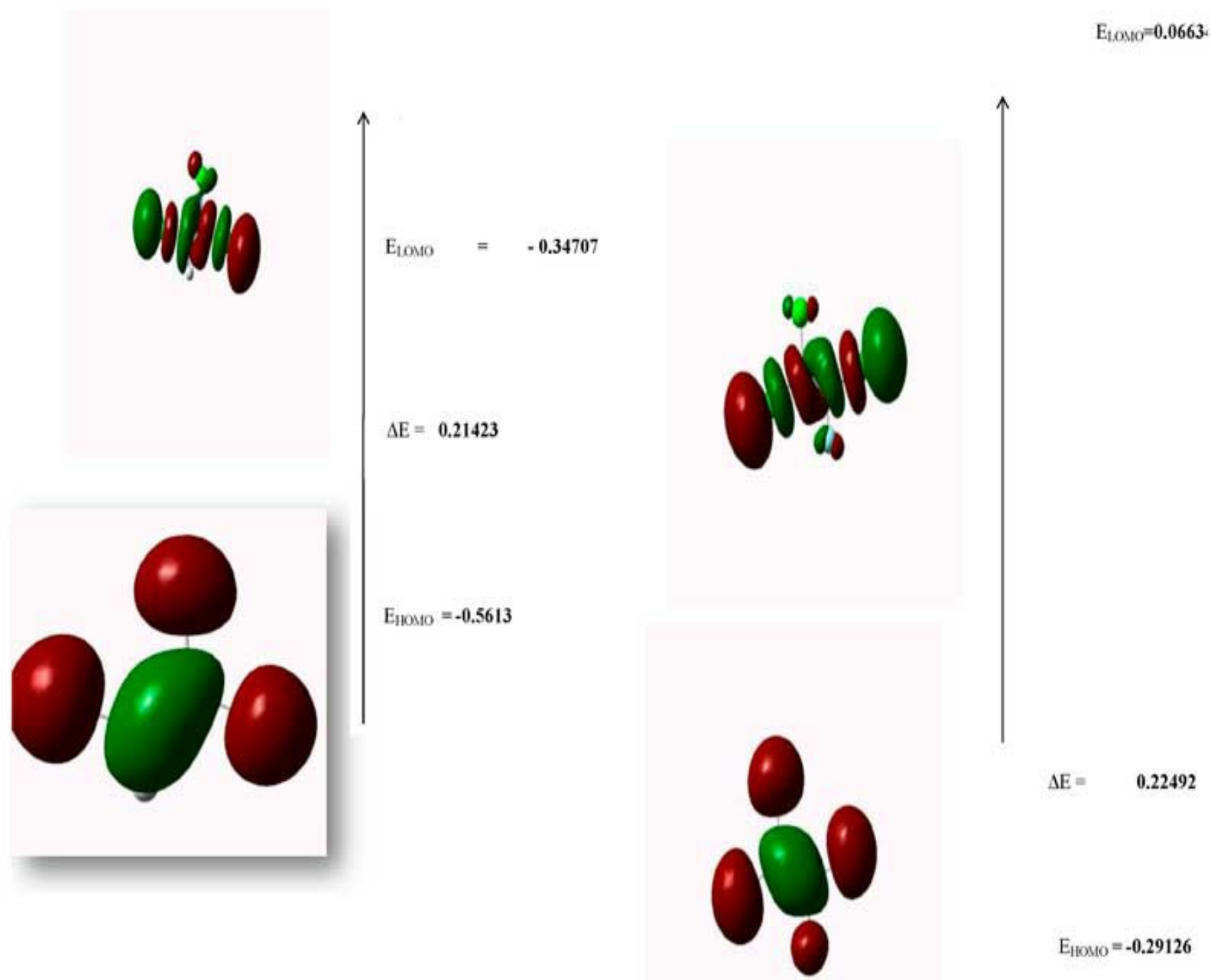


Figure2. The atomic orbital of the frontier molecular orbital for (1) $C_2Cl_3H$ , (2)  $C_2Cl_3F$  at B3LYP/6-311 level of theory

Some thermodynamic parameters Frequencies for (1) $C_2Cl_3H$ , (2) $C_2Cl_3F$  Zero-point Energy, correction Energy, Enthalpy lengths, Gibbs free Energy are calculated and confirmed with other published theoretical data ( Table 4).

Table 4. Some thermodynamic parameters Frequencies for (1) $C_2Cl_3H$ , (2)  $C_2Cl_3F$  Zero-point Energy, correction Energy, Enthalpy lengths, Gibbs free Energy.

	(1)	(2)
$C_2Cl_3HC_2Cl_3F$		
Zero – point correlation	0.015779 (Hartree/particle)	0.012115 (Hartree/particle)
Thermal correction to Energy		0.021407 0.018842
Thermal correction to Enthalpy	0.022351 0.019787	
Thermal correction to Gibbs free Energy	0.015199	0.020598

#### Frontier molecular orbital

The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO energy were calculated by B3LYP/6-311 method. This electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbitals that take part in chemical stability. Therefore, while the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability factor for structures. In addition, 3D plots of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are shown in Figure 2. The HOMO–LUMO energies were also calculated at the 6-311 level and the values are listed in Figure 2, respectively.

#### Conclusion

In this research we are interested and studied on two fluorocarbon compounds were chosen for theoretical studies. The optimized geometries and frequencies of the stationary point and the minimum-energy paths are calculated by using the DFT (B3LYP) methods with 6-311 basis sets. B3LYP/6-311 calculation results indicated that some selected bond length and bond angles values for the  $C_2Cl_3H$  and  $C_2Cl_3F$ . The group point of compounds 1-2 are  $C_1$ .

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\*retained original spelling

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