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Original Research Article

Theoretical Study of M_2X_4 ($M=C$, $X=H$, F and Cl)

Structures by using HOMO, LUMO, NBO and NMR analysis

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ABSTRACT

All calculations were performed within the MP2 / 6-311 G (d, p) method to evaluate the effects of substituent groups which affect the structural stability and molecular energy. A natural bond orbital (NBO) analysis and isotopic, and anisotropic NMR chemistry, were used also for a better understanding of the C_2X_4 electronic structure and its derivatives. The NBO analysis shows that the occupancy of lone pair electrons of halogen atoms in all compounds decreases with increasing p character of the lone pair of halogen atoms. Furthermore, NBO analysis demonstrated the effects of donates substituent groups including (CH₃, NH₂, and OH) that donates some of its electron density into a π system via resonance or inductive effects, thus making the π system more nucleophilic on electron density. The obtained values from NMR tensors parameters shows electronegativity in excellent agreement with the expected chemical shielding values. Therefore, we suggest that is correlations between donates substituent groups with electronegativity along with the total stability energy of the studied molecules. The energies gap of frontier molecular orbital ($\epsilon_{LUMO} - \epsilon_{HOMO}$) is recorded in order to find the suitability correlation between this energy with chemical hardness (η) of the studied molecules.

Keywords: MP2 method, NBO analysis, NMR shielding, HOMO-LUMO

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Introduction

In recent years there has been a great deal of attention paid to the geometric difference between two-dimensional C = C compounds [1, 2]. The simplest C=C compound is ethylene with a formula C₂H₄ that contains four hydrogen atoms bound to a double bond. It is an unsaturated hydrocarbon and also it is a colorless and highly flammable gas. Ethylene can have many different reactions, such as halogen, oxidation, polymerization, and hydration [3]. In these study halogens (fluorine (F), chlorine (Cl)), replacing all H atoms in an ethylene that they are called tetra haloethylene compounds. Tetra flour ethylene (TFE) is a chemical compound with the formula C₂F₄ and this belongs to the fluorocarbon family. In general, tetrafluoroethylene is used to synthesize polytetrafluoroethylene resins, in the synthesis of copolymers as a monomer. When heated to decomposition, tetrafluoroethylene releases a highly toxic fluorocarbon phosphate. The main route of exposure is inhalation. Exposure to activated inhalation with tetrafluoroethylene may cause respiratory inflammation and fluid formation in the lungs (pulmonary edema) [4]. Tetrachloroethylene (also known as PCE, PERC, perchloroethylene or tetrachloroethene, receptivity) is a man-made chemical that is widely used. PERC is a colorless, volatile, non-flammable liquid, carbon dioxide with an ether-like odor that may be exposed to sunlight or toxic flames from phosgene. Tetrachlorethylene is mainly used as a clean solvent in dry cleaning and textile processing and in the production of fluorocarbons. Exposure to this substance stimulates the upper respiratory tract and the eye and causes neurological complications as well as damage to the kidneys and the liver. Tetrachlorethylene is predicted to be a human carcinogen and may be associated with an increased risk of skin, colon, lung, esophagus and urinary tract infections, as well as lymphoma and leukemia [5]. Understanding the halo-ethylene spectroscopy is important for many reasons, including the fact that a number of haloethylenes are toxic pollutants. To this end, many studies have been done in the past, especially experimental studies aimed at understanding the structure of electrons on haloethylenes. Even then, studies of ultraviolet radiation on the ethylene absorption spectrum and its halogen derivatives have long been considered with a large number of transitions, which have not yet been covered by ambiguous transfers due to some fundamental transitions. Therefore, it is best to study these pollutants using modeling structures in chemical calculations [6]. In this work, a comparative study carried out on the structural properties and reactivity of the molecules

(M_2X_4 , $M=C$, $X=H$, F , Cl) using chemical calculation. Also, investigated electron donating substituents effect such as CH_3 , NH_2 and OH on the structural properties and reactivity of the molecules. Is following, the basic study is to analyze the effects of substituents on the structural stability of natural bond orbital (NBO) analysis and Nuclear magnetic resonance (NMR) parameters.

Computational methods

Møller–Plesset calculations are standard levels used in calculating small systems and are implemented in many computational chemistry codes. Systematic studies of MP perturbation theory have shown that it is not necessarily a convergent theory at high orders. Convergence can be slow, rapid, oscillatory, regular, highly erratic or simply non-existent, depending on the precise chemical system or basis set. The density matrix for the first-order and higher MP2 wave function is of the type known as response density, which differs from the more usual expectation value density. The eigenvalues of the response density matrix (which are the occupation numbers of the MP2 natural orbitals) can therefore be greater than 2 or negative. Unphysical numbers are a sign of a divergent perturbation expansion. For open shell molecules, MP_n -theory can directly be applied only to unrestricted Hartree–Fock reference functions (since UHF states are not in general eigenvectors of the Fock operator). However, the resulting energies often suffer from severe spin contamination, leading to large errors. A possible better alternative is to use one of the MP2-like methods based on restricted open-shell Hartree–Fock (ROHF). Unfortunately, there are many ROHF based MP2-like methods because of arbitrariness in the ROHF wave function

Quantum-chemical calculations were carried out with the Gaussian 09 [7] package of the program. All structures were fully optimized at the Møller-Plesset-type theory (MP2) couple-cluster method using 6-311++g (d, p) basis set (show that [Figure.1](#)). The calculated partial atomic charges are achieved theoretically employing the Mulliken approximation (Mulliken, 1955). Also, the change of charge values of filled and the vacant orbitals of NBO analysis describe various second - order interactions which represent the electron transfer. NBO helps to extract natural hybrids (NHOs) and occupancy of the bonding and non-covalent (lone pair) orbitals. The energy contribution of these changes was initially estimated from the second-order mobility approach [8]. The NBO analysis interpretation is an appropriate and detailed theory that

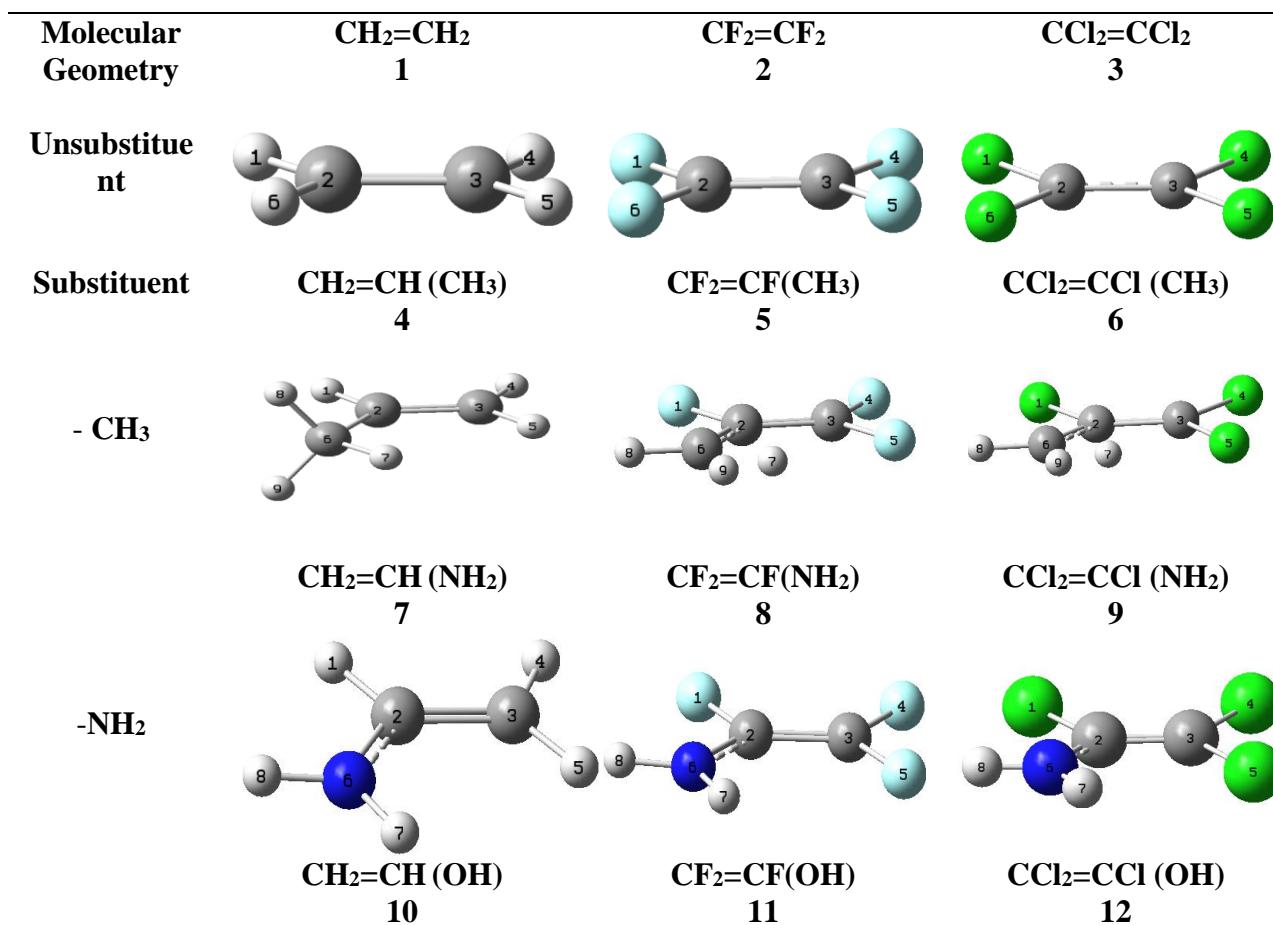
examines quantitatively the effects of hyperconjugation interactions and steric effects on the dynamic behavior of chemical reactions and chemical substances [9]. NMR calculations were done using an optimized structure with the same level of theory by using gauge invariant atomic orbital (GIAO) [10] method for the nuclear magnetic shielding. The values of isotropic chemical shielding (σ_{iso}), anisotropic shielding (Δ_{iso}) and asymmetric shielding (η) were calculated by the following formulas, respectively.

$$\sigma_{iso} = \frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (1)$$

$$\Delta\sigma = \sigma_{33} - \frac{(\sigma_{11} + \sigma_{22})}{2} \quad (2)$$

$$\eta = \frac{|\sigma_{22} - \sigma_{11}|}{|\sigma_{33} - \sigma_{iso}|} \quad (3)$$

Quantum chemical analyses for considering molecules have been used of the frontier orbital (HOMO and LUMO), hardness and electronegativity for contributing us understand the character of molecules.



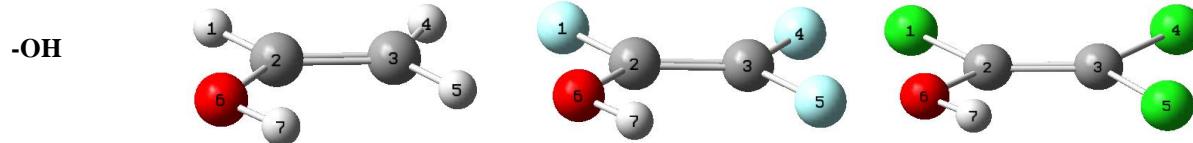


Figure 1. Optimized structures of the molecules (C_2X_4 and C_2X_3Y , X=H, F, and Cl, Y= CH₃, NH₂, and OH)).

Results and Discussion

Molecular geometry

Halogens, CH₃, NH₂ and OH have substituted ethylene with the same performance and the minimum global energy M₂X₄, M = C, X = H, F, Cl is calculated by optimizing the structure 153.428, -474. 638 and -1914.561 Hartree respectively (see Table 1). Structural parameters calculated from compounds such as length (Å), bond angles (°) and dentures (°) are presented in Table 2. According to Table 3, the type of substitution along the length of the bond is indicated that the change in the bond length in C₂Cl₄ is longer than the structure of C₂H₄ and C₂F₄. Based on the interatomic distance and change of the length bonds are over stable the C₂Cl₄ from other molecules. The length of the C-H bond in the structure of C₂H₄ is shorter than other compounds because of that the angle of bonding is less than other compounds and the stress at the θ_{H-C-C} angle is not significant. Subsequently, the replacement in CH₃, NH₂, and OH substitutes indicates that the bond length in C₂H₃CH₃ is longer than C₂H₃NH₂ and C₂H₃OH. Also, the severe effect on the stress angle in C₂H₃CH₃ is more than other compounds.

Table 1: The global minimum energy of the molecules C_2X_4 (X=H, F, and Cl) and C_2X_3Y (X=H, F, and Cl, Y=CH₃, NH₂ and OH) at MP2/6-311++g**

Energy System	Unsubstituent	Substituent		
		CH ₃	NH ₂	OH
CH ₂ =CH ₂	-153.428	-117.466	-133.509	-153.399
CF ₂ =CF ₂	-474. 638	-414.517	-430.748	-450.642
CCl ₂ =CCl ₂	-1914.561	-1494.482	-1510.702	-1530.595

Table 2: The calculated structural parameters of compounds M_2X_4 ($X=H, F$, and Cl) at MP2/6-311++G**.

Compound	H	F	Cl
Bond lengths (Å)			
r_{C-C}	1.339	1.329	1.354
r_{C-X}	1.085	1.318	1.714
Bond angles (°)			
θ_{X-C-C}	121.4	123.2	122.2
θ_{X-C-X}	117.2	113.6	115.7
Torsion Angles (°)			
$\theta_{X-C-C-X}$	0.0	0.0	0.0

Table 3: The calculated structural parameters of compounds M_2X_4 ($X=H, F$, and Cl) and the effect of substitution on the bond lengths (Å) and Bond angles (°).

Compound	bond lengths (Å)	C_2H_4	C_2F_4	C_2Cl_4
Unsubstituted	$r_{1,2}$	1.085	1.318	1.714
	$r_{2,3}$	1.339	1.329	1.354
	$r_{3,4}$	1.085	1.318	1.714
	$r_{2,6}$	1.085	1.318	1.714
	$r_{3,5}$	1.085	1.318	1.714
	bond lengths (Å)	$C_2H_3 CH_3$	$C_2F_3 CH_3$	$C_2Cl_3 CH_3$
	$r_{1,2}$	1.089	1.344	1.723
	$r_{2,3}$	1.341	1.338	1.365
	$r_{3,4}$	1.085	1.321	1.709
	$r_{3,5}$	1.086	1.352	1.743
CH_3	$r_{2,6}$	1.501	1.438	1.423
	$r_{6,7}$	1.093	1.187	1.125
	$r_{6,8}$	1.095	1.076	1.167
	$r_{6,9}$	1.095	1.172	1.078
	bond lengths (Å)	$C_2H_3 NH_2$	$C_2F_3 NH_2$	$C_2Cl_3 NH_2$
	$r_{1,2}$	1.087	1.340	1.723
	$r_{2,3}$	1.347	1.338	1.353
	$r_{3,4}$	1.081	1.324	1.714
	$r_{3,5}$	1.085	1.335	1.372
NH_2	$r_{2,6}$	1.378	1.374	1.403
	$r_{6,7}$	1.00	1.00	1.00
	$r_{6,8}$	1.00	1.00	1.00
	bond lengths (Å)	$C_2H_3 OH$	$C_2F_3 OH$	$C_2Cl_3 OH$

	r 1,2	1.085	1.324	1.707
	r 2,3	1.340	1.331	1.351
OH	r 3,4	1.082	1.319	1.710
	r 3,5	1.086	1.335	1.730
	r 2,6	1.363	1.345	1.350
	r 6,7	0.9635	0.9644	0.9675
	Bond angles (°)	C₂H₄	C₂F₄	C₂Cl₄
	θ1-2-3	121.4	123.2	122.2
	θ2-3-4	121.4	123.2	122.2
Unsubstituted	θ3-4-5	31.4	33.2	32.2
	Bond angles (°)	C₂H₃ CH₃	C₂F₃ CH₃	C₂Cl₃ CH₃
	θ1-2-3	118.8	118.9	119.8
CH ₃	θ2-3-4	121.3	128.3	127.7
	θ3-4-5	31.7	33.8	31.7
	θ1-2-6	116.8	113.4	114.9
	Bond angles (°)	C₂H₃ NH₂	C₂F₃NH₂	C₂Cl₃ NH₂
	θ1-2-3	120.1	119.6	121.3
	θ2-3-4	119.7	125.3	124.2
NH ₂	θ3-4-5	30.8	33.6	31.9
	θ1-2-6	113.7	113.4	114.0
	Bond angles (°)	C₂H₃ OH	C₂F₃OH	C₂Cl₃ OH
	θ1-2-3	122.7	121.0	123.0
OH	θ2-3-4	119.4	121.5	124.2
	θ3-4-5	30.8	33.5	31.7
	θ1-2-6	110.8	111.8	112.1

NBO analysis

The NBO analysis [10] analysis plays a crucial role in the representation of interactions between the electron donors and acceptor orbitals, i.e. delocalization of the electron from filled to empty spaces. This displacement of electrons in the empty spaces can be defined as the "electron transfer process". The effect of delocalization interactions is included changes in energy, geometry, natural atomic charge, occupancy values, mulliken atomic charges and other properties. [11]. As well as, The NBO investigations of the charge transfer or conjugative interactions molecular systems and studying intra- and intermolecular bonding and interaction between bonds [12]. These interactions or energetic stabilizations are referred to as "delocalization" corrections to the zeroth-order natural Lewis structure. The stabilization energy (E2) associated with $i \rightarrow j$ delocalization can be estimated by second-order perturbation theory

$$E_2 = q_i(F_{ij}^2) / (\varepsilon_i - \varepsilon_j)$$

According to the following equation:

Where q_i is the donor orbital occupancy, ε_i and ε_j are diagonal elements (orbital energies) and F_{ij} is the off-diagonal NBO Fock matrix elements [13]. The stabilization energy (E_2) corresponds to the $S^2 / \Delta E$, where S is the orbital overlap, and ΔE is the energy difference between the donor and acceptor orbitals [14]. In principle, each of these parameters can be used to compare these interactions. NBO analysis results show distribution mulliken atomic charges on the carbon atoms C_2H_4 , C_2F_4 and C_2Cl_4 structures are: -0.225877, 0.301096, and -0.824824, respectively. (See Table 4). This result is consistent with energy changes and hyperconjugative interactions because of the C-Cl bonds are better donors than other bonds in these molecules (See Table 5). The result obtained of NBO analysis is consistent with energy changes and hyperconjugative interactions because of the Sigma (σ) bonds of C-Cl have the largest interaction energy values in compared with other compounds bonds. So it can found that these bonds are better donors than other bonds in these molecules.

The analysis shows that C - H bond length in the optimized C_2H_4 structure is shorter than C_2F_4 , C_2Cl_4 because it has a positive natural charge on the H atom of the C_2H_4 molecule in comparing with C_2F_4 and C_2Cl_4 structures. The relative of formed C-X ($X=H$, F, and Cl) bonds with can be illustrated as $SP^{0.02}$, $SP^{2.54}$ and $SP^{4.66}$ respectively. We observed that with increasing p character of the lone pair of existence C_2F_4 and C_2Cl_4 structures the occupancy decreases. The main natural bond orbitals (NBO) analysis showed that total stabilization energy for $LP(X) \rightarrow \pi^*$ or σ^* delocalization increases with increasing p character of considering atoms lone pair [15]. In contrast, the occupancy of the $LP(X)$ decreases with increasing p character of the lone pair of considering atoms. We show that the total stabilization energy for $LP \rightarrow \sigma$ or π^* delocalization decrease with decreasing occupancy values is C_2F_4 and C_2Cl_4 . Total stabilization energy value, also in the structure of C_2F_4 agrees well with the relative calculated electronegativity value for this structure and this is a reason to increase the occupancy value in compared with the other two structures. In contrast, we note that each of which structures of the LP (3) F and Cl with 100 % p character has well donor-acceptor interactions in these structures. The results presented in (Table 6-9) show that the natural charge analysis of the compounds M_2X_4 and M_2X_3Y ($X=H$, F, and Cl, $Y=CH_3$, NH_2 , and OH) structures. As well as, the Elements from the halogen group including F and Cl have pretty high electronegativities that of the charge values increase along with electronegativity because the nature of the intense electron withdrawing of F atoms leads to an increase in self-centered electrons. Generally, the electronegativity of the M_2X_4 and M_2X_3Y ($X=H$, F, and Cl, $Y=CH_3$, NH_2 , and OH) increase with increasing occupancy value of C-X bonds. On the other hand, this trend is correlated the increase in the related total E_2 values for donor-acceptor interactions in these compounds. Finally, Present studies demonstrated an increasing order of occupancy for M_2X_4 and M_2X_3Y ($X=H$, F, and Cl, $Y=CH_3$, NH_2 , and OH) due to the decreasing C-X bonds.

Table 4: (Mulliken atomic charges) of C_2X_4 ($X=H, F$ and Cl ,) at MP2/6-311++g**
Mulliken atomic charges/e

	1	2	3	
1 H	0.112938	1 F	-0.150548	1 Cl
2 C	-0.225877	2 C	0.301096	2 C
3 C	-0.225877	3 C	0.301096	3 C
4 H	0.112938	4 F	-0.150548	4 Cl
5 H	0.112938	5 F	-0.150548	5 Cl
6 H	0.112938	6 F	-0.150548	6 Cl

Table 5: The calculated natural charge of compounds M_2X_4 and M_2X_3Y ($X=H, F$, and Cl , $Y=CH_3, NH_2$, and OH) at MP2/6-311++G**.

Natural Charge						
Compounds	Atom	$CH_2=CH_2$	Atom	$CF_2=CF_2$	Atom	$CCl_2=CCl_2$
Unsubstituted	H	0.17081	F	-0.35488	Cl	0.07373
	C	-0.34163	C	0.70975	C	-0.14747
substituted	Atom	$CH_2=CHCH_3$	Atom	$CF_2=CFCH_3$	Atom	$CCl_2=ClCH_3$
	1 H	0.16736	1 F	-0.37137	1 Cl	0.05251
	2 C	-0.14374	2 C	0.39323	2 C	0.01533
	3 C	-0.37283	3 C	0.65190	3 C	-0.29282
	4 H	0.17682	4 F	-0.36431	4 Cl	0.05591
	5 H	0.16763	5 F	-0.40723	5 Cl	0.02040
CH_3	6 CH₃	0.001	6 CH₃	0.024	6 CH₃	0.037
	Atom	$CH_2=CHNH_2$	Atom	$CF_2=CFNH_2$	Atom	$CCl_2=ClNH_2$
	1 H	0.16415	1 F	-0.37580	1 Cl	0.03490
	2 C	0.11236	2 C	0.53878	2 C	0.19583
	3 C	-0.52811	3 C	0.67052	3 C	-0.24687
	4 H	0.18583	4 F	-0.36709	4 Cl	0.04793
NH_2	5 H	0.16967	5 F	-0.38493	5 Cl	0.01251
	6 NH₂	-0.069	6 NH₂	-0.027	6 NH₂	-0.015
	Atom	$CH_2=CHOH$	Atom	$CF_2=CFOH$	Atom	$CCl_2=C Cl OH$
	1 H	0.15833	1 F	-0.36051	1 Cl	0.05749
	2 C	0.26122	2 C	0.65212	2 C	0.32240
OH	3 C	-0.52285	3 C	0.66814	3 C	-0.24670
	4 H	0.19500	4 F	-0.35785	4 Cl	0.06561
	5 H	0.17323	5 F	-0.38299	5 Cl	0.01834
	6 OH	-0.132	6 OH	-0.109	6 OH	-0.109

Table 6: The Second-Order Perturbation Analysis of the “Hyperconjugative Interactions in (MP2/6-311++G**) M₂X₄ (X=H, F, and Cl)

Compound	Donor Lewis-type NBOs	Occupancy	Hybrid	Acceptor NBO	E ² kcal/mol	ΣE^2 Kcal/mol
¹ C ₂ H ₄	BD (1) H1 - C2	1.98752	SP ^{0.02}	BD*(1) C3 - H5	5.34	
				BD*(2) C2 - C3	0.98	7.22
				BD*(1) C3 - H4	0.90	
	BD (2) C2 - C3	1.99613	SP ^{1.45}	BD* (1) H1 - C2	1.00	4.00
				BD*(1) C2 - H6	1.00	
				BD*(1) C3 - H4	1.00	
				BD*(1) C3 - H5	1.00	
	BD (1) C 2 -H6	1.98752	SP ^{2.36}	BD*(2) C2 - C3	0.98	7.22
				BD*(1) C3 - H4	5.34	
				BD*(1) C3 - H5	0.90	
² CF ₂ =CF ₂	BD (1) C3 - H4	1.98752	SP ^{2.36}	BD* (1) H1 - C2	0.90	7.22
				BD*(2) C2 - C3	0.98	
				BD* (1) C 2 -H6	5.34	
	BD (1) C3 - H5	1.98752	SP ^{2.36}	BD* (1) H1 - C2	5.34	7.22
				BD*(2) C2 - C3	0.98	
				BD*(1) C2 - H6	0.90	
				BD*(1) C2 - H6	0.90	
	Donor Lewis-type NBOs	Occupancy	Hybrid	Acceptor NBO	E ² kcal/mol	
	BD (1) F1 - C 2	1.99624	SP ^{2.54}	BD*(1) C2 - F6	0.71	2.49
	BD (1) C 2 -F6	1.99624	SP ^{2.65}	BD*(1) C3 - F5	1.78	
² LP (1) F 1	BD (1) C3 - F4	1.99624	SP ^{2.65}	BD* (1) F1 - C2	0.71	2.49
				BD*(1) C3 - F4	1.78	
	BD (1) C3 - F5	1.99624	SP ^{2.65}	BD*(1) C2 - F6	1.78	2.49
				BD*(1) C3 - F5	0.71	
	LP (1) F 1	1.99332	SP ^{0.39}	BD* (1) F1 - C2	1.78	2.49
	LP (2) F 1	1.95880	SP ^{99.99}	BD*(1) C3 - F4	0.71	
				BD*(1) C2 - C3	0.82	0.82
				BD*(1) C2 - C3	7.01	18.15
				BD*(1) C2 - F6	17.59	
				BD*(1) C 3 - F5	0.56	
² LP (3) F 1	LP (3) F 1	1.95294	p	BD*(2) C2 - C3	25.44	25.44
	LP (1) F 4	1.99332	SP ^{0.39}	BD*(1) C2 - C3	0.82	0.82
	LP (2) F 4	1.95880	SP ^{99.99}	BD*(1) C2 - C3	7.01	18.15
				BD*(1) C2 - F 6	0.56	
				BD*(1) C3 - F5	17.59	
	LP (3) F 4	1.95294	SP ^{1.00}	BD*(2) C2 - C3	25.44	25.44
	LP (1) F 5	1.99332	SP ^{0.39}	BD*(1) C2 - C3	0.82	0.82
	LP (2) F 5	1.95880	SP ^{99.99}	BD*(1) F1 - C2	0.56	18.13
				BD*(1) C2 - C3	7.01	
				BD*(1) C3 - F4	17.59	
² LP (3) F 5	LP (3) F 5	1.95294	SP ^{1.00}	BD*(2) C2 - C3	25.44	25.44

LP (1) F 6	1.99332	SP ^{0.39}	BD*(1) C2 - C3 BD*(1) F1 - C2	0.82 17.59	0.82 18.13	
LP (2) F 6	1.95880	SP ^{99.99}	BD*(1) C2 - C3 BD*(1) C3 - F4	7.01 0.56		
LP (3) F 6	1.95294	SP ^{1.00}	BD*(2) C2 - C3	25.44	25.44	
Donor Lewis-type NBOs	Occupancy	Hybrid	Acceptor NBO	E ² kcal/mol		
BD (1) Cl 1 - C 2	1.98706	Sp ^{4.66}	BD* (1) C2 - C 3 BD*(1) C2 – Cl 6 BD*(1) C3 –Cl 5	1.52 0.54 5.38	7.44	
BD (1) C 2 –Cl 6	1.98706	Sp ^{2.57}	BD* (1) CL1 -C 2 BD* (1) C2 - C 3 BD* (1) C3- CL 4	0.54 1.52 5.38	7.98	
BD (1) C3 – Cl 4	1.98706	Sp ^{2.57}	BD* (1) C2 - C 3 BD*(1) C2 – Cl 6 BD*(1) C3 –Cl 5	1.52 5.38 0.54	7.44	
BD (1) C3 – Cl 5	1.98706	Sp ^{2.57}	BD* (1) Cl 1 - C 2 BD*(1) C 2 –C3 BD* (1) C 3- CL4	5.38 1.52 0.54	7.44	
<chem>CCl2=CCL2</chem> 3	1.99181	Sp ^{0.22}	BD* (1) C2 - C 3 BD*(1) C2 – Cl 6 BD* (1) C3- Cl 4	2.13 1.70 0.54	4.37	
	1.95998	Sp ^{99.99}	BD* (1) C2 - C 3 BD*(1) C2 – Cl 6 BD* (1) C3- Cl5	5.43 11.69 0.86	17.89	
	1.93552	Sp ^{1.00}	BD* (2) C2 - C 3 BD*(1) C2 – Cl 6	24.31 1.52	24.31 8.42	
LP (1)Cl 4	1.99181	Sp ^{0.22}	BD* (1) C2 - C 3 BD* (1) C3- Cl5 BD* (1) C2 - C 3	5.38 1.52 5.43		
LP (2)Cl 4	1.95998	Sp ^{99.99}	BD*(1) C2 – Cl 6 BD* (1) C3- Cl4	11.69 0.86	17.89	
LP (3)Cl 4	1.93552	Sp ^{1.00}	BD* (2) C2 - C 3 BD* (1) C2 - C 3	24.31 2.13	24.31 4.37	
LP (1)Cl 5	1.99181	Sp ^{0.22}	BD*(1) C2 – Cl 6 BD* (1) C3- Cl 4 BD*(1)Cl 1 - C 2	0.54 1.70 0.86	17.89	
LP (2)Cl 5	1.95998	Sp ^{99.99}	BD* (1) C2 - C 3 BD* (1) C3- Cl 4	5.43 11.69		
LP (3)Cl 5	1.93552	Sp ^{1.00}	BD* (2) C 2 - C3 BD*(1)Cl 1 - C 2	24.31 11.69	24.31 17.89	
LP (1)Cl 6	1.99181	Sp ^{0.22}	BD* (1) C2 - C 3 BD* (1) C3- Cl 4 BD*(1)Cl1 - C 2	5.43 0.86 11.69		
LP (2)Cl 6	1.95998	Sp ^{99.99}	BD* (1) C2 - C 3 BD* (1) C3- Cl 4	5.43 0.86	17.89	
LP (3)Cl 6	1.93552	Sp ^{1.00}	BD* (2) C2 - C 3	24.31	24.31	

Table 7: Occupancy of natural orbitals (NBOs) and hybrids of $C_2X_3CH_3$ (X=H, F, and Cl)

Compound	Donor Lewis-type NBOs	Occupancy	Hybrid	Acceptor NBO	E2 kcal/mol	$\Sigma E2$ Kcal/mol
$CH_2=CHCH_3$ 4	BD (1) H1 – C2	1.97935	SP ^{0.09}	BD*(1) C 2 - C 3	0.98	10.65
				BD*(1) C 3 - H 4	1.08	
				BD*(1) C 3 - H 5	5.92	
				BD*(1) C 6 - H 7	2.67	
	BD (1) C2 - C3	1.99148	SP ^{1.53}	BD*(1) H 1 - C 2	1.35	5.93
				BD*(1) C 2 - C 6	2.20	
				BD*(1) C 3 - H 4	1.34	
				BD*(1) C 3 - H 5	1.04	
	BD (2) C 2 - C 3	1.98216	SP ^{1.00}	BD*(1) C 6 - H 8	4.01	8.02
				BD*(1) C 6 - H 9	4.01	
				BD*(1) C 2 - C 3	2.61	6.6
				BD*(1) C 3 - H 4	2.91	
$BD (1) C2 - C6$	BD (1) C2 - C6	1.98925	SP ^{2.01}	BD*(1) C 6 - H 8	0.54	
				BD*(1) C 6 - H 9	0.54	
				BD*(1) H 1 - C 2	4.98	9.19
	BD (1) C3 - H4	1.98670	SP ^{2.36}	BD*(1) C 2 - C 3	1.53	
				BD*(1) C 2 - C 6	6.85	
				BD*(1) H 1 - C 2	5.95	7.21
	BD (1) C3 - H5	1.98724	SP ^{2.37}	BD*(1) C 2 - C 3	1.26	
				BD*(1) C 2 - C 3	4.98	4.98
				BD*(1) C 2 - C 3	2.21	7.35
	BD (1) C6 - H7	1.99082	SP ^{3.22}	BD*(1) C 2 - C 3	5.14	
				BD*(1) C 2 - C 3	2.21	7.35
				BD*(1) C 2 - C 3	5.14	
$CF_2=CFCH_3$ 5	BD (1) C6 - H8	1.98366	SP ^{3.34}	BD*(1) C 2 - C 3	2.57	
				BD*(1) C 3 - F 5	2.12	5.21
				BD*(1) C 2 - C 6	0.52	
	BD (1) C6 - H9	1.99367	SP ^{3.24}	BD*(1) C 3 - F 4	0.94	7.54
				BD*(1) C 2 - C 6	4.91	
				BD*(1) C 6 - H 8	1.69	
	BD (1) C2 – C6	1.97501	SP ^{1.64}	BD*(1) C 2 - C 3	4.80	20.19
				BD*(1) C 3 - F 4	3.75	
				BD*(1) C 6 - H 8	3.42	
	BD (1) C3 - F4	1.99623	SP ^{2.61}	LP (2) C 6	8.22	
				BD*(1) C 2 - C 3	1.17	3.52
				BD*(1) C 2 - C 6	1.41	
$BD (1) C3 - F5$	BD (1) C3 - F5	1.99512	SP ^{3.03}	BD*(1) C 2 - F 5	0.94	
				BD*(1) F 1 - C 2	3.02	3.79
				BD*(1) C 3 - F 4	0.77	
	BD (1) C6 – H8	1.95703	SP ^{3.10}	BD*(1) F 1 - C 2	1.34	7.55
				BD*(2) C 2 - C 3	2.70	
				BD*(1) C 2 - C 6	2.91	
				BD*(1) C 6 - H 8	0.60	

LP (1) F 1	1.99204	SP ^{0.43}	BD*(1) C 2 - C 6	1.12	1,12	
LP (2) F 1	1.97334	SP ^{99.99}	LP (2) C 6	2.01	16.96	
			BD*(2) C 2 - C 3	7.04		
			BD*(1) C 2 - C 6	6.97		
			BD*(1) C 3 - F 5	0.94		
LP (3) F 1	1.95645	P	BD*(2) C 2 - C 3	24.16	24.16	
LP (1) F 4	1.99291	SP ^{0.41}	BD*(1) C 2 - C 3	1.75	1,75	
LP (2) F 4	1.96212	SP	BD*(2) C 2 - C 3	20.42	20.42	
LP (3) F 4	1.95669	SP ^{99.99}	BD*(1) C 2 - C 3	6.37	25.97	
LP(1) F 5	1.99346	SP ^{0.41}	BD*(1) C 3 - F 5	19.60		
LP (2) F 5	1.96884	SP ^{1.00}	BD*(1) C 2 - C 3	1.20	1,20	
			BD*(2) C 2 - C 3	16.59	16.59	
			BD*(1) F1 - C 2	0.93		
LP (3) F 5	1.96102	SP ^{99.74}	BD*(1) C 2 - C 3	4.43		
			BD*(1) C 3 - F 4	14.72	14,72	
LP(1) C 6	1.83712	P	BD*(2) C 2 - C 3	67.61	67.61	
Donor Lewis-type NBOs	Occupancy	Hybrid	Acceptor NBO	E2 kcal/mol	ΣE2 Kcal/mol	
CCl ₂ =CClCH ₃			BD*(1) C 2 - C 6	7.12	10.61	
BD (1) Cl 1 – C2	1.97920	SP ^{4.46}	BD*(1) C 3 -Cl 4	1.09		
			BD*(1) C 6 - H 8	1.50		
BD (1) C2 - C3	1.98846	SP ^{1.51}	BD*(1) C 6 - H 9	0.90		
BD (2) C2 - C3	1.98309	SP ^{1.00}	BD*(1)Cl 1 - C 2	0.66	1,66	
BD (1) C 2 - C 6	1.96557	SP ^{1.74}	BD*(1) C 3 - C 6	3.80		
6			BD*(2) C 2 - C 3	0.81	0.81	
BD (1) C3 - Cl 4	1.99077	SP ^{2.28}	BD*(1) C 2 - C 3	7.63	18.68	
			BD*(1) C 3 -Cl 4	5.02		
			BD*(1) C 6 - H 8	6.03		
BD (1) C3 – Cl 5	1.98549	SP ^{11.63}	BD*(1) C 2 - C 3	2.34	6.31	
			BD*(1) C 2 - C 3	3.43		
			BD*(1) C 3 -Cl 5	0.64		
BD (1) C6 – H8	1.98040	SP ^{2.21}	BD*(1)Cl 1 - C 2	6.99	7.55	
			BD*(2) C 2 - C 3	0.56		
			BD*(1) C 2 - C 6	1.08		
			BD*(1) C 6 - H 8	4.98		
BD (1) C6 – H9	1.99001	SP ^{3.19}	BD*(1) C 6 - H 9	4.83	17.55	
			BD*(1) C 6 - H 9	0.88		
LP (1) Cl 1	1.99239	SP ^{0.22}	BD*(1)Cl 1 - C 2	5.78		
			BD*(1) C 6 - H 8	2.08	4.75	
LP (2) Cl 1	1.96844	SP ^{99.99}	BD*(1) C 6 - H 8	2.67		
			BD*(1) C 2 - C 3	1.30	4.01	
			BD*(1) C 2 - C 6	2.21		
LP (3) Cl 1	1.94073	P	BD*(1) C 3 -Cl 4	0.50		
			BD*(1) C 2 - C 3	4.99	13.31	
			BD*(1) C 2 - C 6	5.95		
			BD*(1) C 3 -Cl 5	1.18		
			BD*(1) C 6 - H 9	1.19		
			BD*(2) C 2 - C 3	22.37	22.37	

LP (1) Cl 4	1.99261	SP ^{0.22}	BD*(1) C 2 - C 3 BD*(1) C 3 - Cl 3	3.43 1.65	5.08
LP (2) Cl 4	1.96107	SP	BD*(1) C 2 - C 3 BD*(1) C 2 -Cl 5	5.51 14.94	36.20
			BD*(2) C 2 - C 3	15.75	
LP (3) Cl 4	1.95329	SP ^{82.87}	BD*(2) C 2 - C 3	24.80	٢٤,٨٠
LP(1) Cl 5	1.99291	SP ^{0.35}	BD*(1) C 2 - C 3 BD*(1) C 3 - C 14	2.13 0.64	2.77
LP (2) Cl 5	1.96918	P	BD*(2) C 2 - C 3	11.59	11.59
LP (3) Cl 5	1.88397	SP ^{11.63}	BD*(1) Cl 1 - C 2 BD*(1) C 2 - C 3 BD*(1) C 3 -Cl 4	0.91 2.84 9.48	13.2١
LP (1) C 6	1.73446	P	BD*(2) C 2 - C 3	109.53	109.53

Table 8: Occupancy of natural orbitals (NBOs) and hybrids of $C_2X_3NH_2$ (X=H, F, and Cl)

Compound	Donor Lewis-type NBOs	Occupancy	Hybrid	Acceptor NBO	E2 kcal/mol	$\Sigma E2$ Kcal/mol
$CH_2=CHNH_2$	BD (1) H1-C2	1.97758	SP ^{0.1}	BD*(1) C 2 - C 3 BD*(1) C 3 - H 4	1.35 0.89	
				BD*(1) C 3 - H 5 BD*(1) N 6 - H 7	4.99 5.43	12.56
				BD*(1) H 1 - C 2 BD*(1) C 2 - N 6	1.66 2.42	
				BD*(1) C 3 - H 4 BD*(1) C 3 - H 5	1.14 1.03	8.43
				BD*(1) N 6 - H 8	2.18	
	BD (2) C2 - C3	1.98981	SP ^{1.36}	BD*(2) C 2 - C 3 BD*(1) C 2 - C 3	0.79 2.30	0.79
				BD*(1) C 3 - H 4 BD*(1) H 1 - C 2	1.32 0.75	٣,٦٢
				BD*(1) C 2 - N 6 BD*(1) H 1 - C 2	8.71 5.91	
				BD*(1) C 2 - C 3 BD*(1) C 2 - N 6	1.01 0.67	7.59
				BD*(1) H 1 - C 2 BD*(1) C 2 - C 3	3.16 0.75	3.16
7	BD (1) C3 - H4	1.98457	SP ^{2.26}	BD*(1) C 2 - C 3 BD*(1) C 2 - N 6	1.32 8.71	10.78
				BD*(1) H 1 - C 2 BD*(1) C 2 - C 3	5.91 1.01	
				BD*(1) C 2 - N 6 BD*(1) H 1 - C 2	0.67 3.16	7.59
				BD*(1) H 1 - C 2 BD*(1) C 2 - C 3	0.75 4.01	4.76
				BD*(1) C 2 - C 3 BD*(2) C 2 - C 3	59.01	59.01
Compound	Donor Lewis-type NBOs	Occupancy	Hybrid	Acceptor NBO	E2 kcal/mol	$\Sigma E2$ Kcal/mol
$BD (1) F1 - C2$	1.99468	SP ^{2.40}	BD*(1) C 3 - F 5 BD*(1) N 6 -H 7	2.01 1.51		3.52
				BD*(1) C 2 - N 6 BD*(1) N 6 - H 8	2.85 1.81	
				BD*(1) C 2 - C 3 BD*(1) C 3 - F 4	2.54 2.40	4.94
				BD*(1) C 2 - C 3 BD*(1) C 2 - N 6	0.75 1.91	2.51
				BD*(1) C 2 - N 6		
$BD (1) C3 - F 4$	1.99625	SP ^{2.67}	BD*(1) C 2 - C 3 BD*(1) C 2 - N 6	2.01 1.51		3.52
				BD*(1) C 2 - C 3 BD*(1) C 2 - N 6	2.85 1.81	
				BD*(1) C 2 - C 3 BD*(1) C 2 - N 6	2.54 2.40	4.94
				BD*(1) C 2 - C 3 BD*(1) C 2 - N 6	0.75 1.91	2.51
				BD*(1) C 2 - N 6		

<chem>CF2=CFNH2</chem> 8	BD (1) C3 - F 5	1.99563	SP ^{2.84}	BD*(1) C 3 - F 5 BD*(1) F 1 - C 2 BD*(1) C 3 - F 4 BD*(1) F 1 - C 2 BD*(1) F 1 - C 2 BD*(1) C 2 - C 3 BD*(1) C 2 - N 6 BD*(1) C 2 - C 3 BD*(1) C 2 - N 6 BD*(1) C 3 - F 5 BD*(1) N 6 - H 7	0.85 γ,γ ^λ 0.79 5.16 1.80 2.98 0.53 7.06 9.74 0.82 0.59 24.30	3.17 5.16 4.78 18.21 24.30 1.22 21.37 γ4.66 0.95 19.86 γ2.8 ^ξ 52.98
	BD (1) N6 - H8	1.99105	SP ^{2.16}	BD*(1) C 2 - C 3		
	LP (1) F 1	1.99270	SP ^{0.42}	BD*(1) C 2 - N 6 BD*(1) C 2 - C 3 BD*(1) C 2 - N 6 BD*(1) C 3 - F 5 BD*(1) N 6 - H 7	0.53 7.06 9.74 0.82 0.59	1,γ ^γ
	LP (2) F 1	1.97203	SP ^{99.99}	BD*(2) C 2 - C 3 BD*(1) C 2 - C 3 BD*(2) C 2 - C 3 BD*(1) C 2 - C 3 BD*(1) C 3 - F 5 BD*(1) C 2 - C 3 BD*(2) C 2 - C 3 BD*(1) F 1 - C 2 BD*(1) C 2 - C 3 BD*(1) C 3 - F 4	24.30 1.22 21.37 6.49 18.17 0.95 19.86 0.79 5.78 16.37	
	LP (3) F 1	1.95626	P	BD*(2) C 2 - C 3	24.30	
	LP (1) F 4	1.99327	SP ^{0.40}	BD*(1) C 2 - C 3	1.22	
	LP (2) F 4	1.96068	P	BD*(2) C 2 - C 3	21.37	
	LP (3) F 4	1.95900	SP ^{99.99}	BD*(1) C 2 - C 3 BD*(1) C 3 - F 5	6.49 18.17	
	LP(1) F 5	1.99360	SP ^{0.40}	BD*(1) C 2 - C 3	0.95	
	LP (2) F 5	1.96323	P	BD*(2) C 2 - C 3	19.86	
	LP (3) F 5	1.96236	SP ^{99.99}	BD*(1) F 1 - C 2 BD*(1) C 2 - C 3 BD*(1) C 3 - F 4	0.79 5.78 16.37	
	LP (1) N 6	1.88429	P	BD*(2) C 2 - C 3	52.98	

Donor Lewis-type NBOs	Occupancy	Hybrid	Acceptor NBO	E2 kcal/mol	ΣE2 Kcal/mol	
<chem>CCl2=CClNH2</chem> 9	BD (1) Cl 1 – C2	1.98318	Sp ^{4.62}	BD*(1) C 2 - C 3 BD*(1) C 3 - Cl 5 BD*(1) N 6 - H 7 BD*(1) C 2 - N 6	1.26 5.27 1.32 4.32	7.85
	BD (1) C2 - C3	1.98977	SP ^{1.32}	BD*(1) C 3 - Cl 4 BD*(1) N 6 - H 8	·,55 1.91	6.78
	BD (1) C2 – N6	1.99119	SP ^{2.15}	BD*(1) Cl - C 2 BD*(1) C 3 - Cl 4	·,38 ·,·7	7.95
	BD (1) C3 – Cl 4	1.99004	SP ^{2.43}	BD*(1) C 2 - C 3 BD*(1) C 3 - Cl 4	1.50 0.51	5.63
	BD (1) C3 - Cl 5	1.98609	SP ^{2.68}	BD*(1) Cl - C 2 BD*(1) C2 - C 3	6.25 0.98	7.23
	BD (1) N6 – H7	1.98658	SP ^{2.22}	BD*(1) Cl - C 2	·,58	6.58
	BD (1) N6 – H8	1.99192	SP ^{2.28}	BD*(1) C 2 - C 3	4.01	4.01
	LP (1) Cl 1	1.99336	SP ^{0.21}	BD*(1) C 2 - C 3 BD*(1) C 2 - N 6	1.43 1.19	2.62
	LP (2) Cl 1	1.96736	SP ^{99.99}	BD*(1) C 2 - C 3 BD*(1) C 2 - N 6 BD*(1) C 3 - Cl 5 BD*(1) N 6 - H 7	·,14 8.66 ·,95 0.73	·5.48
	LP (3) Cl 1	1.94023	P	BD*(2) C 2 - C 3	·4.45	·4.45
	LP (1) Cl 4	1.99280	SP ^{0.23}	BD*(1) C 2 - C 3 BD*(1) C 3 - Cl 5	2.38 ·,·8	·,·96

				BD*(1) C 2 - C 3 BD*(1) C 3 - Cl 5	◦,56 12.75	
LP (2) Cl 4	1.95867	SP ^{72.56}				18.31
LP (3) Cl 4	1.95538	P		BD*(2) C 2 - C 3 BD*(1) C 2 - C 3	17.91 1.65	17.91
LP(1) Cl 5	1.99303	SP ^{0.23}		BD*(1) C 3 - Cl 4 BD*(1) Cl 1 - C 2	1.59 1.07	3.24
LP (2) Cl 5	1.96046	SP ^{77.10}		BD*(1) C 2 - C 3 BD*(1) C 3 - Cl 4 BD*(1) N 6 - H 7	4.99 10.85 ◦,65	◦,56
LP (3) Cl 5	1.95852	P		BD*(2) C 2 - C 3	16.21	16.21
LP (1) N 6	1.84708	P		BD*(2) C 2 - C 3	67.06	67.06

Table 9 : Occupancy of natural orbitals (NBOs) and hybrids of $C_2X_3 OH$ (x=H, F, and Cl)

Compound	Donor	Occupancy	Hybrid	Acceptor NBO	E2	ΣE2
	Lewis-type NBOs				kcal/mol	Kcal/mol
$CH_2=CHOH$	BD (1) H1 – C2	1.98014	S	BD*(2) C 2 - C 3 BD*(1) C 2 - O 6 BD*(1) C 3 - H 4 BD*(1) C 3 - H 5 BD*(1) O 6 - H 7	◦,28 0.58 ◦,94 5.18 3.48	11.46
	BD (1) C2 - C3	1.99427	SP ^{1.27}	BD*(1) H 1 - C 2 BD*(1) C 3 - H 4 BD*(1) C 3 - H 5	1.66 1.22 0.98	3.86
	BD (2) C2 - C3	1.99599	P	BD*(1) C 2 - C 3	0.50	0.50
	BD (1) C2 – O6	1.99658	SP ^{2.83}	BD*(1) C 2 - C 3 BD*(1) C 3 - H 4	◦,18 1.32	◦,30
	BD (1) C3 - H4	1.98280	SP ^{2.24}	BD*(1) H 1 - C 2 BD*(2) C 2 - C 3 BD*(1) C 2 - O 6	◦,09 ◦,25 9.06	◦,90
	BD (1) C3 - H5	1.98643	SP ^{2.27}	BD*(1) H 1 - C 2 BD*(2) C 2 - C 3 BD*(1) C 2 - O 6	◦,59 0.59 ◦,04	7.22
	BD (1) O6 – H7	1.98923	SP ^{3.75}	BD*(1) H 1 - C 2	3.97	3.97
	LP (1) O 6	1.98286	SP ^{1.23}	BD*(1) H 1 - C 2 BD*(1) C 2 - C 3	2.43 6.55	8.98
	LP (2) O 6	1.91201	P	BD*(2) C 2 - C 3	41.42	41.42
Donor	Lewis-type NBOs	Occupancy	Hybrid	Acceptor NBO	E2	ΣE2
$CF_2=CFOH$	BD (1) F1 – C2	1.99500	SP ^{2.43}	BD*(1) C 3 - F 5 BD*(1) O 6 - H 7	1.96 1.17	3.08
	BD (1) C2 - C3	1.99607	SP ^{1.29}	BD*(1) C 2 - O 6	◦,74	◦,74
	BD (2) C2 - C3	1.99318	P	-	-	-
	BD (1) C2 – O6	1.99538	SP ^{2.28}	BD*(1) C 2 - C 3 BD*(1) C 3 - F 4	1.23 2.18	3.41
	BD (1) C3 - F4	1.99611	SP ^{2.60}	BD*(1) C 2 - C 3 BD*(1) C 2 - O 6 BD*(1) C 3 - F 5	0.67 1.84 0.80	3.31

<i>II</i>	BD (1) C3 – F5	1.99579	SP ^{2.82}	BD*(1) F 1 - C 2 BD*(1) C 3 - F 4	γ,16 0.74	2.90
	BD (1) O6 – H7	1.98177	SP ^{3.61}	BD*(1) F 1 - C 2 BD*(1) C 2 - C 3	7.12 0.93	7.12 ·,64
	LP (1) F 1	1.99293	SP ^{0.41}	BD*(1) C 2 - C 3	7.25	21.33
	LP (2) F 1	1.96536	P	BD*(2) C 2 - O 6 BD*(1) C 3 - F 5	13.31 0.77	
	LP (3) F 1	1.95155	P	BD*(2) C 2 - C 3	26.44	
	LP (1) F 4	1.99316	SP ^{0.40}	BD*(1) C 2 - C 3	1.12	1.12
	LP (2) F 4	1.95741	P	BD*(2) C 2 - C 3	23.08	23.08
	LP (3) F 4	1.95740	SP ^{99.99}	BD*(1) C 2 - C 3	6.85	γ5.50
	LP(1) F 5	1.99364	SP ^{0.39}	BD*(1) C 3 - F 5	18.65	
	LP (2) F 5	1.96211	P	BD*(2) C 2 - C 3	20.63	20.63
	LP (3) F 5	1.96206	SP ^{1.09}	BD*(1) F 1 - C 2 BD*(1) C 2 - C 3	0.74 γ1,γ0	38.91
	LP (1) O 6	1.97506	P	BD*(1) C 3 - F 4	16.22	
	LP (2) O 6	1.92160	P	BD*(1) F 1 - C 2 BD*(2) C 2 - C 3 BD*(1) C 3 - F 4	4.05 5.92 0.54	γ,51
				BD*(2) C 2 - C 3	38.41	38.41
	Donor Lewis-type NBOs	Occupancy	Hybrid	Acceptor NBO	E2 kcal/mol	ΣE2 Kcal/mol
	BD (1) Cl1 – C2	1.98329	SP ^{4.72}	BD*(1) C 2 - C 3 BD*(1) C 3 - Cl 5	1.48 5.26	6.74
<i>CCl₂=CClOH</i> 12	BD (1) C2 - C3	1.99434	SP ^{1.23}	BD*(1) Cl 1 - C 2 BD*(1) C 2 - O 6 BD*(1) C 3 - Cl 4	0.65 1.47 0.52	γ,5‡
	BD (2) C2 - C3	1.98600	P	-	-	-
	BD (1) C2 – O6	1.99366	SP ^{2.58}	BD*(1) C 2 - C 3 BD*(1) C 3 - Cl 4	2.34 3.14	5.48
	BD (1) C3 - Cl4	1.98976	SP ^{2.37}	BD*(1) C 2 - C 3 BD*(1) C 2 - O 6	1.37 4.60	5.9γ
	BD (1) C3 – Cl5	1.98672	SP ^{2.69}	BD*(1) Cl 1 - C 2 BD*(1) C 2 - C 3	5.82 0.70	6.52
	BD (1) O 6 – H 7	1.98052	Sp ^{3.55}	BD*(2) Cl 1 - C 2	8.16	8.16
	LP (1) Cl 1	1.99393	SP ^{0.21}	BD*(1) C 2 - C 3 BD*(1) C 2 - O 6	1.76 0.78	2.54
	LP (2) Cl 1	1.96115	SP ^{99.99}	BD*(1) C 2 - C 3 BD*(1) C 2 - O 6 BD*(1) C 3 - Cl 5	γ,γ· γ,γ· ·,92	γ,γ· γ,γ·
	LP (3) Cl 1	1.93239	P	BD*(2) C 2 - C 3	26.87	0.59
	LP (1) Cl 4	1.99276	SP ^{0.23}	BD*(1) C 2 - C 3 BD*(1) C 3 - Cl 5	2.21 1.67	3.88
	LP (2) Cl 4	1.95613	SP ^{75.31}	BD*(1) C 2 - C 3 BD*(1) C 2 - O 6 BD*(1) C 3 - Cl 5	5.88 ·,54 13.26	19.68
	LP (3) Cl 4	1.95007	P	BD*(2) C 2 - C 3	19.88	19.88
	LP(1) Cl 5	1.99255	SP ^{0.23}	BD*(1) C 2 - C 3 BD*(1) C 3 - Cl 4	γ,45 γ,55	3.00

LP (2) Cl 5	1.96067	P	BD*(6) C 2 - C 3	16.95	16.95
LP (3) Cl 5	1.95594	SP ^{67.26}	BD*(1)Cl 1 - C 2	1.00	19.64
			BD*(1) C 2 - C 3	5.01	
			BD*(1) C 3 -Cl 4	10.84	
			BD*(1) O 6 -H 7	2.79	
LP (1) O 6	1.97945	SP ^{1.22}	BD*(1)Cl 1 - C 2	1.19	8.32
			BD*(1) C 2 - C 3	6.52	
			BD*(1) C 3 -Cl 4	,61	
LP (2) O 6	1.90197	P	BD*(2) C 2 - C 3	45.78	33.06

NMR chemical tensors

The NMR parameters play an important role in studying the molecular structure of compounds. In this work, theoretical studies of NMR properties have been investigated for C_2X_4 ($X=H$, F, and Cl). Table 11 represents the results of NMR shielding tensors of F and Cl atoms in all structures, according to the table it is clear F and Cl substituted which have similar chemical shielding, also provide the same value of asymmetry. It can be noted that C_2Cl_4 is higher than C_2F_4 of the chemical shielding and asymmetry. This shows when low shielding that electronegativity has the largest value. According to the results from NBO interpretation of the C_2Cl_4 and C_2F_4 are reported of the lone pair electrons of C_2F_4 have major occupancy than the C_2Cl_4 . Table 10 indicates that F and Cl in same position 4 at the $C_2Cl_3CH_3$ or $C_2F_3CH_3$ had higher chemical shielding and lower asymmetry. It can also be concluded that presence of CH_3 in substitute at the $C_2Cl_3CH_3$ or $C_2F_3CH_3$ has an impressive effect on the chemical shielding Cl atom and this result with agreeing of $C_2Cl_3NH_2$ or $C_2F_3NH_2$. The following up, the $C_2X_3 OH$ ($X= F$, and Cl) molecules, show that they have the most chemical shielding in position 5 because it has the highest total resonant energy in the bond that related to $LP(3) F5 \rightarrow \sigma^*(F 1 - C 2)$, $(C 2 - C 3)$ and $(C 3 - F 4)$. Our findings demonstrate that the trend of the electron donors with chemical shielding have a same interacting order of $OH > NH_2 > CH_3$. Furthermore, the electronegativity is related directions with chemical shielding.

Table 10: NMR parameters of C_2X_3Y ($X=H$, F, and Cl, $Y=CH_3$, NH_2 and OH) at MP2/6-311++g**

Compounds

C ₂ H ₃ CH ₃	σ iso	σ aniso	η	C ₂ F ₃ CH ₃	σ iso	σ aniso	η	C ₂ Cl ₃ CH ₃	σ iso	σ aniso	η
1 H	25.843	-2.148	-1.680	1 F	314.368	-2.963	11.404	1 Cl	696.956	-196.549	281.731
4 H	26.822	-1.7854	-3.492	4 F	380.715	15.891	-15.414	4 Cl	728.341	-140.763	-31.489
5 H	26.645	-0.9814	-1.938	5 F	333.641	-61.347	12.710	5 Cl	701.534	-198.083	-17.678
6 CH ₃	54.035	-4.940	-2.195	6 CH ₃	68.608	-6.0515	0.185	6 CH ₃	65.287	-10.538	6.536

Compounds											
C ₂ H ₃ NH ₂	σ iso	σ aniso	η	C ₂ F ₃ NH ₂	σ iso	σ aniso	η	C ₂ Cl ₃ NH ₂	σ iso	σ aniso	η
1 H	25.254	-4.340	-1.195	1 F	315.641	-10.870	9.615	1 Cl	695.566	-226.979	273.949
4 H	26.875	-1.104	-3.717	4 F	336.992	-53.345	-9.023	4 Cl	697.591	-217.446	-27.087
5 H	26.263	-0.378	-3.132	5 F	327.627	-48.049	6.223	5 Cl	691.635	-184.694	-22.269
6 NH ₂	97.065	4.971	5.054	6 NH ₂	98.718	1.275	0.760	6 NH ₂	90.199	-4.260	10.966

Compounds											
C ₂ H ₃ OH	σ iso	σ aniso	η	C ₂ F ₃ OH	σ iso	σ aniso	η	C ₂ Cl ₃ OH	σ iso	σ aniso	η
1 H	25.254	-3.729	-1.513	1 F	333.951	-41.384	10.986	1 Cl	749.964	-254.541	256.493
4 H	27.956	-1.860	-2.906	4 F	339.472	-57.392	30.580	4 Cl	761.718	-125.971	-95.835
5 H	27.209	-1.715	-0.738	5 F	339.602	-57.606	20.757	5 Cl	770.125	-159.234	1.343
OH	139.178	15.706	19.852	6 OH	151.049	-8.227	-1.132	6 OH	126.590	6.647	7.204

HOMO- LUMO analysis

The HOMO- LUMO, frontier molecular orbitals are important components and the HOMO-LUMO energy difference (ΔE) is a measure of the intramolecular charge transfer and was used in biological activity studies [16]. The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that largely acts as the electron acceptor. The MOs are defined as eigen functions of the Fock operator, which exhibits the full symmetry of the nuclear point group, they necessarily form a basis for irreducible representations of full point-group symmetry. [17]. According to energies of the HOMO and LUMO orbital's related to the ionization potential (IP) and electron affinities (EA) [18- 21] as in any Eqs.5 and 6.

$$IP = -E_{\text{HOMO}}$$

$$EA = -E_{\text{LUMO}}$$

By using these HOMO–LUMO energy values, the important properties like electronegativity (χ), chemical potential (μ), Chemical hardness (η), Global softness (σ) and electrophilicity index (ω) were calculated.

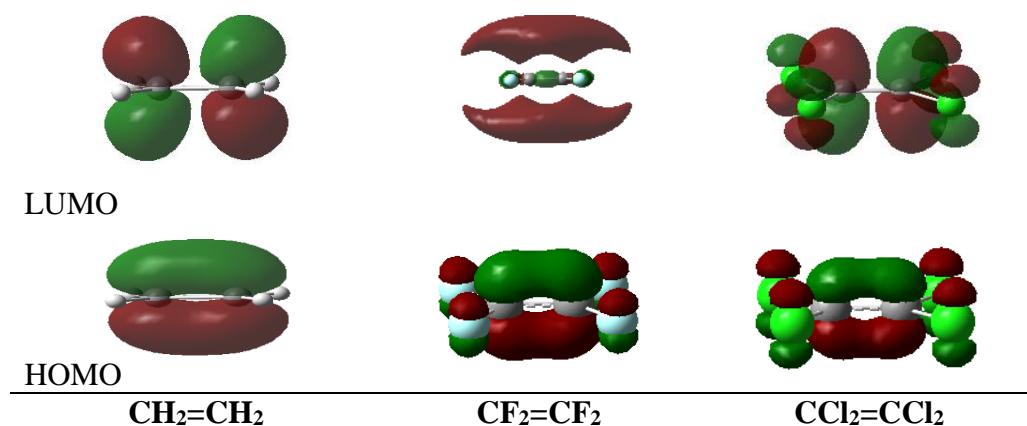
$$\chi = \frac{(IP + EA)}{2} \quad \mu = -\frac{(IP + EA)}{2} \quad \eta = \frac{(IP - EA)}{2} \quad \sigma = \frac{1}{\eta} \quad \omega = \frac{\mu^2}{2\eta}$$

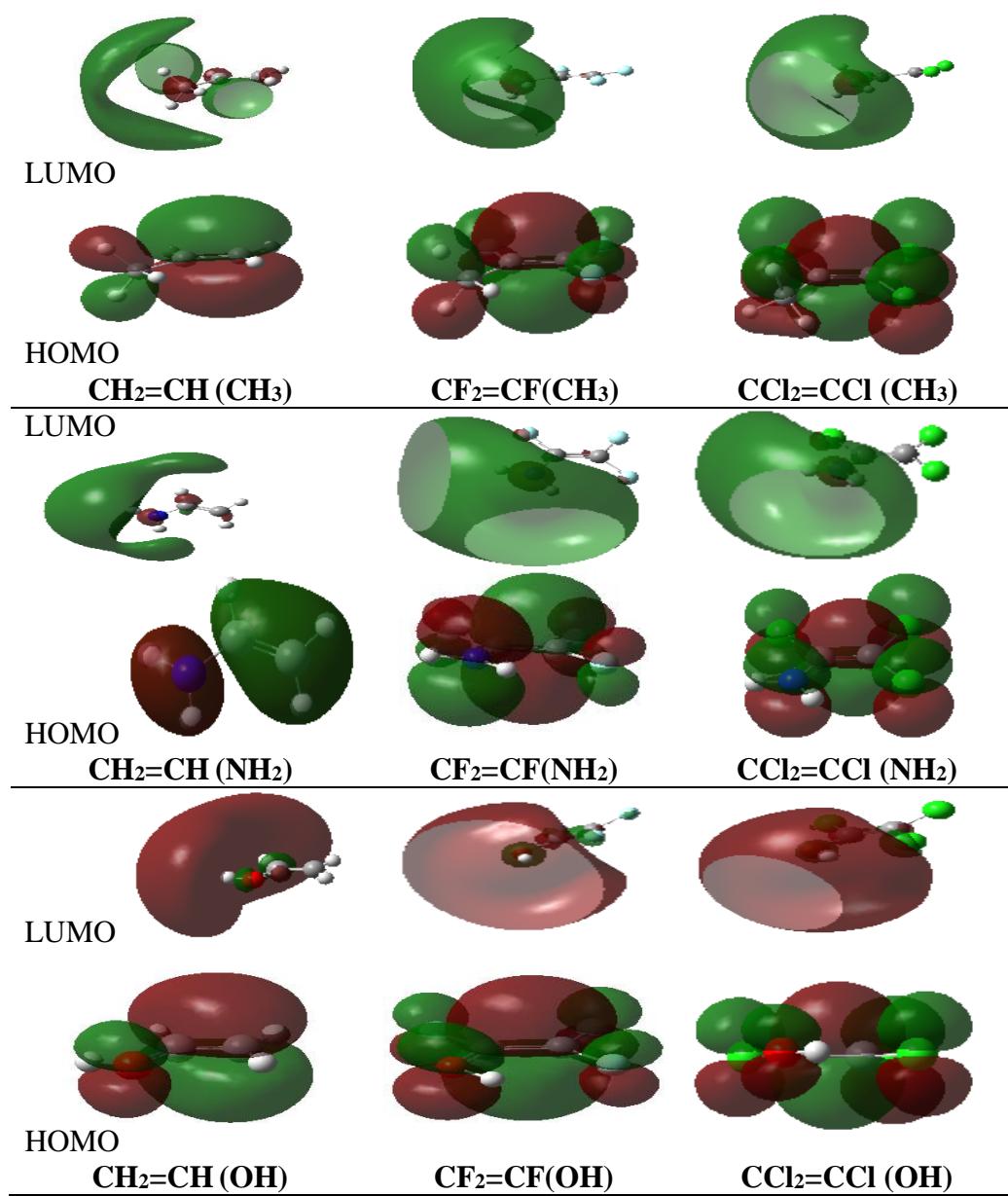
Table 11 indicates that the CCl₂ = CCl₂ and CF₂ = CF₂ have the lowest and the highest values of E_{HOMO} and E_{LUMO}, respectively. Therefore, CF₂=CF₂ system has more electrophilic than CH₂ =

CH_2 and $\text{CCl}_2 = \text{CCl}_2$ structures. Generally, we defined the electrophilicity as the ability of the molecule to accept electrons. The electrophilicity for $\text{CF}_2=\text{CF}_2$, $\text{CCl}_2 = \text{CCl}_2$, and $\text{CH}_2 = \text{CH}_2$ are 0.0303, 0.0551, and 0.0651, respectively. Well, known which molecules with larger HOMO-LUMO gap have kinetic stability and lower chemical *reactivity*. In the present study, the HOMO-LUMO gap are 0.519184, 0.395324 and 0.441977 eV in order: $\text{CF}_2=\text{CF}_2 > \text{CH}_2 = \text{CH}_2 > \text{CCl}_2 = \text{CCl}_2$. Thus, our calculations show that $\text{CCl}_2 = \text{CCl}_2$ compound is more reactive than $\text{CH}_2 = \text{CH}_2$ and $\text{CF}_2=\text{CF}_2$ structures due to it has a small HOMO-LUMO gap (see Fig. 2). The ionization potential (*IP*) is a basic description of the chemical reactivity of atoms and molecules. The slightly higher *IP* for $\text{CH}_2 = \text{CH}_2$ molecule pertains to strong stability.

The energy gap for the molecules obtained by replacing the CH_3 , NH_2 and OH groups in the C_2H_4 molecule showed that the replacement of OH group in the ethylene molecule caused a significant reduction in the energy gap compared to the replacement of the CH_3 and NH_2 gaps. Also, the energy gap for molecules studied by replacing CH_3 , NH_2 and OH groups in C_2F_4 indicates that the replacement of CH_3 group in the molecule significantly reduces the energy gap to replace the chains of CH_3 and NH_2 . Finally, the study of the energy gap in molecules derived from replacing CH_3 , NH_2 and OH in the C_2Cl_4 molecule showed that the CH_3 substitution in the molecule is larger than the replacement of OH and NH_2 in the C_2Cl_4 molecule.

As a result, the energy gap in all molecules, including molecules non-substituted and substituted by groups with similar function, show that the energy gap in the free molecule C_2F_4 is more than other molecules, which indicates the interaction of the charge transfer in the desired molecule and agrees with the stabilization energy (*E₂*).



**Figure 2.** Representation of the frontier molecular orbital in all of these structures**Table 11:** The values of parameters of C_2X_4 ($\text{X}=\text{H}, \text{F}$, and Cl) and $\text{C}_2\text{X}_3\text{Y}$ ($\text{X}=\text{H}, \text{F}$, and Cl , $\text{Y}=\text{CH}_3, \text{NH}_2$ and OH) at MP2/6-311++g**

Compounds	Substituent	HOMO	LUMO	Gap	IP	EA	η	χ	ω	σ	μ
$\text{CH}_2=\text{CH}_2$		-0.38590	0.056074	0.441977	0.385903	-0.056074	0.220989	0.164915	0.0615	4.5251	-0.164915
$\text{CF}_2=\text{CF}_2$	-----	-0.38493	0.134249	0.519184	0.384935	-0.134249	0.259592	0.125343	0.0303	3.5822	-0.125343
		-0.34521	0.050109	0.395324	0.345215	-0.050109	0.197662	0.147553	0.0551	5.0591	-0.147553

CCl ₂ =CCl ₂											
CH ₂ =CH ₂		-0.35715	0.04235	0.39950	0.35715	-0.04235	0.19975	0.1574	0.0620	5.0062	-0.1574
CF ₂ =CF ₂		-0.29347	0.02366	0.31713	0.29347	-0.02366	0.15857	0.13491	0.0574	6.3065	-0.13491
CCl ₂ =CCl ₂	CH ₃	-0.28764	0.02807	0.3171	0.28764	-0.02807	0.15785	0.12979	0.0534	6.3349	-0.12979
CH ₂ =CH ₂		-0.30411	0.04130	0.3454	0.30411	-0.04130	0.17271	0.13141	0.0499	5.7902	-0.13141
CF ₂ =CF ₂	NH ₂	-0.33791	0.03697	0.37488	0.33791	-0.03697	0.18744	0.15047	0.0604	5.3350	-0.15047
CCl ₂ =CCl ₂		-0.32371	0.03717	0.36088	0.32371	-0.03717	0.18044	0.14327	0.0569	5.5420	-0.14327
CH ₂ =CH ₂		-0.35209	0.04517	0.39726	0.35209	-0.04517	0.19863	0.15346	0.0593	5.0345	-0.15346
CF ₂ =CF ₂	OH	-0.38139	0.04156	0.42295	0.38139	-0.04156	0.21148	0.16992	0.0682	4.7286	-0.16992
CCl ₂ =CCl ₂		-0.35551	0.04480	0.40031	0.35551	-0.04480	0.20016	0.15536	0.0603	4.9961	-0.15536

Conclusions

Theoretical calculation with the goal of conscious response was performed to compare the stability of the combinations of C₂X₄ (X = H, F, and Cl) and some of their derivatives. The results reveal that the optimized structural parameters agree well with calculated energies. The total stability energy values for LP (Fs) → σ* and π* delocalization are more than LP (Cls) → σ* and π*. Total stabilization energy for LP (F) → σ* and π* delocalization increases with increasing *p* character of flour lone pair. We also found that that the occupancy values of flour lone pair (3) play a key role in the determination of chemical shielding and it is in relatively good agreement with electron-withdrawing ability, i.e. whatever extent the electronegativities of groups' substituent (CH₃, NH₂, and OH) increase in the same direction *increasing* the chemical shielding the reason for this trend the energy of the total resonance interactions increases upon related bands. Therefore, considering the substituent effect, the Møller-Plesset-Type (MP2) coupled-cluster calculations suggest that the more strongly electron-withdrawing the substituent, the higher occupancy value of C-X bonds in the M₂X₄ molecules. For instance, because the electron-withdrawing ability is ordered F > Cl > H > which has a better correlation with the electronic chemical potential and plays a crucial role in determining the reactivity and it suggested that chemical potential provides a new basis for explaining chemical reactions through the process of charge transfer.

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