DFT Study of the Structural, Electronic, Bonding Nature, NBO Analysis, and Thermodynamic Properties of Halogenated (F, Cl, Br) and Heteroatom (O, N, S) doped Cyclopropane

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Research article

Keywords: Cyclopropane, heteroatoms, halogenation, DFT, thermodynamic

Posted Date: December 31st, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-136338/v1>

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DFT Study of the Structural, Electronic, Bonding Nature, NBO Analysis, and Thermodynamic Properties of Halogenated (F, Cl, Br) and Heteroatom (O, N, S) doped Cyclopropane

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ABSTRACT

Background: The chemistry of cyclopropanes has been widely studied over the years as a result of its high reactivity which is due to its highly strained ring. The cyclopropane ring is highly significant in drug research as the 10th most frequently found ring in small molecules and as such, there is a need for research to improve further the reactivity of cyclopropanes in natural products and pharmaceuticals. In this work, we present an extremely comprehensive and detailed investigation on a variety of properties of cyclopropane including Geometrical properties, bonding nature, bond polarity index (BPI), natural bond orbitals (NBO), orbital charge analysis, Density of states (DOS), molecular electrostatic potential (MEP), UV-spectral analysis, electron ionization, affinity and accompanied process, local reactivity parameters and the effects of substitution of heteroatoms Nitrogen (N-doped C₃H₈), Oxygen (S-doped C₃H₈) and Sulphur (S-doped C₃H₈) each in the place of carbon atom (otherwise known as doping) and also the substitution effects of Fluorine, Chlorine and Bromine each on one hydrogen atom in cyclopropane molecule (halogenation) and investigate how it chemically affects the properties outlined above.

Results: It is observed from conceptual (CDFT) results that S-doped C₃S has the highest reactivity of all the molecules studied. The UV-spectral analysis also predicts doped C₃S as the molecule that gives the highest Bathochromic shift of all the molecules. Some other properties studied also give us the most potential sites for electrophilic and nucleophilic attack by electrophiles and nucleophiles. The NBO investigation revealed the strongest stabilization to the cyclopropane molecule for the heteroatoms follow the trend C₃S<C₃N<C₃O. It is also observed that for the halogens the strongest stabilization for the cyclopropane molecule follows the trend C₃Br<C₃Cl<C₃F<C₃. The strong intra-molecular hyperconjugation interaction of the 2-centered bond (BD) and CR electrons of C-C anti C-C bond in the ring leads to stabilization of the cyclopropane ring as evident from the 2nd order perturbation energy analysis.

Conclusion: The results obtained from the research will help scientists further improve on the reactivity of cyclopropanes as a motif in drug discovery through substitution (halogenation) and doping with heteroatoms (O, S, N)

Keywords: Cyclopropane; heteroatoms; halogenation; DFT; thermodynamic

1.0 Introduction

Cyclopropane is a cycloalkane molecule with the molecular formula C_3H_6 , which consists of 3 carbon atoms joined together to form a ring, with each carbon atom bearing two hydrogen atoms resulting in D_{3h} molecular symmetry [1-3]. The unique reactivity of cyclopropanes due to the high level of strain offers considerable utility in organic synthesis. It is strained because the bent carbon-carbon bonds overlap poorly. Cyclopropane is a versatile synthetic intermediate and a common structural motif in natural products and pharmaceuticals. Cyclopropane analogs have been known to exhibit diverse pharmacological applications that created enormous interest in Bioorganic, Medicinal, and Pharmaceutical chemistry [4-6]. Substituted cyclopropanes have been and still are employed as versatile building blocks in organic synthesis. Activation of the highly strained 3-member rings is necessary for this purpose, electron-donating or accepting substituents are involved in their reactions to make polar processes more favorable. Cyclopropane derivatives substituted by donor and acceptor groups are particularly for synthetic applications since electronic effects of these substituents guarantee activation of the cyclopropane and high versatility of the products after ring cleavage.

In the present work, we have studied global reactivity parameters (ionization potential, electron affinity, electronegativity, chemical potential, hardness, softness, nucleophilicity index, electrophilicity index), local reactivity parameters (Fukui functions and condensed dual descriptors), natural bond orbital analysis, geometrical parameters (bond length, bond angle and bond order), bond polarity index, natural population analysis, the density of states, molecular electrostatic potential and UV-spectral analysis for cyclopropanes with the effects of substitution of heteroatoms Nitrogen, Oxygen and Sulphur each in the place of a carbon atom and also the substitution effects of Fluorine, Chlorine, and Bromine each on one hydrogen atom in cyclopropane molecule as reported in **Fig. 1**. Furthermore, we are interested to study the properties of cyclopropane because of the scarcity of research and also predict the trend in most of the properties outlined above.

Fig 1. The optimized geometrical structure of C3, C3F, C3Cl, C3Br, C3N, C3O and C3S

2.0 Computational details

All calculations involved in this research work were carried out via the restricted DFT-B3LYP correlation functional [7-8]. In DFT methods Becke's three-parameter exchange functional (B3) jointed with gradient-corrected correlation functional of Lee, Yang, and Parr by employing the split-valence polarized 6-311++G (d, p) basis set have been developed for the computation of molecular structure optimization, vibrational frequencies, and energies of the molecular optimized structures [8]. All computational procedure was carried out using Gaussian 09 and Gaussian view 6.0 programs [9]. VEDA 04 software [10] employed results from Gaussian to determine the bond length and bond angles of all the molecules. Unless explicitly noted, all analyses as well as drawing of various kinds of maps were finished via the Multiwfn 3.7(dev) code [11] developed by Tian Lu and co. Some isosurface maps were rendered utilizing the VMD visualization program [12] based on the files exported by Multiwfn.

3.0 RESULTS AND DISCUSSION

3.1 Geometrical Parameters

3.1.1 Bond Length

The optimized structural parameters such as bond lengths, bond angles of C3, and substituted C3 were obtained at B3LYP theory with 6-311++G (d, p) basis set. **Table 1**, compares the theoretically calculated Bond lengths and Bond angles of cyclopropane with experimental data obtained from Computational Chemistry Comparison and Benchmark Database, National Institute of Standard and Technology (NIST) [13]. It is seen that the values of bond lengths for C3 obtained from theoretical calculations are approximately equal to experimental data from NIST. Bond lengths in the cyclopropane ring show values ranging from 1.016-1.525. From **Table 2**, It is observed from the bond length values that $C3-H9 < C3-F9 < C3-Cl9 < C3-Br9$. This is due to the electronegative nature of the halogens as it draws the bonding electrons towards itself and also the size of the halogens to accommodate the bonding electrons. Hence, the increase in size. It is also observed from the values of bond lengths $C1-O7 < C1-N7 < C1-S7$. These will make C3S the better nucleophile since the bonding electrons are not tightly held due to smaller bond length. It is seen from **Table 2**, that substitution of heteroatoms in the cyclopropane ring leads to a reduction in the bond angle of the cyclopropane ring (60°) except for sulfur where there is a deviation from the cyclopropane bond angle to 66.244° . $C1-C2-O7 < C1-C2-C3$ of $F < C1-C2-C3$ of $Br < C1-C2-C3$ of $Cl < C1-C2-N7 < C1-C2-C3$ of $C3 < C1-C2-S7$. The reason for the high deviation of S-substituted cyclopropane may be due to the large size of sulfur when it substitutes a carbon atom in a C3 ring.

TABLE 1: Experimental geometrical parameter of C3

EXPERIMENTAL			EXPERIMENTAL	
BOND LENGTH	VALUE		BOND ANGLE	VALUE
C1-C2	1.501		C1-C2-C3	60
C1-H4	1.083		C1-C2-H6	117.94
C1-H5	1.083		C1-C3-H9	117.94
C2-C3	1.501		C2-C1-H4	117.94
C2-H6	1.083		C2-C3-H8	117.94
C2-H7	1.083		C2-C3-H9	117.94
C3-C1	1.501		C3-C1-H4	117.94
C3-H8	1.083		C3-C1-H5	117.94
C3-H9	1.083		C3-C2-H7	117.94
			H4-C1-H5	114.5
			H6-C2-H7	114.5
			H9-C3-H8	114.5

TABLE 2: Optimized geometrical parameters of C3, C3F, C3Cl, C3Br, C3N, C3O, C3S obtained using VEDA 04 software

C3			C3	
BOND LENGTH	VALUE		BOND ANGLE	VALUE
C1-C2	1.508		C1-C2-C3	60
C1-H4	1.084		C1-C2-H6	118.07
C1-H5	1.084		C1-C3-H9	118.11
C2-C3	1.508		C2-C1-H4	118.06
C2-H6	1.084		C2-C3-H8	118.06
C2-H7	1.084		C2-C3-H9	118.06
C3-C1	1.508		C3-C1-H4	118.07
C3-H8	1.084		C3-C1-H5	118.07
C3-H9	1.084		C3-C2-H7	118.1
			H4-C1-H5	114.15
			H6-C2-H7	114.15
			H9-C3-H8	114.15
C3F			C3F	
BOND LENGTH	VALUE		BOND ANGLE	VALUE
C1-C2	1.525		C1-C2-C3	59.23
C1-H4	1.083		C1-C2-H6	119.36
C1-H5	1.083		C1-C3-F9	117.32
C2-C3	1.49		C2-C1-H4	119.35
C2-H6	1.084		C2-C3-H8	121.09

C2-H7	1.083		C2-C3-F9	117.33
C3-C1	1.49		C3-C1-H4	118.51
C3-H8	1.083		C3-C1-H5	116.54
C3-F9	1.385		C3-C2-H7	118.5
			H4-C1-H5	115.15
			H6-C2-H7	115.15
			F9-C3-H8	110.77
C3Cl			C3Cl	
BOND LENGTH	VALUE		BOND ANGLE	VALUE
C1-C2	1.517		C1-C2-C3	59.54
C1-H4	1.084		C1-C2-H6	119.14
C1-H5	1.083		C1-C3-Cl9	119.52
C2-C3	1.496		C2-C1-H4	119.19
C2-H6	1.084		C2-C3-H8	119.56
C2-H7	1.083		C2-C3-Cl9	119.51
C3-C1	1.496		C3-C1-H4	117.53
C3-H8	1.081		C3-C1-H5	117.41
C3-Cl9	1.788		C3-C2-H7	117.56
			H4-C1-H5	114.93
			H6-C2-H7	114.93
			Cl9-C3-H8	110.22
C3Br			C3Br	
BOND LENGTH	VALUE		BOND ANGLE	VALUE
C1-C2	1.517		C1-C2-C3	59.54
C1-H4	1.084		C1-C2-H6	119.12
C1-H5	1.083		C1-C3-Br9	119.99
C2-C3	1.496		C2-C1-H4	119.16
C2-H6	1.084		C2-C3-H8	119.635
C2-H7	1.082		C2-C3-Br9	119.99
C3-C1	1.496		C3-C1-H4	117.37
C3-H8	1.081		C3-C1-H5	117.83
C3-Br9	1.946		C3-C2-H7	117.39
			H4-C1-H5	114.77
			H6-C2-H7	114.79
			Br9-C3-H8	109.538
C3N			C3N	
BOND LENGTH	VALUE		BOND ANGLE	VALUE
C1-C2	1.485		C1-C2-N7	59.74

C1-H3	1.086		C1-C2-H6	119.92
C1-H4	1.084		C1-N7-H8	110.36
C2-N7	1.472		C1-C2-H5	117.96
C2-H5	1.086		C2-C1-H4	119.89
C2-H6	1.084		C2-N7-H8	110.34
N7-C1	1.473		N7-C1-H3	118.65
N7-H8	1.016		N7-C1-H4	114.8
			N7-C2-H6	114.81
			H3-C1-H4	114.79
			H5-C2-H6	114.71
C3O			C3O	
BOND LENGTH	VALUE		BOND ANGLE	VALUE
C1-C2	1.465		C1-C2-O7	59.23
C1-H3	1.086		C1-C2-H5	119.53
C1-H4	1.086		C1-C2-H6	119.53
C2-O7	1.432		C2-C1-H4	119.56
C2-H5	1.086		O7-C1-H3	115.11
C2-H6	1.084		O7-C1-H4	115.11
O7-C1	1.432		O7-C2-H6	115.03
			H3-C1-H4	115.66
			H5-C2-H6	115.79
C3S			C3S	
BOND LENGTH	Value		BOND ANGLE	VALUE
C1-C2	1.48		C1-C2-S7	66.24
C1-H3	1.084		C1-C2-H5	118.33
C1-H4	1.084		C1-C2-H6	118.33
C2-S7	1.836		C2-C1-H4	118.33
C2-H5	1.084		S7-C1-H3	144.93
C2-H6	1.084		S7-C1-H4	114.93
S7-C1	1.836		S7-C2-H6	114.95
			H3-C1-H4	118.33
			H5-C2-H6	115.02

3.1.2 Bond Order

Bond order is an important geometrical concept for understanding the nature of a chemical bond. It is used to compare the stability and reactivity of molecules by comparing the bond orders of the respective atoms in a molecule. A high bond order indicates more attraction between electrons i.e the higher the pull between the atoms and the shorter the bond length. Hence, the greater the stability and vice versa for Lower bond order. In this work, we are particularly interested in a type of bond order known as Laplacian Bond Order (LBO), which is defined as a scaled integral of negative parts of the Laplacian of electron density in fuzzy overlap space as reported in **Table S1** of the supporting information. It is shown that LBO has a direct correlation with the bond polarity, the bond dissociation energy, and the bond vibrational frequency. LBO has a surprisingly good correlation with Bond Dissociation energy i.e LBO predicts bonding strength fairly well.

From **Table S1**, it is observed that the C1-C3 and C2-C3 bond order for the halogen-substituted cyclopropane molecules are found to be increased than the normal cyclopropane molecule. The reason for selecting these bond orders is because the C3 carbon is directly connected to each of the halogens. Therefore, there is increased bond dissociation energy of the C1-C2 and C2-C3 bond and it increases in the following order C3<CBr<C3Cl<C3F. Moreover, LBO also predicts that the sequence of the C-X bonding strength in the 3 substituted halogen cyclopropanes as C3-F9<C3-Br9<C3-Cl9<C3-H9. For the heteroatoms, it is observed that the C-C bond strength increases in the following order C3N7 (0.77) <C3O7 (0.805) <C3S7 (0.97). Moreover, LBO also predicts that the sequence of the BDE of the C-Y bond where Y is a heteroatom will increase in the order C2-O7<C2-S7<C2-N7.

3.1.3 Energy Index and Bond Polarity Index

The energy index of an atom is regarded as the average energy per valence electron of the atom. The energy index for atom A in a molecule is defined as follows;

$$E.I_A = \frac{\sum_i^{val} \varepsilon_i \eta_i \theta_{i,A}}{\sum_i^{val} \eta_i \theta_{i,A}} \quad (1)$$

Where $\theta_{i,A}$ denotes the composition of atom A in MO i, η_i and ε_i are the occupation and energy of MO i, respectively. The denominator is defined as the number of valence electrons of atom A, and the numerator corresponds to the total energy of its valence electrons. The BPI between atoms A and B in a molecule is defined as

$$BPI_{AB} = (E.I_A - E.I_A^{ref}) - (E.I_B - E.I_B^{ref}) \quad (2)$$

Where $E.I^{ref}$ is the reference E.I value derived from calculations of homonuclear species.

TABLE 3: energy index and bond polarity index of C3, C3F, C3Cl, C3Br, C3N, C3O, C3S

	INTERACTING ATOMS	ENERGY INDEX OF	ENERGY INDEX OF	ENERGY INDEX OF	ENERGY INDEX OF	BOND POLARITY INDEX
MOLECULES	(X and Y)	ATOM X	ATOM Y	REFERENCE ATOM X	REFERENCE ATOM Y	XY
C3F	F9		-0.634678	-0.659349	-0.992515	
	F9-C3	-0.585744				-0.285928
C3Cl	Cl9		-0.468232	-1.651864	-0.697793	
	Cl9-C3	-0.506427				-0.076639
C3Br	Br9		-1.715235	-0.659349	-2.17115	
	Br9-C3	-50.96				-0.306171
C3N	N7		-0.497651	-0.659349	-0.718132	
	C1-N7	-0.522679				-0.083811
	C2-N7	-0.522747				-0.08387
C3O	O7		-0.554331	-0.659349	-0.905877	
	C1-O7	-0.543286				-0.235583
	C2-O7	-0.543236				-0.235533
C3S	S7		-0.41756	-0.659349	-0.61704	
	C1-S7	-0.524603				-0.064734
	C2-S7	-0.524594				-0.064725

The energy index of all the molecules in **Table 3**, shows that C3Br has the highest energy index of all the studied molecules. Therefore, it has the strongest capacity to attract electrons than other molecules. The energy index value increases in the following order C3S<C3Cl<C3N<C3O<C3F<C3Br. The Bond Polarity Index for C3Br is more negative and so C-Br bond in C3Br is more polar than the bonds in the other substituted cyclopropane molecules while the least polar will be C3S, indicating that the C-S bond in C3S has the least polarity of the studied molecules. The increase in BPI follows the trend C3S<C3Cl<C3N<C3O<C3F<C3Br

3.2 Natural Bond Orbital (NBO) Analysis

Natural bond orbital (NBO) investigations provide the information about nature of hydrogen bonding and interaction among bonds, and also give insight about the nature of charge transfer or conjugative interaction of molecular systems in addition to second-order perturbation energy analysis [14-16]. The electron donor orbital, acceptor orbital, and interacting stabilizing energy resulting from 2nd order perturbation theory obtained from NBO calculation. The higher the stabilization energy $E_j^{(2)}$ value the higher is the interaction between the electron filled and unfilled orbitals i.e the greater donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (anti-bond or Rydberg) non-Lewis NBO orbitals corresponds to a stabilizing donor-acceptor interaction [17-19]. NBO analysis has been carried out on the molecules at the B3LYP/6-

311++G(d,p) level to explain the intramolecular, re-hybridization, and delocalization of electron density within the molecule. $E^{(2)}$ means energy hyper conjugative interaction (stabilization energy). $E(i)-E(j)$ is the energy difference between donor and acceptor i and j NBO orbitals. $F(i,j)$ is the Fock matrix element between I and j NBO orbitals. The electron density (ED), donor and acceptor electrons, second-order perturbation energy (E2), and the interaction energies of C3, C3F, C3Cl, C3Br, C3N, C3O, and C3S is represented in Tables 4(a)-(g) respectively.

TABLE 4(a). Second order perturbation theory analysis of C3 using B3LYP/6-311++G functional

Donor NBO (i)	ED(e)	Acceptor NBO (j)	ED(e)	E(2)	E(j)-E(i)	F(i, j)
				kcal/mol	a.u	a.u
1. BD (1) C 1 - C 2	1.96554	RY*(1) C 3	0.00498	2.72	1.28	0.053
1. BD (1) C 1 - C 2		BD*(1) C 1 - C 3	0.02316	5.90	0.88	0.064
1. BD (1) C 1 - C 2		BD*(1) C 2 - C 3	0.02316	5.90	0.88	0.064
1. BD (1) C 1 - C 2		BD*(1) C 3 - H 8	0.01192	2.21	0.96	0.041
1. BD (1) C 1 - C 2		BD*(1) C 3 - H 9	0.01192	2.21	0.96	0.041
2. BD (1) C 1 - C 3	1.06555	RY*(1) C 2	0.00498	2.72	1.28	0.053
2. BD (1) C 1 - C 3		BD*(1) C 1 - C 2	0.02317	5.89	0.88	0.064
2. BD (1) C 1 - C 3		BD*(1) C 2 - C 3	0.02316	5.90	0.88	0.064
2. BD (1) C 1 - C 3		BD*(1) C 2 - H 6	0.01192	2.21	0.96	0.041
2. BD (1) C 1 - C 3		BD*(1) C 2 - H 7	0.01192	2.21	0.96	0.041
3. BD (1) C 1 - H 4	1.98830	BD*(1) C 2 - H 6	0.01192	0.55	0.94	0.020
3. BD (1) C 1 - H 4		BD*(1) C 2 - H 7	0.01192	1.19	0.94	0.030
3. BD (1) C 1 - H 4		BD*(1) C 3 - H 8	0.01192	1.19	0.94	0.030
3. BD (1) C 1 - H 4		BD*(1) C 3 - H 9	0.01192	0.55	0.94	0.020
4. BD (1) C 1 - H 5	1.98830	BD*(1) C 2 - H 6	0.01192	1.19	0.94	0.030
4. BD (1) C 1 - H 5		BD*(1) C 2 - H 7	0.01192	0.55	0.94	0.020
4. BD (1) C 1 - H 5		BD*(1) C 3 - H 8	0.01192	0.55	0.94	0.020
4. BD (1) C 1 - H 5		BD*(1) C 3 - H 9	0.01192	1.19	0.94	0.030
5. BD (1) C 2 - C 3	1.96555	RY*(1) C 1	0.00498	2.72	1.28	0.053
5. BD (1) C 2 - C 3		BD*(1) C 1 - C 2	0.02317	5.90	0.88	0.064
5. BD (1) C 2 - C 3		BD*(1) C 1 - C 3	0.02316	5.89	0.88	0.064
5. BD (1) C 2 - C 3		BD*(1) C 1 - H 4	0.01192	2.21	0.96	0.041
5. BD (1) C 2 - C 3		BD*(1) C 1 - H 5	0.01192	2.21	0.96	0.041
6. BD (1) C 2 - H 6	1.98830	BD*(1) C 1 - H 4	0.01192	0.55	0.94	0.020
6. BD (1) C 2 - H 6		BD*(1) C 1 - H 5	0.01192	1.19	0.94	0.030
6. BD (1) C 2 - H 6		BD*(1) C 3 - H 8	0.01192	1.19	0.94	0.030
6. BD (1) C 2 - H 6		BD*(1) C 3 - H 9	0.01192	0.55	0.94	0.020
7. BD (1) C 2 - H 7	1.98830	BD*(1) C 1 - H 4	0.01192	1.19	0.94	0.030
7. BD (1) C 2 - H 7		BD*(1) C 1 - H 5	0.01192	0.55	0.94	0.020
7. BD (1) C 2 - H 7		BD*(1) C 3 - H 8	0.01192	0.55	0.94	0.020
7. BD (1) C 2 - H 7		BD*(1) C 3 - H 9	0.01192	1.19	0.94	0.030

8. BD (1) C 3 - H 8	1.98830	BD*(1) C 1 - H 4	0.01192	1.19	0.94	0.030
8. BD (1) C 3 - H 8		BD*(1) C 1 - H 5	0.01192	0.55	0.94	0.020
8. BD (1) C 3 - H 8		BD*(1) C 2 - H 6	0.01192	1.19	0.94	0.030
8. BD (1) C 3 - H 8		BD*(1) C 2 - H 7	0.01192	0.55	0.94	0.020
9. BD (1) C 3 - H 9	1.98830	BD*(1) C 1 - H 4	0.01192	0.55	0.94	0.020
9. BD (1) C 3 - H 9		BD*(1) C 1 - H 5	0.01192	1.19	0.94	0.030
9. BD (1) C 3 - H 9		BD*(1) C 2 - H 6	0.01192	0.55	0.94	0.020
9. BD (1) C 3 - H 9		BD*(1) C 2 - H 7	0.01192	1.19	0.94	0.030
10. CR (1) C 1	1.99931	RY*(1) C 2	0.00498	0.70	10.78	0.077
10. CR (1) C 1		RY*(1) C 3	0.00498	0.70	10.78	0.077
11. CR (1) C 2	1.99931	RY*(1) C 1	0.00498	0.70	10.78	0.077
11. CR (1) C 2		RY*(1) C 3	0.00498	0.70	10.78	0.077
12. CR (1) C 3	1.99931	RY*(1) C 1	0.00498	0.70	10.78	0.077
12. CR (1) C 3		RY*(1) C 2	0.00498	0.70	10.78	0.077

TABLE 4(b): Second order perturbation theory analysis of C3F using B3LYP/6-311++G functional

Donor NBO (i)	ED(e)	Acceptor NBO (j)	ED(e)	E(2)	E(i)-E(j)	F(i, j)
				kcal/mol	a.u.	a.u.
1. BD (1) C 1 - C 2	1.95752	RY*(2) C 3	0.00538	1.51	1.61	0.045
1. BD (1) C 1 - C 2		BD*(1) C 1 - C 3	0.03919	5.34	0.87	0.061
1. BD (1) C 1 - C 2		BD*(1) C 2 - C 3	0.03919	5.34	0.87	0.061
1. BD (1) C 1 - C 2		BD*(1) C 3 - H 8	0.02904	3.65	0.92	0.052
1. BD (1) C 1 - C 2		BD*(1) C 3 - F 9	0.03709	4.22	0.77	0.051
2. BD (1) C 1 - C 3	1.96799	RY*(1) C 2	0.00512	2.68	1.29	0.053
2. BD (1) C 1 - C 3		BD*(1) C 1 - C 2	0.02251	5.46	0.88	0.062
2. BD (1) C 1 - C 3		BD*(1) C 2 - C 3	0.03919	5.69	0.91	0.064
2. BD (1) C 1 - C 3		BD*(1) C 2 - H 6	0.01175	2.41	0.98	0.044
2. BD (1) C 1 - C 3		BD*(1) C 2 - H 7	0.00984	1.72	0.99	0.037
2. BD (1) C 1 - C 3		BD*(1) C 3 - H 8	0.02904	0.62	0.96	0.022
3. BD (1) C 1 - H 4	1.95514	BD*(1) C 2 - H 7	0.00984	1.07	0.94	0.028
3. BD (1) C 1 - H 4		BD*(1) C 3 - F 9	0.03709	2.39	0.76	0.038
4. BD (1) C 1 - H 5	1.98311	BD*(1) C 2 - H 6	0.01175	1.21	0.94	0.030
4. BD (1) C 1 - H 5		BD*(1) C 2 - H 7	0.00984	0.52	0.94	0.020
4. BD (1) C 1 - H 5		BD*(1) C 3 - H 8	0.02904	1.28	0.91	0.031
4. BD (1) C 1 - H 5		BD*(1) C 3 - F 9	0.03709	1.34	0.76	0.029
5. BD (1) C 2 - C 3	1.96799	RY*(1) C 1	0.00512	2.68	1.29	0.053
5. BD (1) C 2 - C 3		BD*(1) C 1 - C 2	0.02251	5.46	0.88	0.062
5. BD (1) C 2 - C 3		BD*(1) C 1 - C 3	0.03919	5.69	0.91	0.064
5. BD (1) C 2 - C 3		BD*(1) C 1 - H 4	0.01175	2.41	0.98	0.044
5. BD (1) C 2 - C 3		BD*(1) C 1 - H 5	0.00984	1.72	0.99	0.037

5. BD (1) C 2 - C 3		BD*(1) C 3 - H 8	0.02904	0.62	0.96	0.022
6. BD (1) C 2 - H 6	1.98514	BD*(1) C 1 - H 5	0.00984	1.06	0.94	0.028
6. BD (1) C 2 - H 6		BD*(1) C 3 - F 9	0.03709	2.39	0.76	0.038
7. BD (1) C 2 - H 7	1.98311	BD*(1) C 1 - H 4	0.01175	1.21	0.94	0.030
7. BD (1) C 2 - H 7		BD*(1) C 1 - H 5	0.00984	0.52	0.94	0.020
7. BD (1) C 2 - H 7		BD*(1) C 3 - H 8	0.02904	1.28	0.91	0.031
7. BD (1) C 2 - H 7		BD*(1) C 3 - F 9	0.03709	1.34	0.76	0.029
8. BD (1) C 3 - H 8	1.98929	BD*(1) C 1 - H 5	0.00984	1.09	0.96	0.029
8. BD (1) C 3 - H 8		BD*(1) C 2 - H 7	0.00984	1.08	0.96	0.029
8. BD (1) C 3 - H 8		BD*(1) C 3 - F 9	0.03709	1.40	0.78	0.030
9. BD (1) C 3 - F 9	1.99568	RY*(1) C 3	0.00638	0.67	1.78	0.031
10. CR (1) C 1	1.99930	RY*(1) C 2	0.00512	0.62	10.77	0.073
10. CR (1) C 1		RY*(2) C 3	0.00638	0.64	11.13	0.076
11. CR (1) C 2	1.99930	RY*(1) C 1	0.00512	0.62	10.77	0.073
11. CR (1) C 2		RY*(2) C 3	0.00538	0.64	11.13	0.076
12. CR (1) C 3	1.99865	RY*(1) C 1	0.00512	0.70	10.86	0.078
12. CR (1) C 3		RY*(1) C 2	0.00512	0.70	10.86	0.078
12. CR (1) C 3		BD*(1) C 1 - C 3	0.03919	0.68	10.48	0.076
12. CR (1) C 3		BD*(1) C 2 - C 3	0.03919	0.68	10.48	0.076
12. CR (1) C 3		BD*(1) C 3 - F 9	0.03709	2.86	10.38	0.155
13. CR (1) F 9	1.99994	RY*(1) C 3	0.00638	2.24	25.25	0.213
14. LP (1) F 9	1.99216	RY*(1) C 3	0.00638	7.48	1.87	0.106
15. LP (2) F 9	1.97003	RY*(2) C 3	0.00538	1.06	1.48	0.036
15. LP (2) F 9		BD*(1) C 1 - C 3	0.03919	2.38	0.74	0.038
15. LP (2) F 9		BD*(1) C 2 - C 3	0.03919	2.39	0.74	0.038
15. LP (2) F 9		BD*(1) C 3 - H 8	0.02904	6.52	0.79	0.064
16. LP (3) F 9	1.96790	RY*(4) C 3	0.00208	1.18	1.88	0.042
16. LP (3) F 9		BD*(1) C 1 - C 3	0.03919	5.25	0.74	0.056
16. LP (3) F 9		BD*(1) C 2 - C 3	0.03919	5.24	0.74	0.056

TABLE 4(c). Second order perturbation theory analysis of C3Cl using B3LYP/6-311++G functional

Donor NBO (i)	ED(e)	Acceptor NBO (j)	ED(e)	E(2)	E(i)-E(j)	F(i, j)
					kcal/mol	a.u. a.u.
1. BD (1) C 1 - C 2	1.95596	RY*(1) C 3	0.00751	1.22	1.30	0.036
1. BD (1) C 1 - C 2		RY*(3) C 3	0.00226	0.81	1.41	0.031
1. BD (1) C 1 - C 2		BD*(1) C 1 - C 3	0.03929	5.65	0.87	0.063
1. BD (1) C 1 - C 2		BD*(1) C 2 - C 3	0.03927	5.64	0.87	0.063
1. BD (1) C 1 - C 2		BD*(1) C 3 - H 8	0.02670	3.06	0.95	0.048
1. BD (1) C 1 - C 2		BD*(1) C 3 -Cl 9	0.03865	6.05	0.66	0.057

2. BD (1) C 1 - C 3	1.96668	RY*(1) C 2	0.00459	2.03	1.24	0.045
2. BD (1) C 1 - C 3		RY*(1) Cl 9	0.00286	0.69	1.27	0.027
2. BD (1) C 1 - C 3		BD*(1) C 1 - C 2	0.02010	5.07	0.88	0.060
2. BD (1) C 1 - C 3		BD*(1) C 1 - H 5	0.01102	0.55	0.99	0.021
2. BD (1) C 1 - C 3		BD*(1) C 2 - C 3	0.03927	6.14	0.91	0.067
2. BD (1) C 1 - C 3		BD*(1) C 2 - H 6	0.01244	2.37	0.99	0.043
2. BD (1) C 1 - C 3		BD*(1) C 2 - H 7	0.01103	1.94	0.99	0.039
2. BD (1) C 1 - C 3		BD*(1) C 3 - H 8	0.02670	0.60	0.99	0.022
3. BD (1) C 1 - H 4	1.98355	RY*(1) C 2	0.00252	0.55	1.19	0.023
3. BD (1) C 1 - H 4		RY*(1) C 3	0.00751	0.59	1.28	0.025
3. BD (1) C 1 - H 4		BD*(1) C 2 - H 7	0.01103	1.08	0.94	0.028
3. BD (1) C 1 - H 4		BD*(1) C 3 - Cl 9	0.03865	3.01	0.65	0.040
4. BD (1) C 1 - H 5	1.98494	RY*(2) C 2	0.00252	0.52	1.23	0.023
4. BD (1) C 1 - H 5		RY*(1) C 3	0.00751	0.65	1.28	0.026
4. BD (1) C 1 - H 5		BD*(1) C 2 - H 6	0.01244	1.20	0.94	0.030
4. BD (1) C 1 - H 5		BD*(1) C 2 - H 7	0.01103	0.54	0.94	0.020
4. BD (1) C 1 - H 5		BD*(1) C 3 - H 8	0.02670	1.41	0.94	0.033
5. BD (1) C 2 - C 3	1.96670	RY*(1) C 1	0.00459	2.03	1.24	0.045
5. BD (1) C 2 - C 3		RY*(1) Cl 9	0.00286	0.69	1.27	0.027
5. BD (1) C 2 - C 3		BD*(1) C 1 - C 2	0.02010	5.07	0.88	0.060
5. BD (1) C 2 - C 3		BD*(1) C 1 - C 3	0.03929	6.13	0.91	0.067
5. BD (1) C 2 - C 3		BD*(1) C 1 - H 4	0.01243	2.37	0.99	0.043
5. BD (1) C 2 - C 3		BD*(1) C 1 - H 5	0.01102	1.94	0.99	0.039
5. BD (1) C 2 - C 3		BD*(1) C 2 - H 7	0.01103	0.55	0.99	0.021
5. BD (1) C 2 - C 3		BD*(1) C 3 - H 8	0.02670	0.60	0.99	0.022
6. BD (1) C 2 - H 6	1.98355	RY*(1) C 1	0.00459	0.55	1.19	0.023
6. BD (1) C 2 - H 6		RY*(1) C 3	0.00751	0.59	1.28	0.025
6. BD (1) C 2 - H 6		BD*(1) C 1 - H 5	0.00102	1.08	0.94	0.028
6. BD (1) C 2 - H 6		BD*(1) C 3 - Cl 9	0.03865	3.01	0.65	0.040
7. BD (1) C 2 - H 7	1.98493	RY*(2) C 1	0.00252	0.52	1.23	0.023
7. BD (1) C 2 - H 7		RY*(1) C 3	0.00751	0.65	1.28	0.026
7. BD (1) C 2 - H 7		BD*(1) C 1 - H 4	0.01243	1.21	0.94	0.030
7. BD (1) C 2 - H 7		BD*(1) C 1 - H 5	0.01102	0.54	0.94	0.020
7. BD (1) C 2 - H 7		BD*(1) C 3 - H 8	0.02670	1.40	0.94	0.032
8. BD (1) C 3 - H 8	1.98721	RY*(1) C 1	0.00459	0.59	1.21	0.024
8. BD (1) C 3 - H 8		RY*(1) C 2	0.00459	0.59	1.21	0.024
8. BD (1) C 3 - H 8		RY*(2) Cl 9	0.00205	0.67	1.22	0.026
8. BD (1) C 3 - H 8		BD*(1) C 1 - H 4	0.01243	0.54	0.96	0.020
8. BD (1) C 3 - H 8		BD*(1) C 1 - H 5	0.01102	1.26	0.96	0.031
8. BD (1) C 3 - H 8		BD*(1) C 2 - H 6	0.01244	0.54	0.96	0.020
8. BD (1) C 3 - H 8		BD*(1) C 2 - H 7	0.01103	1.26	0.96	0.031

8. BD (1) C 3 - H 8		BD*(1) C 3 -Cl 9	0.03865	1.14	0.67	0.025
9. BD (1) C 3 -Cl 9	1.99092	RY*(2) C 1	0.00252	0.60	1.38	0.026
9. BD (1) C 3 -Cl 9		RY*(2) C 2	0.00252	0.60	1.38	0.026
9. BD (1) C 3 -Cl 9		BD*(1) C 1 - H 4	0.01243	0.68	1.09	0.024
9. BD (1) C 3 -Cl 9		BD*(1) C 2 - H 6	0.01244	0.69	1.09	0.024
10. CR (1) C 1	1.99922	RY*(1) C 2	0.00459	0.68	10.71	0.076
10. CR (1) C 1		RY*(1) C 3	0.00751	1.16	10.81	0.100
10. CR (1) C 1		BD*(1) C 3 -Cl 9	0.03865	0.55	10.18	0.068
11. CR (1) C 2	1.99922	RY*(1) C 1	0.00459	0.68	10.71	0.076
11. CR (1) C 2		RY*(1) C 3	0.00751	1.16	10.81	0.100
11. CR (1) C 2		BD*(1) C 3 -Cl 9	0.03865	0.55	10.18	0.068
12. CR (1) C 3	1.99891	RY*(1) C 1	0.00459	0.69	10.78	0.077
12. CR (1) C 3		RY*(1) C 2	0.00459	0.69	10.78	0.077
12. CR (1) C 3		RY*(4) H 8	0.00016	0.50	11.94	0.069
12. CR (1) C 3		BD*(1) C 1 - C 3	0.03929	0.52	10.45	0.067
12. CR (1) C 3		BD*(1) C 2 - C 3	0.03927	0.52	10.45	0.067
12. CR (1) C 3		BD*(1) C 3 -Cl 9	0.03865	2.41	10.24	0.141
14. CR (2) Cl 9	1.99978	RY*(2) C 3	0.00300	0.99	11.44	0.095
14. CR (2) Cl 9		RY*(3) C 3	0.00226	0.77	11.31	0.083
18. LP (1) Cl 9	1.99512	RY*(2) C 3	0.00300	1.68	1.91	0.051
18. LP (1) Cl 9		RY*(3) C 3	0.00226	0.87	1.79	0.035
19. LP (2) Cl 9	1.97192	RY*(1) C 3	0.00751	1.02	1.07	0.030
19. LP (2) Cl 9		BD*(1) C 1 - C 3	0.03929	1.80	0.65	0.031
19. LP (2) Cl 9		BD*(1) C 2 - C 3	0.03927	1.80	0.65	0.031
19. LP (2) Cl 9		BD*(1) C 3 - H 8	0.02670	4.42	0.73	0.051
20. LP (3) Cl 9	1.97138	RY*(4) C 3	0.00190	0.63	1.58	0.028
20. LP (3) Cl 9		BD*(1) C 1 - C 3	0.03929	3.54	0.64	0.043
20. LP (3) Cl 9		BD*(1) C 2 - C 3	0.03927	3.54	0.64	0.043

TABLE 4(d). Second-order perturbation theory analysis of C3Br using B3LYP/6-311++G functional

Donor NBO (i)	ED(e)	Acceptor NBO (j)	ED(e)	E(2)	E(i)-E(j)	F(i, j)
				kcal/mol	a.u	a.u
1. BD (1) C 1 - C 2	1.95390	RY*(1) C 3	0.00763	1.41	1.24	0.038
1. BD (1) C 1 - C 2		RY*(4) C 3	0.00169	0.90	1.35	0.032
1. BD (1) C 1 - C 2		BD*(1) C 1 - C 3	0.03636	5.77	0.87	0.063
1. BD (1) C 1 - C 2		BD*(1) C 2 - C 3	0.03635	5.76	0.87	0.063
1. BD (1) C 1 - C 2		BD*(1) C 3 - H 8	0.02380	3.03	0.96	0.048
1. BD (1) C 1 - C 2		BD*(1) C 3 -Br 9	0.04287	6.80	0.61	0.057
2. BD (1) C 1 - C 3	1.96706	RY*(1) C 2	0.00463	2.00	1.24	0.045
2. BD (1) C 1 - C 3		RY*(1) Br 9	0.00223	0.51	1.20	0.022

2. BD (1) C 1 - C 3	BD*(1) C 1 - C 2	0.01971	5.01	0.89	0.060
2. BD (1) C 1 - C 3	BD*(1) C 1 - H 5	0.01164	0.60	0.99	0.022
2. BD (1) C 1 - C 3	BD*(1) C 2 - C 3	0.03635	6.05	0.91	0.066
2. BD (1) C 1 - C 3	BD*(1) C 2 - H 6	0.01274	2.39	0.99	0.044
2. BD (1) C 1 - C 3	BD*(1) C 2 - H 7	0.01165	1.97	0.99	0.040
2. BD (1) C 1 - C 3	BD*(1) C 3 - H 8	0.02380	0.52	1.00	0.020
3. BD (1) C 1 - H 4 1.98262	RY*(1) C 2	0.00463	0.60	1.19	0.024
3. BD (1) C 1 - H 4	RY*(1) C 3	0.00763	0.58	1.23	0.024
3. BD (1) C 1 - H 4	BD*(1) C 2 - H 7	0.01165	1.05	0.94	0.028
3. BD (1) C 1 - H 4	BD*(1) C 3 -Br 9	0.04287	3.36	0.60	0.040
4. BD (1) C 1 - H 5 1.98504	RY*(2) C 2	0.00289	0.53	1.19	0.022
4. BD (1) C 1 - H 5	RY*(1) C 3	0.00763	0.66	1.23	0.025
4. BD (1) C 1 - H 5	RY*(2) C 3	0.00298	0.50	1.48	0.024
4. BD (1) C 1 - H 5	BD*(1) C 2 - H 6	0.01274	1.20	0.94	0.030
4. BD (1) C 1 - H 5	BD*(1) C 2 - H 7	0.01165	0.55	0.94	0.020
4. BD (1) C 1 - H 5	BD*(1) C 3 - H 8	0.02380	1.43	0.95	0.033
5. BD (1) C 2 - C 3 1.96708	RY*(1) C 1	0.00463	2.00	1.24	0.045
5. BD (1) C 2 - C 3	RY*(1) Br 9	0.00223	0.51	1.20	0.022
5. BD (1) C 2 - C 3	BD*(1) C 1 - C 2	0.01971	5.01	0.89	0.060
5. BD (1) C 2 - C 3	BD*(1) C 1 - C 3	0.03636	6.05	0.91	0.066
5. BD (1) C 2 - C 3	BD*(1) C 1 - H 4	0.01274	2.39	0.99	0.044
5. BD (1) C 2 - C 3	BD*(1) C 1 - H 5	0.01164	1.97	0.99	0.040
5. BD (1) C 2 - C 3	BD*(1) C 2 - H 7	0.03635	0.60	0.99	0.022
5. BD (1) C 2 - C 3	BD*(1) C 3 - H 8	0.02380	0.52	1.00	0.020
6. BD (1) C 2 - H 6 1.98262	RY*(1) C 1	0.00463	0.60	1.19	0.024
6. BD (1) C 2 - H 6	RY*(1) C 3	0.00763	0.58	1.23	0.024
6. BD (1) C 2 - H 6	BD*(1) C 1 - H 5	0.01164	1.05	0.94	0.028
6. BD (1) C 2 - H 6	BD*(1) C 3 -Br 9	0.04287	3.36	0.60	0.040
7. BD (1) C 2 - H 7 1.98504	RY*(2) C 1	0.00289	0.53	1.19	0.022
7. BD (1) C 2 - H 7	RY*(1) C 3	0.00763	0.66	1.23	0.025
7. BD (1) C 2 - H 7	RY*(2) C 3	0.00298	0.50	1.48	0.024
7. BD (1) C 2 - H 7	BD*(1) C 1 - H 4	0.01274	1.20	0.94	0.030
7. BD (1) C 2 - H 7	BD*(1) C 1 - H 5	0.01164	0.55	0.94	0.020
7. BD (1) C 2 - H 7	BD*(1) C 3 - H 8	0.02380	1.43	0.95	0.033
8. BD (1) C 3 - H 8 1.98699	RY*(1) C 1	0.00463	0.67	1.20	0.025
8. BD (1) C 3 - H 8	RY*(1) C 2	0.00463	0.67	1.20	0.025
8. BD (1) C 3 - H 8	BD*(1) C 1 - H 4	0.01274	0.55	0.96	0.021
8. BD (1) C 3 - H 8	BD*(1) C 1 - H 5	0.01164	1.29	0.96	0.031
8. BD (1) C 3 - H 8	BD*(1) C 2 - H 6	0.01274	0.55	0.96	0.021
8. BD (1) C 3 - H 8	BD*(1) C 2 - H 7	0.03635	1.29	0.96	0.031
8. BD (1) C 3 - H 8	BD*(1) C 3 -Br 9	0.04287	1.30	0.62	0.025

9. BD (1) C 3 -Br 9	1.98682	RY*(2) C 1	0.00289	0.85	1.28	0.029
9. BD (1) C 3 -Br 9		RY*(2) C 2	0.00289	0.85	1.28	0.029
9. BD (1) C 3 -Br 9		BD*(1) C 1 - H 4	0.01274	0.80	1.02	0.026
9. BD (1) C 3 -Br 9		BD*(1) C 2 - H 6	0.01274	0.81	1.02	0.026
10. CR (1) C 1	1.99921	RY*(1) C 2	0.00463	0.67	10.71	0.076
10. CR (1) C 1		RY*(1) C 3	0.00763	1.22	10.75	0.102
10. CR (1) C 1		BD*(1) C 3 -Br 9	0.04287	0.66	10.12	0.074
11. CR (1) C 2	1.99921	RY*(1) C 1	0.00463	0.67	10.71	0.076
11. CR (1) C 2		RY*(1) C 3	0.00463	1.22	10.75	0.102
11. CR (1) C 2		BD*(1) C 3 -Br 9	0.04287	0.66	10.12	0.074
12. CR (1) C 3	1.99893	RY*(1) C 1	0.00169	0.67	10.77	0.076
12. CR (1) C 3		RY*(1) C 2	0.00763	0.67	10.77	0.076
12. CR (1) C 3		BD*(1) C 3 -Br 9	0.04287	2.43	10.18	0.142
15. CR (3) Br 9	1.99982	RY*(4) C 3	0.00169	1.08	12.26	0.103
27. LP (1) Br 9	1.99627	RY*(2) C 3	0.00298	0.55	1.90	0.029
27. LP (1) Br 9		RY*(4) C 3	0.00169	1.05	1.77	0.038
28. LP (2) Br 9	1.97747	RY*(1) C 3	0.00763	0.71	0.99	0.024
28. LP (2) Br 9		BD*(1) C 1 - C 3	0.03636	1.38	0.62	0.026
28. LP (2) Br 9		BD*(1) C 2 - C 3	0.03635	1.39	0.62	0.026
28. LP (2) Br 9		BD*(1) C 3 - H 8	0.02380	3.17	0.72	0.043
29. LP (3) Br 9	1.97676	BD*(1) C 1 - C 3	0.03636	2.71	0.62	0.037
29. LP (3) Br 9		BD*(1) C 2 - C 3	0.03635	2.70	0.62	0.037

TABLE 4(e). Second-order perturbation theory analysis of C3N using B3LYP/6-311++G functional

Donor NBO (i)	ED(e)	Acceptor NBO (j)	ED(e)	E(2)	E(i)-E(j)	F(i, j)
				kcal/mol	a.u.	a.u.
1. BD (1) C 1 - C 2	1.97385	RY*(1) N 7	0.00288	0.94	1.25	0.031
1. BD (1) C 1 - C 2		RY*(2) N 7	0.00237	1.37	1.43	0.040
1. BD (1) C 1 - C 2		BD*(1) C 1 - N 7	0.02104	3.24	0.85	0.047
1. BD (1) C 1 - C 2		BD*(1) C 2 - N 7	0.02101	3.24	0.85	0.047
1. BD (1) C 1 - C 2		BD*(1) N 7 - H 8	0.00967	1.00	0.99	0.028
2. BD (1) C 1 - H 3	1.99132	BD*(1) C 2 - H 5	0.01594	0.58	0.93	0.021
2. BD (1) C 1 - H 3		BD*(1) C 2 - H 6	0.02050	1.44	0.94	0.033
3. BD (1) C 1 - H 4	1.99014	RY*(1) N 7	0.00288	0.62	1.21	0.025
3. BD (1) C 1 - H 4		BD*(1) C 2 - H 5	0.01594	1.16	0.93	0.029
3. BD (1) C 1 - H 4		BD*(1) C 2 - H 6	0.02050	0.53	0.94	0.020
3. BD (1) C 1 - H 4		BD*(1) N 7 - H 8	0.00967	1.15	0.94	0.029
4. BD (1) C 1 - N 7	1.97414	RY*(1) C 2	0.00605	2.13	1.43	0.049
4. BD (1) C 1 - N 7		BD*(1) C 1 - C 2	0.01404	4.05	0.96	0.056
4. BD (1) C 1 - N 7		BD*(1) C 2 - H 5	0.01594	1.71	1.01	0.037

4. BD (1) C 1 - N 7		BD*(1) C 2 - H 6	0.02050	1.65	1.02	0.037
4. BD (1) C 1 - N 7		BD*(1) C 2 - N 7	0.02101	4.75	0.90	0.058
5. BD (1) C 2 - H 5	1.99132	BD*(1) C 1 - H 3	0.01589	0.58	0.93	0.021
5. BD (1) C 2 - H 5		BD*(1) C 1 - H 4	0.02043	1.44	0.94	0.033
6. BD (1) C 2 - H 6	1.99013	RY*(1) N 7	0.00258	0.62	1.21	0.025
6. BD (1) C 2 - H 6		BD*(1) C 1 - H 3	0.01589	1.16	0.93	0.029
6. BD (1) C 2 - H 6		BD*(1) C 1 - H 4	0.02043	0.53	0.94	0.020
6. BD (1) C 2 - H 6		BD*(1) N 7 - H 8	0.06967	1.15	0.94	0.029
7. BD (1) C 2 - N 7	1.97419	RY*(1) C 1	0.00605	2.12	1.43	0.049
7. BD (1) C 2 - N 7		BD*(1) C 1 - C 2	0.01404	4.04	0.96	0.056
7. BD (1) C 2 - N 7		BD*(1) C 1 - H 3	0.01589	1.70	1.01	0.037
7. BD (1) C 2 - N 7		BD*(1) C 1 - H 4	0.02043	1.64	1.02	0.037
7. BD (1) C 2 - N 7		BD*(1) C 1 - N 7	0.02104	4.74	0.90	0.058
8. BD (1) N 7 - H 8	1.98389	RY*(1) C 1	0.00605	0.65	1.43	0.027
8. BD (1) N 7 - H 8		RY*(2) C 1	0.00223	0.80	1.66	0.033
8. BD (1) N 7 - H 8		RY*(1) C 2	0.00605	0.65	1.43	0.027
8. BD (1) N 7 - H 8		RY*(2) C 2	0.00223	0.80	1.67	0.033
8. BD (1) N 7 - H 8		BD*(1) C 1 - H 3	0.01589	0.76	1.01	0.025
8. BD (1) N 7 - H 8		BD*(1) C 1 - H 4	0.02043	1.08	1.02	0.030
8. BD (1) N 7 - H 8		BD*(1) C 2 - H 5	0.01594	0.76	1.01	0.025
8. BD (1) N 7 - H 8		BD*(1) C 2 - H 6	0.02050	1.08	1.02	0.030
9. CR (1) C 1	1.99934	RY*(1) C 2	0.00605	0.91	10.89	0.089
10. CR (1) C 2	1.99934	RY*(1) C 1	0.00605	0.91	10.89	0.089
11. CR (1) N 7	1.99956	RY*(1) C 1	0.00605	0.72	14.96	0.093
11. CR (1) N 7		RY*(1) C 2	0.00605	0.72	14.96	0.093
11. CR (1) N 7		RY*(4) H 8	0.00014	0.72	16.41	0.097
12. LP (1) N 7	1.95517	RY*(1) C 1	0.00605	1.04	1.21	0.032
12. LP (1) N 7		RY*(3) C 1	0.00154	0.67	1.64	0.030
12. LP (1) N 7		RY*(1) C 2	0.00605	1.04	1.21	0.032
12. LP (1) N 7		RY*(3) C 2	0.00154	0.67	1.64	0.030
12. LP (1) N 7		RY*(1) H 8	0.00196	1.74	1.42	0.045
12. LP (1) N 7		RY*(2) H 8	0.00089	0.55	1.54	0.026
12. LP (1) N 7		BD*(1) C 1 - H 3	0.01589	2.17	0.79	0.037
12. LP (1) N 7		BD*(1) C 1 - H 4	0.02043	2.56	0.80	0.041
12. LP (1) N 7		BD*(1) C 2 - H 5	0.01594	2.18	0.79	0.037
12. LP (1) N 7		BD*(1) C 2 - H 6	0.02050	2.57	0.80	0.041

TABLE 4(f). Second-order perturbation theory analysis of C3O using B3LYP/6-311++G functional

Donor NBO (i)	ED(e)	Acceptor NBO (j)	ED(e)	E(2)	E(i)-E(j)	F(i, j)
				kcal/mol	a.u.	a.u.
1. BD (1) C 1 - C 2	1.98085	RY*(2) O 7	0.00120	1.09	1.67	0.038
1. BD (1) C 1 - C 2		BD*(1) C 1 - O 7	0.02085	1.18	0.84	0.028
1. BD (1) C 1 - C 2		BD*(1) C 2 - O 7	0.02089	1.19	0.84	0.028
2. BD (1) C 1 - H 3	1.99196	RY*(3) C 2	0.00736	0.54	1.57	0.026
2. BD (1) C 1 - H 3		BD*(1) C 2 - H 5	0.02199	0.57	0.93	0.021
2. BD (1) C 1 - H 3		BD*(1) C 2 - H 6	0.02199	1.40	0.93	0.032
2. BD (1) C 1 - H 3		BD*(1) C 2 - O 7	0.02089	0.87	0.78	0.023
3. BD (1) C 1 - H 4	1.99196	RY*(3) C 2	0.00134	0.54	1.57	0.026
3. BD (1) C 1 - H 4		BD*(1) C 2 - H 5	0.02199	1.40	0.93	0.032
3. BD (1) C 1 - H 4		BD*(1) C 2 - H 6	0.02199	0.57	0.93	0.021
3. BD (1) C 1 - H 4		BD*(1) C 2 - O 7	0.02089	0.87	0.78	0.023
4. BD (1) C 1 - O 7	1.97975	RY*(1) C 2	0.00736	1.04	1.50	0.035
4. BD (1) C 1 - O 7		BD*(1) C 1 - C 2	0.00803	2.71	1.04	0.047
4. BD (1) C 1 - O 7		BD*(1) C 2 - H 5	0.02199	1.20	1.08	0.032
4. BD (1) C 1 - O 7		BD*(1) C 2 - H 6	0.02199	1.20	1.08	0.032
4. BD (1) C 1 - O 7		BD*(1) C 2 - O 7	0.02080	5.23	0.92	0.062
5. BD (1) C 2 - H 5	1.99197	RY*(3) C 1	0.00134	0.54	1.57	0.026
5. BD (1) C 2 - H 5		BD*(1) C 1 - H 3	0.02210	0.57	0.93	0.021
5. BD (1) C 2 - H 5		BD*(1) C 1 - H 4	0.02210	1.40	0.93	0.032
5. BD (1) C 2 - H 5		BD*(1) C 1 - O 7	0.02085	0.87	0.78	0.023
6. BD (1) C 2 - H 6	1.99197	RY*(3) C 1	0.00134	0.54	1.57	0.026
6. BD (1) C 2 - H 6		BD*(1) C 1 - H 3	0.02210	1.40	0.93	0.032
6. BD (1) C 2 - H 6		BD*(1) C 1 - H 4	0.02210	0.57	0.93	0.021
6. BD (1) C 2 - H 6		BD*(1) C 1 - O 7	0.02085	0.87	0.78	0.023
7. BD (1) C 2 - O 7	1.97969	RY*(1) C 1	0.00737	1.05	1.50	0.035
7. BD (1) C 2 - O 7		BD*(1) C 1 - C 2	0.00803	2.72	1.04	0.048
7. BD (1) C 2 - O 7		BD*(1) C 1 - H 3	0.02210	1.21	1.07	0.032
7. BD (1) C 2 - O 7		BD*(1) C 1 - H 4	0.02210	1.21	1.07	0.032
7. BD (1) C 2 - O 7		BD*(1) C 1 - O 7	0.02085	5.24	0.92	0.062
8. CR (1) C 1	1.99928	RY*(1) C 2	0.00736	0.98	10.91	0.093
8. CR (1) C 1		RY*(6) C 2	0.00010	0.64	10.99	0.075
8. CR (1) C 1		BD*(1) C 2 - O 7	0.02089	0.88	10.34	0.086
9. CR (1) C 2	1.99928	RY*(1) C 1	0.00737	0.98	10.91	0.093
9. CR (1) C 2		RY*(6) C 1	0.00010	0.64	10.98	0.075
9. CR (1) C 2		BD*(1) C 1 - O 7	0.02085	0.88	10.34	0.086
10. CR (1) O 7	1.99988	RY*(1) C 1	0.00737	0.80	19.75	0.113
10. CR (1) O 7		RY*(4) C 1	0.00083	0.51	20.46	0.091
10. CR (1) O 7		RY*(1) C 2	0.00736	0.80	19.75	0.112

10. CR (1) O 7		RY*(4) C 2	0.00083	0.51	20.46	0.091
11. LP (1) O 7	1.99003	RY*(1) C 1	0.00737	3.04	1.55	0.061
11. LP (1) O 7		RY*(5) C 1	0.00390	0.51	2.58	0.033
11. LP (1) O 7		RY*(1) C 2	0.00736	3.03	1.55	0.061
11. LP (1) O 7		RY*(5) C 2	0.00590	0.52	2.57	0.033
12. LP (2) O 7	1.92793	RY*(2) C 1	0.00236	1.63	2.07	0.053
12. LP (2) O 7		RY*(2) C 2	0.00236	1.63	2.07	0.053
12. LP (2) O 7		BD*(1) C 1 - H 3	0.02210	5.30	0.68	0.054
12. LP (2) O 7		BD*(1) C 1 - H 4	0.02210	5.30	0.68	0.054
12. LP (2) O 7		BD*(1) C 2 - H 5	0.02210	5.27	0.68	0.054
12. LP (2) O 7		BD*(1) C 2 - H 6	0.02210	5.27	0.68	0.054

TABLE 4(g). Second-order perturbation theory analysis of C3S using B3LYP/6-311++G functional

Donor NBO (i)	ED(e)	Acceptor NBO (j)	ED(e)	E(2)	E(i)-E(j)	F(i, j)
				kcal/mol	a.u.	a.u.
1. BD (1) C 1 - C 2	1.96918	RY*(1) S 7	0.00476	2.89	1.36	0.056
2. BD (1) C 1 - H 3	1.99073	RY*(2) C 2	0.00204	0.65	1.23	0.025
2. BD (1) C 1 - H 3		BD*(1) C 2 - H 5	0.01974	0.63	0.95	0.022
2. BD (1) C 1 - H 3		BD*(1) C 2 - H 6	0.01974	1.81	0.95	0.037
3. BD (1) C 1 - H 4	1.99073	RY*(2) C 2	0.00204	0.65	1.23	0.025
3. BD (1) C 1 - H 4		BD*(1) C 2 - H 5	0.01974	1.81	0.95	0.037
3. BD (1) C 1 - H 4		BD*(1) C 2 - H 6	0.01974	0.63	0.95	0.022
4. BD (1) C 1 - S 7	1.96396	RY*(1) C 2	0.00656	3.39	1.21	0.058
4. BD (1) C 1 - S 7		BD*(1) C 1 - C 2	0.00593	2.02	0.87	0.038
4. BD (1) C 1 - S 7		BD*(1) C 2 - H 5	0.01974	1.65	0.90	0.035
4. BD (1) C 1 - S 7		BD*(1) C 2 - H 6	0.01974	1.65	0.90	0.035
4. BD (1) C 1 - S 7		BD*(1) C 2 - S 7	0.02657	7.75	0.60	0.061
5. BD (1) C 2 - H 5	1.99073	RY*(2) C 1	0.00204	0.65	1.23	0.025
5. BD (1) C 2 - H 5		BD*(1) C 1 - H 3	0.01973	0.64	0.95	0.022
5. BD (1) C 2 - H 5		BD*(1) C 1 - H 4	0.01973	1.81	0.95	0.037
6. BD (1) C 2 - H 6	1.99073	RY*(2) C 1	0.00204	0.65	1.23	0.025
6. BD (1) C 2 - H 6		BD*(1) C 1 - H 3	0.01973	1.81	0.95	0.037
6. BD (1) C 2 - H 6		BD*(1) C 1 - H 4	0.01973	0.64	0.95	0.022
7. BD (1) C 2 - S 7	1.96397	RY*(1) C 1	0.00204	3.39	1.21	0.058
7. BD (1) C 2 - S 7		BD*(1) C 1 - C 2	0.00593	2.02	0.87	0.038
7. BD (1) C 2 - S 7		BD*(1) C 1 - H 3	0.01973	1.65	0.90	0.035
7. BD (1) C 2 - S 7		BD*(1) C 1 - H 4	0.01973	1.65	0.90	0.035
7. BD (1) C 2 - S 7		BD*(1) C 1 - S 7	0.02656	7.74	0.60	0.061
8. CR (1) C 1	1.99927	RY*(4) C 2	0.00068	0.74	11.26	0.081
8. CR (1) C 1		BD*(1) C 1 - S 7	0.02656	0.58	10.19	0.069

9. CR (1) C 2	1.99927	RY*(4) C 1	0.00656	0.74	11.26	0.081
9. CR (1) C 2		BD*(1) C 2 - S 7	0.02657	0.58	10.19	0.069
11. CR (2) S 7	1.99959	RY*(1) C 1	0.00656	0.65	9.50	0.070
11. CR (2) S 7		RY*(1) C 2	0.00656	0.65	9.50	0.070
15. LP (1) S 7	1.99730	RY*(1) C 1	0.00656	0.59	1.43	0.026
15. LP (1) S 7		RY*(1) C 2	0.00656	0.59	1.43	0.026
15. LP (1) S 7		BD*(1) C 1 - S 7	0.02656	0.51	0.81	0.018
15. LP (1) S 7		BD*(1) C 2 - S 7	0.02657	0.51	0.81	0.018
16. LP (2) S 7	1.94618	RY*(3) C 1	0.00122	0.52	1.98	0.029
16. LP (2) S 7		RY*(3) C 2	0.00122	0.52	1.98	0.029
16. LP (2) S 7		BD*(1) C 1 - H 3	0.01973	3.02	0.64	0.040
16. LP (2) S 7		BD*(1) C 1 - H 4	0.01973	3.02	0.64	0.040
16. LP (2) S 7		BD*(1) C 2 - H 5	0.01974	3.03	0.64	0.040
16. LP (2) S 7		BD*(1) C 2 - H 6	0.01974	3.03	0.64	0.040

In **Tables 4(a)-(g)**, the perturbation energies of donor-acceptor interaction are presented. In Cyclopropane $BD(C1-C2) \rightarrow BD^*(C1-C3)$, $BD(C1-C2) \rightarrow BD^*(C2-C3)$, $BD(C2-C3) \rightarrow BD^*(C1-C2)$, $BD(C2-C3) \rightarrow BD^*(C1-C3)$ have stabilization energies of 5.90 kcal/mol, 5.90 kcal/mol, 5.90 kcal/mol, and 5.89 kcal/mol respectively. Hence, they give stronger stabilization to the molecule. It is also reported from **Table 4(a)**, that the maximum occupancy occurs at CR(C1), CR(C2), and CR(C3) of 1.99931 which suggest that CR(C1), CR(C2), and CR(C3) are essentially controlled by the p-character of the hybrid orbitals. For **Table 4(b)**, $LP(F9) \rightarrow RY^*(C3)$, $LP(F9) \rightarrow BD^*(C3-H8)$ have stabilization energies of 7.48 kcal/mol and 6.52 kcal/mol respectively. Hence, they give stronger stabilization to the molecule. This stronger interaction around the ring could enhance the activity of C3F. It is noted that the maximum occupancy occurs at 1.99994, 1.99930, 1.99930 which are obtained for CR(F9), CR(C1), and CR(C2) respectively. The results suggest that CR(F9), CR(C1), and CR(C2) are essentially controlled by the p-character of the hybrid orbitals.

Table 4(c), $(C3Cl)$ gives $BD(C1-C3) \rightarrow RY^*(C2-C3)$, $BD(C2-C3) \rightarrow RY^*(C1-C3)$, $BD(C1-C2) \rightarrow BD^*(C3-Cl9)$ having 6.14kcal/mol, 6.13kcal/mol and 6.05kcal/mol stabilization energies. These stabilization energies are the strongest of any interactions in Table. The maximum occupancies occur at 1.99978, 1.99922, 1.99922 which corresponds to CR(Cl9), CR(C1), and CR(C2) respectively. For **Table 4(d)**, the interactions $BD(C1-C3) \rightarrow BD^*(C2-C3)$, $BD(C2-C3) \rightarrow BD^*(C1-C3)$ with stabilization energies, 6.05kcal/mol and 6.05kcal/mol respectively gives the strongest stabilization to the molecule. The maximum occupancies occur at CR(BR9) (1.99982), and CR(C1) (1.99921). Therefore, CR(BR9) and CR(C1) are essentially controlled by the p-character of the hybrid orbitals. From **Table 4(e)**, the interactions $BD(C1-N7) \rightarrow BD^*(C1-C2)$, $BD(C1-N7) \rightarrow BD^*(C2-N7)$, $BD(C2-N7) \rightarrow BD^*(C1-C2)$, $BD(C2-N7) \rightarrow BD^*(C1-N7)$ with stabilization energies of 4.05 kcal/mol, 4.75 kcal/mol, 4.04 kcal/mol, 4.74 kcal/mol respectively give the strongest stabilization to the molecule. It is also seen from **Table 4(e)**, that the maximum occupancies occur at CR(C1) (1.99934), CR(C2) (1.99934), and CR (N7) (1.99956). From **Table**

4(f), the interactions $LP(O7) \rightarrow BD^*(C1 - H3)$, $LP(O7) \rightarrow BD^*(C1 - H4)$, $LP(O7) \rightarrow BD^*(C2 - H5)$, $LP(O7) \rightarrow BD^*(C2 - H6)$ has stabilization energy 5.30kcal/mol, 5.30 kcal/mol, 5.27 kcal/mol, 5.27 kcal/mol respectively. Hence, the interactions give the strongest stabilization to the molecule. The maximum occupancies occur at CR(C1) (1.99928), CR(C2) (1.99928), and CR(O7) (1.99988). Therefore, CR(C1), CR(C2), and CR(O7) are essentially controlled by the p-character of the hybrid orbitals. As reported in **Table 4(g)**, the interactions $LP(S7) \rightarrow BD^*(C1 - H3)$, $LP(S7) \rightarrow BD^*(C1 - H4)$, $LP(S7) \rightarrow BD^*(C2 - H5)$, $LP(S7) \rightarrow BD^*(C2 - H6)$ give stabilization energies of 3.02 kcal/mol, 3.02 kcal/mol, 3.03 kcal/mol, and 3.03 kcal/mol respectively. Hence, these give the strongest stabilization to the molecule. The maximum occupancies occur at CR(C1) (1.99927), CR(C2) (1.99927), and CR(S7) 1.99950. Hence, CR(C1), CR(C2), and CR(C3) are essentially controlled by the p-character of the hybrid orbitals.

Therefore, it can be generalized that the strongest stabilization to the cyclopropane molecule for the heteroatoms will follow the trend $C3S < C3N < C3O$. It is also observed that for the halogens the strongest stabilization for the cyclopropane molecule follows the trend $C3Br < C3Cl < C3F < C3$. The strong intra-molecular hyperconjugation interaction of the BD and CR electrons of C-C anti C-C bond in the ring leads to stabilization of the cyclopropane ring as evident from the 2nd order perturbation analysis.

3.3 Atomic Dipole Corrected Hirshfield (ADCH) Population Analysis

In the ADCH method proposed by Tian Lu [20] the atomic dipole moments of each atom are expanded to correction charges placed at neighbor atoms, then ADCH charge is just the sum of original Hirshfield charge and correction charge. ADCH charges have an important role in the application of quantum chemical calculation to the molecular system because of the atomic charge effect, molecular polarizability, and other molecular properties that characterize a system. The charge distribution over the atoms suggests the formation of donor and acceptor pairs involving the charge transfer in the molecule. The ADCH distribution of the molecule is calculated on B3LYP at 6-311++G(d, p) level theory and the charges are presented in **Table 5**.

TABLE 5. ADCH calculated charges of C3, C3F, C3Cl, C3Br, C3N, C3O, C3S

	C3	C3F	C3Cl	C3Br	C3N	C3O	C3S
Atom	At. CHARGES	At. CHARGES	At. CHARGES	At. CHARGES	At. CHARGES	At. CHARGES	At. CHARGES
C (1)	-0.21160595	-0.21830166	-0.1984685	-0.19471156	-0.11513078	-0.11085671	-0.18549534
C (2)	-0.2115842	-0.21829324	-0.19840915	-0.19466349	-0.11488541	-0.11110678	-0.18559933
C (3)	-0.21152227	0.02650321	-0.07726481	-0.10892618			
H (4)	0.10579042	0.12255563	0.12717517	0.12818269	0.11075019	0.11916845	0.13603914
H (5)	0.10579043	0.11916354	0.11240628	0.11180341	0.11044202	0.11934645	0.13605037
H (6)	0.1057887	0.12254937	0.12716454	0.12816903	0.11061105	0.11934645	0.13605037
H (7)	0.1057887	0.11915565	0.11242609	0.11182239			
N (7)					-0.53076702		
O (7)						-0.2550663	
S (7)							-0.17308435
H (8)	0.10577709	0.11514411	0.12278405	0.12827548	0.3184429		
H (9)	0.10577709						
F (9)		-0.1884766					
Cl (9)			-0.12781402				
Br (9)				-0.10995086			
H (3)					0.11053705	0.11934645	0.13603914

The charge distribution of the title compound show that all the halogens and heteroatoms have negative charges and the highest negative value is found with Nitrogen (-0.53076702) making it the best candidate to undergo nucleophilic substitution reactions. It increases in the following order Br9<Cl9<S7<F9<O7<N7. Besides, negative charges spread over C1, C2. This is due to the position of the atoms attached to the molecule.

3.4 Density of States (DOS)

Density-of-states (DOS) is an important concept of solid physics, which represents the number of states in-unit energy interval since energy level is proximate, so DOS can be plotted as a curve matrix [21]. **Fig. 2**, the OPDOS, T-DOS, and P-DOS of C3, C3F, C3Cl, C3Br, C3Cl, C3Br are reported. In cyclopropane, only two fragments are corresponding to the contribution by carbon and hydrogen respectively. It can be seen that in most valence molecular orbitals fragment 1 (carbons) has the highest amount of contribution. Fragment 2 (hydrogens) contributes to the valence Molecular orbitals (MOs) but not as much as frag 1. The green curve corresponds to the overlap partial density of states (OPDOS) between fragments 1 and 2, its positive value indicates that the MOs in the corresponding energy range show bonding character between the two fragments while the negative value of OPDOS behave as anti-bonding orbital between the two fragments. Since there is little or no negative value of OPDOS in C3. Therefore, its orbitals constitute MOs which show bonding character between the two fragments.

Fig. 2. OPDOS, PDOS and TDOS for C₃, C₃F, C₃Cl, C₃Br, C₃N, C₃O and C₃S

In C₃F, the axis at the left side corresponds to T-DOS and P-DOS, while the one at the R.H.S corresponds to OPDOS. It can be seen that in most valence MOs, fragment 2 (Fluorine) has the highest amount of contribution. Fragment 1 (Carbons) also contributes significantly to the valence MOs, but the contribution mainly comes between -0.47 to -0.35 a.u. Fragment 3

(hydrogens) contributes significantly to the MOs but the main contribution comes from -0.46 to -0.34 a.u. OPDOS between fragments 1 and 2 shows bonding character -0.60 to -0.45 a.u. and displays anti-bonding character between -0.35 and -0.25 a.u. For C3Cl, it can be observed that in most valence MOs fragment 2 (chlorine) has the highest amount of contribution. Fragment 1 mainly contributes to the valence MOs between -0.45 and -0.35 a.u. The bonding character between the two fragments (1 and 2) i.e positive OPDOS occurs at -0.45 a.u to -0.34 a.u while the negative OPDOS between fragments 1 and 2 occurs between -0.34 a.u to -0.20 a.u.

For C3Br, in most valence MOs, fragment 2(Bromine) has the highest amount of contribution. Fragment 1 mainly contributes to the MOs between -0.45 a.u to -0.20 a.u and also between -0.85 a.u to -0.70 a.u. Fragment 3 (hydrogens) also contributes to the valence MOs but the contribution is less than that from fragment 2 and fragment 1. The green curve is the OPDOS between fragment 1 and 2, It's positive value implies that the MOs in the corresponding energy range show bonding character between the two fragments while the negative part implies that the MOs in the corresponding energy range shows antibonding character. The bonding character occurs more than the antibonding character.

In C3N, it can be observed that in most valence MOs that fragment 3 has the highest amount of contribution with fragment 2 (Nitrogen) almost having the same amount of contribution in valence MOs. Fragment 3 also contributes to the MOs, but the contribution is less when compared to the other 2 fragments. The green curve is the OPDOS between fragments 1 and 2. It's positive and negative values indicate that the MOs in the corresponding energy range show bonding and anti-bonding character respectively. For the C3O molecule, fragment 2 (oxygen) contributes the highest in the most valence MOs while fragment 3 contributes the least. Fragment 1 contributes mainly between -0.45 a.u to -0.20 a.u to the valence MOs. The green curve gives the OPDOS between fragments 1 and 2. It shows the bonding and anti-bonding character between the 2 fragments and gives their corresponding energy range. The C3S fragment 2 (Sulphur) contributes the most to the valence MOs. Fragment 1 also contributes to the valence MOs but the highest contribution occurs in the energy range -0.40 a.u to -0.34 a.u and -0.34 a.u to -0.20 a.u. Fragment 3 (hydrogens) gives the least contribution to the valence MOs. The green curve (OPDOS) for C3S between fragments 1 and 2 shows bonding and anti-bonding character, but the bonding character is more prevalent than the anti-bonding character.

3.5 Molecular Electrostatic Potential (MEP)

The molecular electrostatic potential is a quantum-molecular descriptor, which is used to determine or identify molecular sites possibly prone to electrophilic and nucleophilic attacks [22]. MEP, $V(r)$ at a given point $r(x,y,z)$ in the vicinity of a molecule, is defined in terms of the interaction energy between the electrical charge generated from the molecule's electrons and nuclei and a positive charge (a proton) located at r . MEP analyses enable the identification of high susceptible interactive center with a proton in the surrounding space of a molecule [23-24]. The MEP map of C3, C3F, C3Cl, C3Br, C3N, C3O, C3S are reported in **Fig. 3**. The negative (red and orange) area of the MEP is relative to the electrophilic reactivity and the positive blue area is related to the nucleophilic activity. In other words, the blue color indicates the strongest attraction and the red color indicates the strongest repulsion towards electrophiles.

Fig. 3. Representative MEP of C3, C3F, C3Cl, C3Br, C3N, C3O and C3S

For C3, MEP is almost evenly distributed as there are no points or regions for maximum and minimum esp. i.e regions for attack by nucleophiles and electrophiles could evenly occur in any carbon of C3. The MEP map of C3F, shows that the near vicinity of the fluorine atom is more prone to electrophilic attack, while the hydrogens are more sensitive to nucleophilic attacks. For C3Cl, it is observed that the vicinity of the chlorine atom is also more sensitive to electrophilic attack, while the hydrogens are more prone to nucleophilic attacks. The MEP map of C3Br also shows the same effect. Therefore, according to the MEP maps of halogen-substituted cyclopropanes, it can be said that C3X where X is a halogen act as highly nucleophilic sites or regions for electrophilic attacks. In C3N the near vicinity of the Nitrogen atom is prone to electrophilic attacks i.e highly nucleophilic region. For C3O and C3S the MEP diagrams show that the heteroatoms O and S are highly nucleophilic regions and represent sites for attacks by electrophiles

3.6 UV Spectral analysis

In UV spectral analysis absorption maxima and oscillator strengths of cyclopropane molecule has been reported in the **Table S2** of the supporting information. To study the effect of the substituents in cyclopropane molecule the electronic properties such as wavelengths (λ_{max}), oscillator strength and energy values were calculated and given in the table for the molecule, cyclopropane, and Substituted derivatives of cyclopropane molecule. The UV-Vis spectra of all the structures were given in **Figure 4**. UV spectrum of cyclopropane shows 3 transitions and absorption maxima (λ_{max}) observed at 172.35nm with 0.00091 oscillator strength due to transition from HOMO (11) to LUMO (14) as shown in **Figure 4**. In the case of the C3F molecule, there are 3 absorption bands, primary absorption band (166.30nm) with oscillator strength 0.0137, secondary absorption band (176.25nm) with oscillator strength 0.0049, tertiary

absorption band (167.15nm) with oscillator strength 0.0015. The primary and tertiary absorption band show a decrease in wavelength while the secondary absorption band increases in wavelength when compared to the original molecule C3. In the case of C3Cl two absorption bands are observed, the primary absorption band with absorption maxima of 186.2nm with oscillator strength 0.0150nm and secondary absorption band with absorption maxima of 177.6nm and oscillator strength 0.0015. Therefore is an increase in wavelength (λ_{max}) for C3Cl i.e a Bathochromic shift is observed as Cl is substituted in the original molecule. In the case of C3Br, there are also 2 absorption bands observed, the primary absorption band (194.7nm) with oscillator strength of 0.0259 and secondary absorption band (210.9nm) with oscillator strength of 0.0027. It is also seen that there is an increase in wavelength (λ_{max}) for C3Br i.e a Bathochromic shift is observed greater than that of C3Cl when the UV-spectra of substituted Br-C3 is observed.

Fig 4. UV-vis spectra of C3, C3F, C3Cl, C3Br, C3N, C3O and C3S

In the case of N-Cyclopropane three absorption bands are observed, the primary absorption band (195.4nm) with oscillator strength 0.0241, secondary absorption band (188.475nm) with oscillator strength 0.0277, and tertiary absorption band (217.45nm) with oscillator strength 0.0277. Here, also there an increase in the absorption maxima of the wavelength indicating a positive Bathochromic shift when N is substituted in the cyclopropane ring. Also, in the case of C3O 2 absorption bands are observed, the primary absorption band (184.85nm) with oscillator strength of 0.0277 and the secondary absorption band (174.00) with oscillator strength of 0.0277. There is also a positive Bathochromic shift when the UV-spectra of O-substituted cyclopropane molecule is observed due to an increase in absorption maxima of the primary and secondary absorption bands. In C3S only one absorption band is observed, with λ_{max} of 219.675nm with oscillator strength of 0.0316. These also show a positive Bathochromic shift. Comparing the λ_{max} of the primary absorption bands for each of the substituted molecules, the extent of Bathochromic shift increases in the following order, C3F<C3O<C3Cl<C3Br<C3N<C3S.

3.7 Quantum Chemical Descriptors

Conceptual DFT developed by Robert Parr is used to study the reactivity of various chemical systems. The DFT-based global reactivity descriptors are sufficient to describe the stability and reactivity of chemical systems. Electronegativity is one of the most important chemical properties which describe the ability or power of a species (atom, molecule, or ion) to attract electrons towards itself. Chemical hardness (η) measures the chemical activity of an element by determining the resistance to charge transfer in electron number. [25-26]. Chemical potential and chemical hardness are the first and second derivatives of the total energy of a chemical system

respectively. It is expressed as a function of the electron density [27-29] concerning the number of electrons when the external potential is kept constant. The chemical hardness (η) can be thought of as a resistance of a molecule to exchange electron density with the environment. On the other hand, softness was introduced as the inverse of the chemical hardness. Therefore, a hard molecule will be less polarizable and reactivity is less and vice versa. The electrophilicity w index is the ability of an electron loving specie to acquire an extra amount of electron density, given by μ , and the resistance of a molecule to exchange electron density with the environment, given by $\omega = \frac{\mu^2}{\eta}$. Thus, a good electrophile is a species characterized by high chemical potential and low hardness value. The quantum descriptors for the studied structures are presented in **Table 6**.

Table 6. Global reactivity descriptors of C3, C3F, C3Cl, C3Br, C3N, C3O, C3S obtained at B3LYP functional with 6-311++G (d, p) basis set

VIP	2 nd VIP	VEA	ME	CP	HARDNESS	SOFTNESS	EI	NI	CEI	cpds
10.6239	19.7972	-5.1626	2.7307	-2.7307	15.7866	0.0633	0.2362	1.3136	0.4495	C3
10.2545	19.1568	-4.7384	2.7581	-2.7581	14.9929	0.0667	0.2537	1.703	0.4586	C3F
9.9074	17.7768	-3.2769	3.3152	-3.3152	13.1842	0.0758	0.4168	0.8047	0.6407	C3Cl
9.5508	17.1569	-2.6794	3.4357	-3.4357	12.2301	0.0818	0.4826	2.159	0.692	C3Br
9.1002	19.2027	-4.6839	2.2081	-2.2081	13.7841	0.0725	0.1769	2.968	0.2835	C3N
10.3603	21.7778	-4.4822	2.9391	-2.9391	14.8425	0.0674	0.291	1.8141	0.4075	C3O
8.9816	18.3535	-2.647	3.1673	-3.1673	11.6286	0.086	0.4313	2.9267	0.5292	C3S

VIP: Vertical Ionization Potential; VEA: Vertical Electron Affinity; ME: Mulliken Electronegativity;

EI: Electrophilicity Index; NI: Nucleophilicity Index; CEI: Cubic Electrophilicity Index

From **Table 6**, it is observed that the molecule with the highest electronic chemical potential is C3Br, $\mu = -3.4357$, and C3N, $\mu = -2.2081$ has the smallest electronic potential. Therefore, C3Br will act as the strongest electron acceptor of all the molecules while the strongest electron donor will be C3N. **Table 6** shows that halogens increase the size of electronic chemical potential and an increase in the size of the halogens increases the value of the electronic chemical potential. C3 also shows an increase in μ as heteroatoms O and S are substituted in the ring and C3O < C3S, but C3 shows a decrease in μ when N is substituted in the ring. These may be due to the small size of N compared to the other heteroatoms.

As reported in **Table 6**, it is observed that C3S has the least value of hardness 11.6286, and has the greatest value of softness. Hence, it is the most reactive, while C3 has the highest value of hardness and the least value of softness making it the least reactive of the molecules. Therefore, the substitution of halogens and heteroatoms in a C3 ring increases the reactivity of the ring. It increases in the following order C3 < C3F < C3O < C3N < C3Cl < C3Br < C3S. The electrophilicity index has become a very powerful tool for the study of the reactivity of organic molecules participating in polar reactions [30] From **Table 6**, it is seen that the molecule with the highest electrophilic value will be C3Br, while the molecule with the least electrophilic value will be C3N. These molecules have the highest and lowest value of chemical potential respectively. Electrophilicity increases in the following order C3N < C3 < C3F < C3O < C3Cl < C3S < C3Br. Furthermore, the molecule with the highest value of nucleophilicity from the table will be C3N, while C3Cl will be the molecule with the least value of nucleophilicity. Therefore, these make C3N the best nucleophile of all the molecules. Nucleophilicity increases in the following order. C3Cl < C3 < C3F < C3O < C3Br < C3S < C3N.

3.8 Condensed Dual Descriptor and Electrophilic Fukui Functions

Martinez-Araya has explained in recent research [31] that the condensed expression for the dual descriptor will be more useful for the prediction of the preferred sites of a reaction than the nucleophilic and electrophilic Fukui functions in the Hirshfield population analysis. The dual descriptor can be condensed over atomic sites: when $\Delta f_k > 0$ the process is driven by nucleophilic attack on atom k and then that atom k act as electrophilic species; conversely, when $\Delta f_k < 0$ the process is driven by an electrophilic attack over atom k and then atom k act as a nucleophilic species. As can be seen from the table, electrophilic f_k^+ Fukui functions give the three C atoms of cyclopropane equal electrophilic values while the CDD gives C2 as the most nucleophilic atom of the three C atoms. **Table S3** of the supporting information, it is observed that electrophilic f_k^+ Fukui functions give C3 and C1 as the most electrophilic center of C3F, while the nucleophilic f_k^- Fukui function predicts C3 and F9 as the most nucleophilic center for electrophiles. CDD further confirms F as the most nucleophilic center as it has the highest value of CDD of all the atoms in C3F. Similarly, for C3Cl, electrophilic f_k^+ Fukui function predicts Cl9 and C3 as the most electrophilic center for attack by nucleophiles while nucleophilic f_k^- Fukui functions also predict that C3 and Cl9 maintain the position as the most nucleophilic center for electrophiles. Cl9 has the least negative value for CDD making it the most electrophilic center for nucleophilic species. Furthermore, electrophilic f_k^+ and nucleophilic f_k^- functions of C3Br predicts Br9 as the most nucleophilic and electrophilic attack for electrophiles

and nucleophiles while CDD predicts Br9 with the highest negative value as the most nucleophilic center for attack by electrophiles. For the electron-rich C3N, nucleophilic f_k^- Fukui functions predict N7 as the most nucleophilic center for attack by electrophiles. The CDD also predicts N7 as the most nucleophilic center for attack by electrophiles having the highest negative value of CDD. Similarly, electrophilic f_k^+ and nucleophilic f_k^- Fukui functions predict O7 as the most electrophilic and nucleophilic center for attack by both electrophiles and nucleophiles in C3O while CDD predicts O7 as the most nucleophilic center for electrophiles having the highest negative value of CDD. Finally, electrophilic f_k^+ and nucleophilic f_k^- Fukui functions predict S7 as the most electrophilic and nucleophilic center for attack by both electrophiles and nucleophiles in C3S while CDD predicts S7 as the most nucleophilic center due to S7 having the highest negative value of CDD for C3S.

3.9 Thermodynamic properties

The enthalpy (H) of a system is defined as the sum of its internal energy (Q) plus the product of its pressure (p) and volume (V), i.e. $\Delta H = PV$ [32]. The enthalpy of reaction is the difference between the products and reactants of a system [33]. It is a common understanding that when $\Delta H^o_r = > 0$ the reaction is endothermic and when $\Delta H^o_r = < 0$ the reaction is said to be exothermic. In this paper, the thermodynamic properties in the form of enthalpy of reaction of halogen-substituted cyclopropane (C_3H_5X , where X represents F, Cl, and Br), O, N, and S doped cyclopropane are studied and reported in **Tables 7(a) to (f)** respectively. Enthalpy reactions is classified into Endothermic (heat absorption) and Exothermic (heat releasing). Data obtained from our research which was gotten through the density functional theory (DFT) method at the B3LYP/aug-cc-pVDZ and Shermo [34] for enthalpy and free energy calculations shows that for C_3H_5X series, bromocyclopropane, (C_3H_5Br) possesses the highest enthalpy of reaction of the C_3H_5X series at -10.99kcal/mol which is trailed by chlorocyclopropane (C_3H_5Cl) at -28.75kcal/mol while fluorocyclopropane (C_3H_5F) possesses the lowest enthalpy of reaction of the series at -108.5kcal/mol. This is to say that bromocyclopentane is the most exothermic of the series while fluorocyclopentane is the least exothermic of the series. For the O, N, and S doped-cyclopropane, thiirane (C_2H_4S) possesses the highest enthalpy of reaction at 226560.75kcal/mol which is trailed by aziridine (C_2H_5N) at 45.51kcal/mol while oxirane (C_2H_4O) possesses the lowest enthalpy of reaction at -84.61kcal/mol, therefore, thiirane is extremely endothermic of the series, more endothermic than aziridine while oxirane is the most exothermic of the series.

Gibbs free energy (ΔG) is related to the chemical reaction needed to do work [35]. The free energy of a system is the sum of its enthalpy plus the product of temperature and entropy [36]. Gibbs free energy of reaction refers to the change in enthalpy (ΔH) of the system minus the product of the temperature (K) and the change in entropy (ΔS) of the system [37]. Just as the reactions in enthalpy which is classified into Endothermic (absorbs heat) and Exothermic (releases heat), Gibbs free energy is also classified into Endergonic (non-spontaneous) $\Delta G = > 0$ and Exergonic (spontaneous) $\Delta G = < 0$. Data obtained for the free energy calculation shows that for C_3H_5X series, bromocyclopropane possesses the highest enthalpy of reaction at -11.77kcal/mol which is trailed by chlorocyclopropane at -11.77kcal/mol and fluorocyclopropane at -109kcal/mol. For O, N, and S doped cyclopropane, Thiirane (C_2H_4S) possesses the highest free energy of reaction of the series at 226561.32kcal/mol which is trailed by Aziridine (C_2H_5N)

at 43.89kcal/mol while Oxirane (C_2H_4O) possesses the lowest free energy of reaction of the series at -86.63kcal/mol. This is to say that thiirane is highly endergonic while oxirane is the most exergonic of the series.

Table 7(a). Thermodynamic properties of C_3H_7F

	C_3H_6	F_2	C_3H_5F	HF
ε_0	-117.9077120	-199.5354060	-217.1548990	-100.4607620
ε_{ZPE}	0.080721	0.002329	0.072939	0.009249
E_{tot}	0.084116	0.004724	0.076909	0.011609
H_{corr}	0.085060	0.005668	0.077853	0.012553
G_{corr}	0.058108	-0.017298	0.046891	-0.007165
$\varepsilon_0 + \varepsilon_{ZPE}$	-117.8269912	-199.5330767	-217.0819598	-100.4515134
$\varepsilon_0 + E_{tot}$	-117.8235963	-199.5306824	-217.0779904	-100.4491529
$\varepsilon_0 + H_{corr}$	-117.8226521	-199.5297382	-217.0770462	-100.4482087
$\varepsilon_0 + G_{corr}$	-117.8496039	-199.5527035	-217.1080085	-100.4679270

Table 7(b). Thermodynamic properties of C_3H_7Cl

	C_3H_6	Cl_2	C_3H_5Cl	HCl
ε_0	-117.9077120	-920.4038110	-577.5267610	-460.8276990
ε_{ZPE}	0.080721	0.001197	0.071813	0.006632
E_{tot}	0.084116	0.003764	0.076011	0.008992
H_{corr}	0.085060	0.004708	0.076955	0.009936
G_{corr}	0.058108	-0.020654	0.044742	-0.011269
$\varepsilon_0 + \varepsilon_{ZPE}$	-117.8269912	-920.4026138	-577.4549480	-460.8210672
$\varepsilon_0 + E_{tot}$	-117.8235963	-920.4000475	-577.4507499	-460.8187067
$\varepsilon_0 + H_{corr}$	-117.8226521	-920.3991033	-577.4498057	-460.8177626
$\varepsilon_0 + G_{corr}$	-117.8496039	-920.4244646	-577.4820192	-460.8389681

Table 7(c). Thermodynamic properties of C_3H_7Br

	C_3H_6	Br_2	C_3H_5Br	HBr
ε_0	-117.9077120	-5148.3053220	-2691.4636990	-2574.7631890
ε_{ZPE}	0.080721	0.000703	0.071270	0.005937
E_{tot}	0.084116	0.003473	0.075629	0.008297
H_{corr}	0.085060	0.004417	0.076574	0.009241
G_{corr}	0.058108	-0.023481	0.043027	-0.013299
$\varepsilon_0 + \varepsilon_{ZPE}$	-117.8269912	-5148.3046185	-2691.3924290	-2574.7572524
$\varepsilon_0 + E_{tot}$	-117.8235963	-5148.3018488	-2691.3880696	-2574.7548919

$\varepsilon_0 + H_{\text{corr}}$	-117.8226521	-5148.3009046	-2691.3871254	-2574.7539477
$\varepsilon_0 + G_{\text{corr}}$	-117.8496039	-5148.3288028	-2691.4206719	-2574.7764877

Table 7(d). Thermodynamic properties of $\text{C}_2\text{H}_5\text{N}$

	C_3H_6	N_2	$\text{C}_2\text{H}_5\text{N}$	HCN
ε_0	-117.9077120	-109.5428260	-133.9407150	-93.4370530
ε_{ZPE}	0.080721	0.005568	0.069815	0.016162
E_{tot}	0.084116	0.007929	0.073069	0.018727
H_{corr}	0.085060	0.008873	0.074013	0.019671
G_{corr}	0.058108	-0.012880	0.045631	-0.003223
$\varepsilon_0 + \varepsilon_{\text{ZPE}}$	-117.8269912	-109.5372578	-133.8709003	-93.4208913
$\varepsilon_0 + E_{\text{tot}}$	-117.8235963	-109.5348973	-133.8676461	-93.4183263
$\varepsilon_0 + H_{\text{corr}}$	-117.8226521	-109.5339531	-133.8667019	-93.4173821
$\varepsilon_0 + G_{\text{corr}}$	-117.8496039	-109.5557057	-133.8950837	-93.4402759

Table 7(e). Thermodynamic properties of $\text{C}_2\text{H}_4\text{O}$

	C_3H_6	O_2	$\text{C}_2\text{H}_4\text{O}$	H_2CO
ε_0	-117.9077120	-150.2881920	-153.8094900	-114.5205580
ε_{ZPE}	0.080721	0.003725	0.057026	0.026439
E_{tot}	0.084116	0.006088	0.060198	0.029309
H_{corr}	0.085060	0.007032	0.061142	0.030253
G_{corr}	0.058108	-0.015207	0.033578	0.005421
$\varepsilon_0 + \varepsilon_{\text{ZPE}}$	-117.8269912	-150.2844673	-153.7524643	-114.4941190
$\varepsilon_0 + E_{\text{tot}}$	-117.8235963	-150.2821041	-153.7492918	-114.4912493
$\varepsilon_0 + H_{\text{corr}}$	-117.8226521	-150.2811599	-153.7483476	-114.4903052
$\varepsilon_0 + G_{\text{corr}}$	-117.8496039	-150.3033991	-153.7759124	-114.5151370

Table 7(f). Thermodynamic properties of $\text{C}_2\text{H}_4\text{S}$

	C_3H_6	S_2	$\text{C}_2\text{H}_4\text{S}$	H_2S
ε_0	-117.9077120	-796.3746470	-153.8094900	-399.4151190
ε_{ZPE}	0.080721	0.001588	0.057026	0.014895
E_{tot}	0.084116	0.004062	0.060198	0.017745
H_{corr}	0.085060	0.005006	0.061142	0.018689
G_{corr}	0.058108	-0.019902	0.033578	-0.004689
$\varepsilon_0 + \varepsilon_{\text{ZPE}}$	-117.8269912	-796.3730593	-153.7524643	-399.4002245

$\varepsilon_0 + E_{\text{tot}}$	-117.8235963	-796.3705849	-153.7492918	-399.3973738
$\varepsilon_0 + H_{\text{corr}}$	-117.8226521	-796.3696407	-153.7483476	-399.3964297
$\varepsilon_0 + G_{\text{corr}}$	-117.8496039	-796.3945485	-153.7759124	-399.4198081

Conclusion

The computed predicted geometrical parameters of cyclopropane viz., bond lengths, bond angles compared with experimental values from NIST. The calculated bond length values of the substituted and doped cyclopropanes proved the electron-withdrawing effects of the substituents and dopants, as the bond length values decrease when there are attached to the C3 molecule. The NBO analysis shows the interactions that give the strongest stabilizations to the molecule. ADCH proved that doped C3N shows the greatest tendency to undergo nucleophilic substitution reaction. The MEP studies proved that substituted and doped cyclopropanes have higher reactivity than normal cyclopropane molecule. MEP maps also show that doped cyclopropanes have higher reactivity than substituted cyclopropanes. DOS analyses show the contributions of the various substituents and dopants to the valence MOs and also the percentage of bonding and anti-bonding character between the various molecules. The UV-Spectral analyses tell us that the substituted and doped cyclopropane molecules have greater absorption maxima than the normal cyclopropane. It also reports that doped C3S has the greatest absorption maxima. Hence, gives the greatest bathochromic shift. The Conceptual DFT results compare the reactivity of all the molecules and showed that the substituted and doped cyclopropanes have higher reactivity than the normal cyclopropane. Fukui functions and Condensed Dual Descriptors help in identifying the electrophilic/nucleophilic nature of a specific site within a molecule.

Ethics approval and consent to participate

Not applicable

Consent for publication

All authors agreed for the manuscript publication

Competing Interests

All authors declare no conflict of interest

Funding

No funding from any external agency

Authors' Contributions

Mr. E.I. Ubana conducted detailed theoretical calculations and first manuscript draft, H. Louis conceptualized, designed, and Supervised the research work, O.C. Enudi analyzed the results and offered scientific insight, M.M. Edim conducted details of NBO calculations and analysis, P. David calculated the thermodynamic properties, I.P. Samuel provided the methodology, and Be.I. Ita revised the manuscript.

Acknowledgments

Even though this research work did not receive funding from any external agencies, however, the authors are thankful to the Computational Quantum Chemistry research team leader, Dr. H. Louis, for the scientific contribution, leadership, and motivation.

Data availability

All data generated or analyzed during this study are included in this published article (and its supplementary information files)

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Figures

Figure 1

The optimized geometrical structure of C₃, C₃F, C₃Cl, C₃Br, C₃N, C₃O and C₃S

Figure 2

OPDOS, PDOS and TDOS for C3, C3F, C3Cl, C3Br, C3N, C3O and C3S

Figure 3

Representative MEP of C3, C3F, C3Cl, C3Br, C3N, C3O and C3S

Figure 4

UV-vis spectra of C3, C3F, C3Cl, C3Br, C3N, C3O and C3S

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