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Structural Properties, Natural Bond Orbital, Density Functional Theory (DFT) and Energy Calculations for Fluorous Compound: $C_{13}H_{12}F_7ClN_2O$

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ABSTRACT

In this study, the optimized geometries, frequencies of the stationary point and the minimum-energy paths of $C_{13}H_{12}F_7ClN_2O$ are calculated by using the DFT (B3LYP) methods with LANL2DZ basis sets. B3LYP/LANL2DZ calculation results indicated some selected bond length and bond angles values for the fluorous compound $C_{13}H_{12}F_7ClN_2O$.

Key words: Fluorous compound ($C_{13}H_{12}F_7ClN_2O$), LUMO, HOMO, DFT

INTRODUCTION

Fluorous molecules comprise an organic domain and a highly fluorinated domain. Ideally, the organic domain controls reactivity and the fluorinated domain controls separation. Generally, >60% fluorine by weight is called a “heavy fluorous” compound. These materials have limited solubility in non-fluorous media, typically require perfluorinated solvents and are expensive, all of which limits practical adoption. “Light fluorous” compounds (<40% by weight) are miscible in organic solvents and cost less. Since, they typically will not form a separate fluorous liquid phase, light fluorous compounds are separated using a companion fluorous stationary phase.

Whereas, compounds bearing light fluorous tags are miscible in organic solvents, heavy fluorous compounds are soluble in perfluorinated solvents and form a distinct liquid phase. Fluorous stationary phases exhibit high selectivity for retention of fluorous versus non-fluorous molecules. In addition, fluorous sorbents are able to resolve fluorous molecules of differing fluorine content (Zhang, 2004a, b; Curran and Matsugi, 2005; Dandapani *et al.*, 2005; Gladysz and Curran, 2002).

During this study, we report the optimized geometries, assignments and electronic structure calculations for the compound. The structure of the compound has been optimized by using the DFT (B3LYP) method with the LANL2DZ basis sets, using the Gaussian 98 program Frisch and Trucks (1998). The comparison between theory and experiment is made. Density functional theory methods were employed to determine the optimized structures of $C_{13}H_{12}F_7ClN_2O$ and initial calculations were performed at the DFT level and split valence plus polarization LANL2DZ basis sets were used. Local minima were obtained by full geometrical optimization have all positive frequencies (Vrajmasu *et al.*, 2004; Smith *et al.*, 2005).

METHODS

All computational are carried out using Gaussian 98 program. Energy minimum molecular geometries were located by minimizing energy with respect to all geometrical coordinates without imposing any symmetrical constraints (Ghammamy *et al.*, 2011).

RESULTS AND DISCUSSION

Molecular properties: The structures of compounds are shown in Fig. 1. All calculations were carried out using the computer program Gaussian 98. Theoretical calculation of bond length and angle for the compound was determined by optimizing the geometry (Table 1).

The NBO calculated hybridizations are presensted in Table 2. We could not compare the calculation results given in bond lengths and bond angle values with the experimental data because the crystal structure of the title compound is not available till now.

NBO study on structures: Natural charges have been computed using Natural Bond Orbital (NBO) module implemented in Gaussian 98. The NBO calculated hybridizations are significant parameters for our investigation. These quantities are derived from the NBO population analysis. The former provides an orbital picture that is closer to the classical Lewis structure. The NBO analysis involving hybridizations of selected bonds are calculated at B3LYP methods and LANL2DZ level of theory (Table 2).

These data shows the hyperconjugation of electrons between ligand atoms with central metal atom. The NBO calculated hybridization for $C_{13}H_{12}F_7ClN_2O$ shows that all of complexes have Sp^x hybridization and non-planar configurations. The total hybridization of these molecules are Sp^x that was confirmed by structure. The amount of bond hybridization showed the inequality

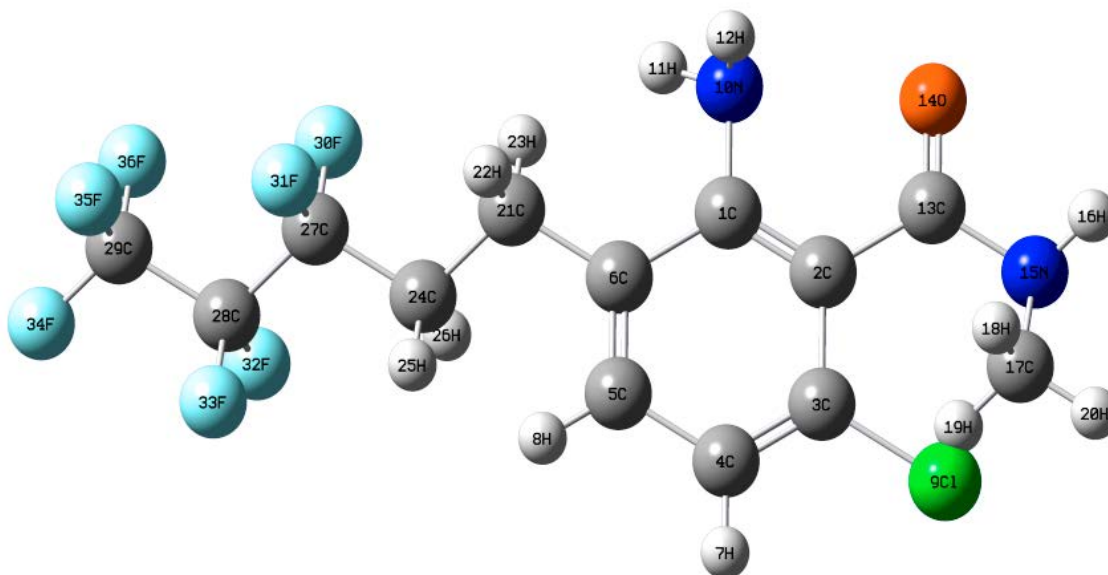


Fig. 1: Schematic structure of the $C_{13}H_{12}F_7ClN_2O$

Table 1: Geometrical parameters optimized for $C_{13}H_{12}F_7ClN_2O$, some selected bond lengths (Å) and angles (°)

Bond definition	Optimized parameters (Å and °)	Bond definition	Optimized parameters (Å and °)
C ₁ -C ₂	1.3552	C ₆ -C ₂₁	1.54
C ₁ -C ₆	1.54	Cl ₉ -C ₁₇	1.6343
C ₁ -N ₁₀	1.47	Cl ₉ -H ₁₉	0.6421
C ₂ -C ₃	1.54	N ₁₀ -H ₁₁	1.0
C ₂ -C ₁₃	1.54	N ₁₀ -H ₁₂	1.0
C ₃ -C ₄	1.3552	C ₁₃ -O ₁₄	1.2584
C ₃ -Cl ₉	1.76	C ₁₃ -N ₁₅	1.47
C ₄ -C ₅	1.54	N ₁₅ -H ₁₆	1.0
C ₄ -H ₇	1.07	N ₁₅ -C ₁₇	1.47
C ₅ -C ₆	1.3552	C ₁₇ -H ₁₈	1.07
C ₅ -H ₈	1.07	C ₁₇ -H ₁₉	1.07
C ₁₇ -H ₂₀	1.07	C ₂₈ -F ₃₃	1.35
C ₂₁ -H ₂₂	1.07	C ₂₉ -F ₃₄	1.35
C ₂₁ -H ₂₃	1.07	C ₂₉ -F ₃₅	1.35
C ₂₁ -C ₂₄	1.54	C ₂₉ -F ₃₆	1.35
C ₂₄ -H ₂₅	1.07	C ₂₇ -F ₃₀	1.35
C ₂₄ -H ₂₆	1.07	C ₂₇ -F ₃₁	1.35
C ₂₄ -C ₂₇	1.54	C ₂₈ -C ₂₉	1.54
C ₂₇ -C ₂₈	1.54	C ₂₈ -F ₃₂	1.35
C ₂ -C ₁ -C ₆	120	C ₄ -C ₅ -C ₆	120
C ₂ -C ₁ -N ₁₀	120	C ₄ -C ₅ -H ₈	120
C ₆ -C ₁ -N ₁₀	120	C ₆ -C ₅ -H ₈	120
C ₁ -C ₂ -C ₃	120	C ₁ -C ₆ -C ₅	120
C ₁ -C ₂ -C ₁₃	120	C ₁ -C ₆ -C ₂₁	120
C ₃ -C ₂ -C ₁₃	120	C ₅ -C ₆ -C ₂₁	120
C ₂ -C ₃ -C ₄	120	C ₃ -Cl ₉ -C ₁₇	97.271
C ₂ -C ₃ -C ₄	120	C ₃ -Cl ₉ -H ₁₉	75.8778
C ₂ -C ₃ -Cl ₉	120	C ₁ -N ₁₀ -H ₁₁	109.4712
C ₄ -C ₃ -Cl ₉	120	C ₁ -N ₁₀ -H ₁₂	109.4712
C ₃ -C ₄ -C ₅	120	H ₁₁ -N ₁₀ -H ₁₂	109.4712
C ₃ -C ₄ -H ₇	120	C ₂ -C ₁₃ -O ₁₄	120
C ₅ -C ₄ -H ₇	120	C ₂ -C ₁₃ -N ₁₅	120
C ₄ -C ₅ -H ₈	120	O ₁₄ -C ₁₃ -N ₁₅	120
C ₁₃ -N ₁₅ -H ₁₆	109.4712	C ₂₇ -C ₂₈ -F ₃₂	109.4712
C ₁₃ -N ₁₅ -C ₁₇	109.4712	C ₂₉ -C ₂₈ -F ₃₂	109.4712
H ₁₆ -N ₁₅ -C ₁₇	109.4712	F ₃₄ -C ₂₉ -F ₃₅	109.4712
Cl ₉ -C ₁₇ -N ₁₅	119.4712	F ₃₅ -C ₂₇ -F ₃₆	109.4712
Cl ₉ -C ₁₇ -H ₁₈	111.0302	C ₆ -C ₂₁ -H ₂₃	109.4712
Cl ₉ -C ₁₇ -H ₂₀	97.0271	C ₂₁ -C ₂₄ -C ₂₇	109.4712
N ₁₅ -C ₁₇ -H ₁₈	109.4712	C ₂₄ -C ₂₇ -F ₃₀	109.4712
N ₁₅ -C ₁₇ -H ₁₉	109.4712	C ₂₈ -C ₂₇ -F ₃₀	109.4712
H ₁₈ -C ₁₇ -H ₂₀	109.4712	F ₃₀ -C ₂₇ -F ₃₁	109.4712

between central atoms angles, Table 2 shows distortion from octahedral and VSEPR structural and confirmed deviation from VSEPR structures. Second order perturbation theory analysis of Fock matrix in NBO basis for $C_{13}H_{12}F_7ClN_2O$ means energy of hyperconjugative interaction (stabilization energy) Table 3.

Table 2: NBO calculated hybridizations for C₁₃H₁₂F₇ClN₂O acalculated at B3LYP/LANL2DZ

C ₁₃ H ₁₂ F ₇ ClN ₂ O			C ₁₃ H ₁₂ F ₇ ClN ₂ O		
Bond	Atom No.	B3LYP	Bond	Atom No.	B3LYP
C-C	C ₁ -C ₂	S ¹ P ^{1.55} , S ¹ P ^{1.47}	C-N	C ₁₃ -N ₁₅	S ¹ P ^{2.38} , S ¹ P ^{2.38}
C-C	C ₁ -C ₆	S ¹ P ^{2.01} , S ¹ P ^{2.18}	N-H	N ₁₅ -H ₁₆	S ¹ P ^{2.87} , S ¹
C-N	C ₁ -N ₁₀	S ¹ P ^{2.65} , S ¹ P ^{2.19}	N-C	N ₁₅ -C ₁₇	S ¹ P ^{2.71} , S ¹ P ^{2.49}
C-C	C ₂ -C ₃	S ¹ P ^{2.25} , S ¹ P ^{1.30}	C-H	C ₁₇ -H ₁₈	S ¹ P ^{2.18} , S ¹
C-C	C ₂ -C ₁₃	S ¹ P ^{2.48} , S ¹ P ^{1.60}	C-H	C ₁₇ -H ₂₀	S ¹ P ^{3.38} , S ¹
C-C	C ₃ -C ₄	S ¹ P ^{1.38} , S ¹ P ^{1.60}	C-H	C ₂₁ -H ₂₂	S ¹ P ^{3.26} , S ¹
C-C	C ₄ -C ₅	S ¹ P ^{2.06} , S ¹ P ^{2.16}	C-H	C ₂₁ -H ₂₃	S ¹ P ^{3.25} , S ¹
C-H	C ₄ -H ₇	S ¹ P ^{2.48} , S ¹	C-C	C ₂₁ -C ₂₄	S ¹ P ^{2.88} , S ¹ P ^{2.72}
C-C	C ₅ -C ₆	S ¹ P ^{1.60} , S ¹ P ^{1.67}	C-H	C ₂₄ -H ₂₅	S ¹ P ^{3.12} , S ¹
C-H	C ₅ -H ₈	S ¹ P ^{2.35} , S ¹	C-H	C ₂₄ -H ₂₆	S ¹ P ^{3.11} , S ¹
C-C	C ₆ -C ₂₁	S ¹ P ^{2.22} , S ¹ P ^{2.68}	C-C	C ₂₄ -C ₂₇	S ¹ P ^{3.07} , S ¹ P ^{2.19}
Cl-C	Cl ₉ -C ₁₇	S ¹ P ^{4.635} , S ¹ P ^{5.01}	C-C	C ₂₇ -C ₂₈	S ¹ P ^{2.72} , S ¹ P ^{2.32}
Cl-H	Cl ₉ -H ₁₉	S ¹ P ^{1.29} , S ¹	C-F	C ₂₇ -F ₃₀	S ¹ P ^{3.77} , S ¹ P ^{2.69}
N-H	N ₁₀ -H ₁₁	S ¹ P ^{2.93} , S ¹	C-F	C ₂₇ -F ₃₁	S ¹ P ^{3.79} , S ¹ P ^{2.69}
N-H	N ₁₀ -H ₁₂	S ¹ P ^{3.10} , S ¹	C	C ₁	S ¹ P ^{0.00}
C-O	C ₁₃ -O ₁₄	S ¹ P ^{0.00}	N	N ₁₀	S ¹ P ^{0.00}
C-F	C ₂₈ -F ₃₃	S ¹ P ^{3.58} , S ¹ P ^{2.93}	C	C ₁₃	S ¹
C-F	C ₂₉ -F ₃₄	S ¹ P ^{3.43} , S ¹ P ^{3.33}	O	O ₁₄	S ¹ P ^{0.00}
C-F	C ₂₉ -F ₃₅	S ¹ P ^{3.34} , S ¹ P ^{3.38}	N	N ₁₅	S ¹ P ^{0.00}
C-F	C ₂₉ -F ₃₆	S ¹ P ^{3.34} , S ¹ P ^{3.39}	F	F ₃₀	S ¹
C-C	C ₂₈ -C ₂₉	S ¹ P ^{2.82} , S ¹ P ^{2.19}	F	F ₃₁	S ¹
C-F	C ₂₈ -F ₃₂	S ¹ P ^{3.58} , S ¹ P ^{2.94}	C	C ₃	S ¹

Table 3: Second order perturbation theory analysis of Fock matrix in NBO basis for C₁₃H₁₂F₇ClN₂O

Donor (i)	Type	ED/e	Acceptor (j)	Type	ED/e	E(2) (kJ mol ⁻¹)	E(j) E(i) ^a (a.u)	F(i,j) ^b (a.u)
C1-C2	σ	1.9679	C3	σ [*]	1.2605	4.06	0.69	0.076
C1-C6	σ	1.9664	N10	σ [*]	0.0039	0.60	1.37	0.026
C1-N10	σ	1.9841	C5-C6	σ [*]	0.0176	2.07	1.32	0.047
C2-C3	σ	1.9707	C1-N10	σ [*]	0.0231	4.81	0.96	0.061
C2-C13	σ	1.9713	N15	σ [*]	0.0065	0.56	1.28	0.024
C3-C4	σ	1.9812	Cl9	σ [*]	0.0134	1.95	4.94	0.091
C4-C5	σ	1.9699	Cl9	σ [*]	0.0134	1.35	5.27	0.076
Cl9-C17	σ	1.8274	Cl9	σ [*]	0.0134	16.49	5.14	0.271
Cl9-H19	σ	1.9233	C17	σ [*]	0.0250	8.06	1.45	0.098
N10-H11	σ	1.9847	C1-C2	σ [*]	0.0294	3.80	1.26	0.062
C13-O14	σ	1.9775	N15	σ [*]	0.0065	0.57	1.64	0.027
C13-N15	σ	1.9864	O14	σ [*]	0.0040	0.90	1.75	0.036
N15-H16	σ	1.9606	C17	σ [*]	0.0250	1.11	1.0	0.030
N15-C17	σ	1.9841	Cl9-C17	σ [*]	0.5203	0.60	0.69	0.021
C27-F30	σ	1.9912	C27	σ [*]	0.0148	0.54	1.55	0.026
C28-F32	σ	1.9917	C27-F31	σ [*]	0.0744	1.81	1.23	1.043
N10	n	1.9995	C1-C2	σ [*]	0.0294	0.52	14.79	0.079
O14	n	1.9998	C13	σ [*]	0.0172	4.10	19.38	0.253
F30	n	1.9999	C27	σ [*]	0.0148	1.14	24.98	0.151
F35	n	1.9999	C29	σ [*]	0.0123	0.71	25.01	0.120
C3	n	1.9989	Cl9	σ [*]	0.0134	127.74	4.70	0.868

^aEnergy difference between donor and acceptor i and j NBO orbital's, ^bF(i, j) is the fock matrix element between i and j NBO

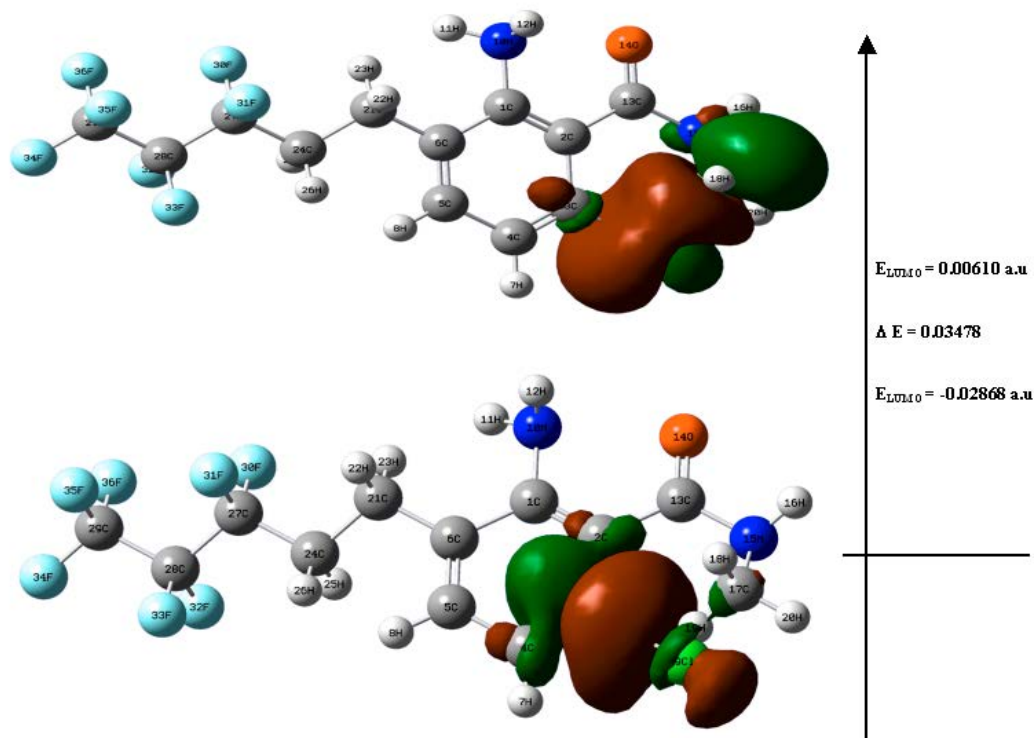


Fig. 2: Atomic orbital of the frontier molecular orbital for $C_{13}H_{12}F_7ClN_2O$ B3LYP/LANL2DZ level of theory

Frontier molecular orbital: Energy difference between HOMO and LUMO orbital is called as “energy gap” that is an important stability for structures. In addition, 3D plots of Highest Occupied Molecular Orbitals (HOMOs) and Lowest Unoccupied Molecular Orbitals (LUMOs) are shown in Fig. 2. The HOMO-LUMO energies were also calculated at the LANL2DZ and the values are listed in Fig. 2, respectively.

CONCLUSION

In this study, we are interested in study on fluorous compound. Organic compound was chosen for theoretical studies. In this study, the optimized geometries and frequencies of the stationary point and the minimum-energy paths are calculated by using the DFT (B3LYP) methods with LANL2DZ basis sets. B3LYP/LANL2DZ calculation results indicated some selected bond length and bond angles values for the $C_{13}H_{12}F_7ClN_2O$.

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