Original Article

Structural Parameters, NLO Properties, Thermodynamic Functions, NBO Analysis And Fukui Functions Of Benzyl(3-Fluoro-4-Morpholinophenyl)Carbamate By Density Functional Theory

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Abstract

This work deals with the study of Benzyl(3-fluoro-4-morpholinophenyl)carbamate with the help of Density Functional Theory (DFT) calculations. The B3LYP method with 6-311++G(d,p) and cc-pVDZ basis sets are used in DFT calculations. The structural parameters (Bond length and Bond Angle) of the titled molecule are calculated theoretically by DFT. The thermodynamic parameters (Heat capacity, Entropy and Enthalpy) are calculated for temperatures between 100 to 1000 Kelvin. The hybridization and covalent effects are investigated using Natural Bond Orbital (NBO) calculations with the help of the charge delocalization energies and hyperconjugative interactions. The Non-linear optical (NLO) properties of the molecule are calculated by DFT using 6-311++G(d,p) and cc-pVDZ basis sets. The Fukui function is used as a local density functional descriptor to model chemical reactivity and site selectivity.

Keywords: NBO, NLO, DFT, Thermodynamic Functions, Fukui Function.

1. INTRODUCTION

Morpholine and its derivatives have been studied by researchers due to their vast applications in various fields. C. Cheng et al. discussed the production of potash fertilizer at low temperatures by morpholine surfactant [1]. R. R. Sagam et al. synthesized a morpholine derivative that can be used as an anticancer agent [2]. Morpholine amides can be used for the synthesis of ketones and aldehydes [3]. S.chiff base ligands and their metal complexes chemistry has attracted a lot of interest due to their facile synthesis and wide range of applications including antimicrobial [4-6] and catalytic oxidation [7]. R.H. Mennen at al. studied morpholines as gene regulators in the cardiac embryonic stem cell test [8]. F. Arshad et al. [9] studied morpholine derivatives as anticancer agents.

Due to the various applications of morpholine derivatives, the present study deals with the study of Benzyl(3-fluoro-4-morpholinophenyl)carbamate (BFMC). DFT calculations for the molecule BFMC are used to analyze structural parameters, thermodynamic functions, Natural Bond Orbital (NBO) analysis, Non-linear optical (NLO) properties and Fukui function analysis. These parameters are studied by various researchers. V.S. Jeba Reeda et al. [10] analyze morpholine derivatives by vibrational, fukui and molecular docking studies. The structural and thermodynamic properties of the binary mixtures of morpholine glycol are studied by Z. Fakhri et al. [11].

2. COMPUTATIONAL ANALYSIS

Computational calculations are performed using Density functional theory (DFT) by the Gaussian 09 program package [12]. DFT calculations can be performed at various basis sets. A basis set is a linear combination of molecular orbitals. The basis sets B3LYP/6-311++G(d,p) and B3LYP/cc-pVDZ are used in this study which gives better results as compared to other basis sets. B3LYP employs Becke’s three-parameter exchange functional B3 and Lee-Yang-Parr correlation functional LYP) [13]. Gauss View interface program [14] is used to view the molecular structure of the molecule and helps to analyze the parameters calculated by DFT. The thermodynamic parameters Heat capacity, Entropy and Enthalpy are calculated for a temperature range of 100 K to 1000 K at B3LYP/6-311++G(d,p) basis set. The Natural Bond Orbital (NBO) analysis is performed at B3LYP/6-311++G(d,p) basis set. The Non-linear optical (NLO) properties are calculated at B3LYP/6-311++G(d,p) and B3LYP/cc-pVDZ basis sets. Fukui functions are calculated by Density Functional Theory. The drug likeliness study is performed by SwissADME program to check the biological activity of the molecule BFMC.

3. DRUG LIKELINESS

Drug-likeliness helps in computing physiochemical descriptors and to study pharmacokinetic properties to be used in medicinal industry and thereby supporting drug discovery. For a high possibility of drug likeness, the compound must obey Lipinski's rule of five [15]. The BFMC molecule shows a good bioavailability score of 0.55 and shows no violation of Lipinski's rule as shown in table 1. All these physiochemical descriptors were calculated with the help of Swiss ADME program [16]. Hence it can be stated that BFMC molecule qualifies to be used in the medicinal field.

Table 1: Drug likeliness of BFMC molecule.

Descriptor value	Value
Hydrogen Bond Donor (HBD)	1
Hydrogen Bond Acceptor (HBA)	4
AlogP[1]	3.25
Topological polar surface area (TPSA) [Å^2]	50.80
Number of atoms	43
Number of rotatable bonds	6
Molecular weight	330.35
Bioavailability score	0.55

4. NONLINEAR OPTICAL (NLO) PROPERTIES

Nonlinear optical (NLO) properties are necessary for the development of electronic device applications. The NLO properties arise with respect to changes in the molecular optical properties like; phase, amplitude and frequency in the presence of an electromagnetic field [17]. The mean polarizability $<\alpha>$, anisotropy of the polarizability $\Delta\alpha$, total first-order hyperpolarizability $\beta_{total,}$ second–order hyperpolarizability and dipole moment μ are studied by various researchers [18–21] and can be calculated by the following equations.

$<\alpha> = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/ 3$

$\Delta\alpha = [\{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6 (\alpha_{xy}^2 + \alpha_{zy}^2 + \alpha_{xz}^2)\}/2]^{1/2}$

$\beta_{total} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$ where

$\beta_x = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})$, $\beta_y = (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})$, $\beta_z = (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})$

$<\gamma> = (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz})/ 5$

$\mu = (\mu_x + \mu_y + \mu_z)^{1/2}$

The dipole moment, polarizabilities α and hyperpolarizabilities β in atomic mass units (a.u.) for BFMC molecule are calculated at B3LYP/6-311++G(d,p) and B3LYP/cc-pVDZ basis sets as shown in Table 2. The component α_{zz} of polarizability has the maximum negative value of –135.7161 a.u. with respect to the maximum positive value of the component α_{yz} which is equal to 4.4186 a.u. The component β_{xxy} of first–order hyperpolarizability has a maximum value of 44.6661a.u. and the value of β_{Total} is 207.3537 and 172.8988 a.u. respectively in B3LYP/6-311++G(d,p) and B3LYP/cc-pVDZ basis sets which are quite large and show that this molecule can be used in non-linear optical applications. The total dipole moment is 2.8869 debye in the B3LYP/6-311++G(d,p) basis set and 2.7896 debye in the B3LYP/cc-pVDZ basis set. All the values of various parameters are slightly more in the B3LYP/6-311++G(d,p) basis set as compared to B3LYP/cc-pVDZ basis sets. The component γ_{xxxx} of the second order hyperpolarizability has the maximum negative value of –21421.8866 a.u. while the maximum positive value for the component γ_{xxyz} which is equal to 163.3684 a.u and total value of second order hyperpolarizability is –7495.6328 a.u.

Table 2: Non-linear Optical Parameters (Dipole moment, Polarizability, First order Hyperpolarizability and Second order Hyperpolarizability) of Benzyl(3-Fluoro-4-morpholinophenyl)carbamate calculated in B3LYP/6-311++G(d,p) and B3LYP/cc-pVDZ basis sets.

Parameters	B3LYP/cc-pVDZ	B3LYP/6-311++
	Dipole Moments (Debye)	
μ_x	–2.4782	–2.6614
μ_y	1.2467	1.0825
μ_z	0.2930	2.2815
μ_{Total}	2.7896	2.8869
	Molecular Polarizability (a.u)	
α_{xx}	–131.2748	–135.3723
α_{xy}	–7.6695	–8.6068
α_{yy}	–138.5021	–141.5623
α_{xz}	–0.2956	–0.7396
α_{yz}	3.7205	4.4186
α_{zz}	–135.7161	–137.5994

Mean polarizability<α>	–135.1643	–138.1780
Anisotropic polarizabilityΔα	16.9485	18.1934
	Hyperpolarizability (a.u)	
β_{xxx}	–189.5448	–223.7715
β_{xxy}	37.9594	44.6661
β_{xyy}	39.7285	41.9716
β_{yyy}	11.2879	9.4309
β_{xxz}	–27.3340	–33.1185
β_{xyz}	7.5105	10.9043
β_{yyz}	–0.6193	–0.1580
β_{xzz}	–11.8160	–14.5377
β_{yzz}	3.6827	3.7594
β_{zzz}	–1.3194	–1.2735
β_x	–161.6323	–196.3376
β_y	52.9300	57.8564
β_z	–29.2727	–34.5428
β_{Total}	172.8988	207.3765
	Second Order Hyperpolarizability	
γ_{xxxx}	–20875.0318	–21421.8866
γ_{yyyy}	–1108.3168	–1150.2375
γ_{zzzz}	–493.4258	–508.6644
γ_{xxxy}	–277.0752	–313.5188
γ_{xxxz}	–94.2412	–150.3295
γ_{yyyx}	17.2053	10.7385
γ_{yyyz}	–2.2071	–2.9739
γ_{zzzx}	–3.6478	–4.9703
γ_{zzzy}	–3.8482	–1.0491
γ_{xxyy}	–3507.5210	–3556.9599
γ_{xxzz}	–3346.5453	–3365.8510
γ_{yyzz}	–265.5990	–275.8769
γ_{xxyz}	142.8667	163.3684
γ_{yyxz}	4.1088	5.9524
γ_{zzxy}	19.0468	17.6377
Average second order hyperpolarizability <γ>	–7343.2210	–7495.6328

5. STRUCTURAL PARAMETERS

DFT calculations are performed to obtain the optimized structure of the BFMC molecule. This optimized molecule is used to calculate the structural parameters bond lengths and bond angles. The molecular structure of Benzyl(3-Fluoro-4-morpholinophenyl)carbamate with the numbering of atoms is shown in Figure 1. The optimized bond lengths and bond angles for the molecule are calculated at B3LYP/6-311++G (d,p) and B3LYP/cc-pVDZ basis sets as shown in Table 3.

The value of bond lengths between N-C atoms ranges from 1.4729-1.3700 Å for both basis sets. The bond lengths between C3-F5 are 1.3576 Å and 1.3596 Å respectively for B3LYP/6-311++G (d,p) and B3LYP/cc-pVDZ basis sets. Bond lengths between C-C atoms range from 1.3788-1.5248 Å for both the basis sets. The bond length between C-H atoms ranges from 1.0791- 1.1124 Å. The bond length between C-O atoms ranges from 1.2110 Å to 1.4538 Å for both basis sets. The bond lengths calculated at B3LYP/cc-pVDZ basis sets are slightly greater than that calculated at B3LYP/6-311++G(d,p) basis set. The bond angles between the atoms in the ring range from 109.5660° to 123.2518°. The bond angles between the atoms C-C-H range from 106.5065° for O_6-C_{14}-H_{31} to 121.7509° for C_1-C_2-H_{34}. The bond angle between C-C-F is 117.5878° and 119.1602°. The bond angle is maximum between C_1-N_{10}-C_{17} and is equal to 128.1788° calculated at B3LYP/cc-pVDZ basis set. The bond angle between O_7–C_{17}–O_8 is 124.4509°.

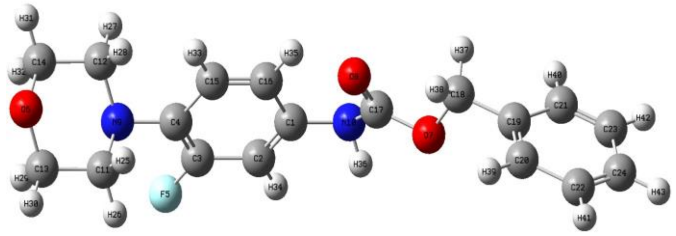


Figure 1: The optimized structure of BFMC with atom numbering.

Table 3: Optimized structural parameters (Bond Length and Bond Angle) calculated at B3LYP/cc-pVDZ and B3LYP/6-311++G (d,p) basis sets.

Bond Length (Å)	B3LYP/ cc–pVDZ	B3LYP/ 6-311G++(d, p)	Bond Angle (°)	B3LYP/ 6-311G++(d, p)	B3LYP/ cc–pVDZ
C1-C2	1.4059	1.4014	C2-C1-N10	117.4350	117.2464
C1-N10	1.4080	1.4094	C2–C1–C16	118.6602	118.6750
C1-C16	1.4012	1.3960	N10–C1–C16	123.9045	124.0778
C2-C3	1.3840	1.3788	C1–C2–C3	119.9827	119.8560
C2-H34	1.0922	1.0843	C1–C2–H34	121.7509	121.6815
C3-C4	1.4084	1.4036	C3–C2–H34	118.2518	118.4497
C3-F5	1.3576	1.3596	C2–C3–C4	123.2518	123.5235
C4-N9	1.4128	1.4104	C2–C3–F5	117.5878	117.2939
C4-C15	1.4060	1.4020	C4–C3–F5	119.1602	119.1756
O16-C13	1.4213	1.4239	C3–C4–N9	120.3678	120.6991
O6–C14	1.4193	1.4218	C3–C4–C15	115.3426	115.1206
O7-C17	1.3616	1.3596	N9–C4–C15	124.2391	124.1273
O7–C18	1.4505	1.4538	C13–O6–C14	110.4343	110.8833
O8-C17	1.2154	1.2110	C17–O7–C18	114.8296	115.5170
N9-C11	1.4716	1.4729	C4–N9–C11	116.5608	116.5977
C9-C12	1.4604	1.4616	C4–N9–C12	117.2148	117.2397
N10-C17	1.3728	1.3700	C11–N9–C12	111.0359	111.1215
N10-H36	1.0130	1.0089	C1–N10–C17	127.9998	128.1788
C11-C13	1.5248	1.5236	C1–N10–H36	117.1269	116.9746
C11-H25	1.1115	1.1028	C17–N10-H36	114.8733	114.8457
C11-H26	1.0970	1.0890	N9–C11–C13	109.5660	109.7408
C12-C14	1.5279	1.5265	N9–C11–H25	110.5746	110.3010
C12-H27	1.1011	1.0929	N9–C11–H26	109.5978	109.6693
C12-H28	1.1124	1.1037	C13–C11–H25	109.2880	109.4083
C13-H29	1.1092	1.0994	C13–C11–H26	109.4844	109.3342
C13-C30	1.1002	1.0914	H25–C11–H26	108.3072	108.3623
C14-H31	1.1003	1.0916	N9–C12–C14	109.3921	109.4803
C14-H32	11094	1.0997	N9–C12–H27	109.2127	109.8166
C15-C16	1.3980	1.3942	N9–C12–H28	112.0192	111.9043
C15–H33	1.0899	1.0820	C14–C12–H27	109.3652	109.1338
C16–H35	1.0868	1.0791	C14–C12–H28	108.8075	108.8770
C18–C19	1.5047	1.5028	H27–C12–H28	108.0030	108.2126
C18–H37	1.1005	1.0915	O6–C13–C11	111.5789	111.5039
C18–H38	1.1003	1.0914	O6–C13–H29	110.1439	109.7954
C19–C20	1.4025	1.3981	O6–C13–H30	106.5503	106.4424
C19–C21	1.4019	1.3978	C11–C13–H29	109.2826	109.6390
C20–C22	1.3967	1.3929	C11–C13–H30	110.4390	110.4606
C20–H39	1.0932	1.0852	H29–C13–H30	108.7838	108.9256
C21–C23	1.3973	1.3932	O6–C14–C12	111.6668	111.6074
C21–H40	1.0932	1.0852	O6–C14–H31	106.6135	106.5065
C22–C24	1.3986	1.3943	O6–C14–H32	110.2051	109.8573
C22–H41	1.0924	1.0842	C12–C14–H31	110.2868	110.3311
C23–**C**24	1.3980	1.3941	C12–C14–H32	109.2684	109.5761
C23–H42	1.0924	1.0842	H31–C14–H32	108.7336	108.8893
C24–H43	1.0924	1.0842	C4–C15–C16	122.8894	122.9438
			C4–C15–H33	119.2257	119.1796
			C16–C15–H33	117.8848	117.8766
			C1–C16–C15	119.8544	119.8667
			C1–C16–H35	119.5894	119.8856
			C15–C16–H35	120.5514	120.2426
			O7–C17–O8	124.4509	124.4304
			O7–C17–N10	108.3887	108.5686
			O8–C17–N10	127.1604	127.0010
			O7–C18–C19	107.7422	107.8704
			O7–C18–H37	108.8276	108.5441
			O7–C18–H38	108.7388	108.5339
			C19–C18–H37	111.7690	111.7560
			C19–C18–H38	111.8828	111.7961
			H37–C18–H38	107.8069	108.2460
			C18–C19–C20	120.4686	120.4912
			C18–C19–C21	120.6196	120.5403
			C20–C19–C21	118.9044	118.9651
			C19–C20–C22	120.6354	120.6015

C19–C20–H39	119.4452	119.5233
C22–C20–H39	119.9193	119.8751
C19–C21–C23	120.6363	120.6003
C19–C21–H40	119.4565	119.5219
C23–C21–H40	119.9071	119.8778
C20–C22–H40	120.0152	120.0029
C20–C22–H41	119.8946	119.9065
C24–C22–H41	120.0898	120.0901
C21–C23–C24	120.0136	120.0032
C21–C23–H42	119.8870	119.9037
C24–C23–H42	120.0992	120.0927
C22–C24–C23	119.7950	119.8266
C22–C24–H43	120.0987	120.0861
C23–C24–H43	120.1059	120.0867

6. THERMODYNAMIC FUNCTIONS

The thermodynamic functions of BFMC molecule such as heat capacity, entropy and enthalpy are observed at temperatures varying from 100 K to 1000 K by using Perl script. The plot of temperature variation with the calculated thermodynamic functions is shown in Figure 2 and the corresponding values are enlisted in Table 4. These calculations are computed using DFT calculations at B3LYP/cc-pVDZ basis set. It can be seen in the graph that all three thermodynamic parameters increase with the increase in temperature. These thermodynamic parameters have been studied by many researchers [22–24].

Table 4: Variation of Entropy(S), Heat capacity **(**C_p**)** and Enthalpy ddH content with temperature using B3LYP/6–311++G(d,p)basis set of BFMC molecule.

T (K)	S (J/mol.K)	Cp (J/mol.K)	ddH (kJ/mol)
100	422.942	144.902	9.607
150	490.414	191.347	18.005
200	552.119	240.581	28.789
250	611.408	293.277	42.122
298.15	667.55	345.881	57.507
300	669.696	347.908	58.149
350	727.412	402.023	76.904
400	784.495	453.544	98.307
450	840.71	501.241	122.195
500	895.805	544.646	148.36
550	949.585	583.801	176.588
600	1001.919	619.015	206.674
650	1052.74	650.699	238.431
700	1102.026	679.277	271.692
750	1149.787	705.136	306.313
800	1196.057	728.617	342.166
850	1240.881	750.009	379.14
900	1284.312	769.554	417.136
950	1326.406	787.459	456.068
1000	1367.222	803.899	495.858

The correlation equations for entropy, heat capacity, and enthalpy content with temperature variation have been fitted in the quadratic equation and the corresponding fitting factors R^2 have been shown by the following equations.
$S = 293.0771 + 1.3376T - 2.6232 \times 10^{-4}T^2$ ($R^2 = 0.9999$)
$C_P = 537.4075 + 527.1408T - 5.5211 \times 10^{-4} T^2$ ($R^2 = 0.9996$)
$ddH = -14.0572 + 0.1385T + 3.7759 \times 10^{-4} T^2$ ($R^2 = 0.9997$)

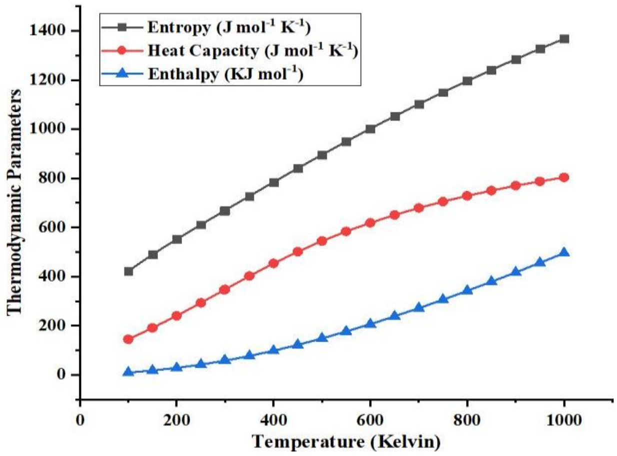


Figure 2: Variation of computed thermodynamic parameters with temperature of BFMC molecule.

7. NATURAL BOND ORBITAL (NBO)

The Natural Bond Orbital (NBO) helps in studying the hybridization and covalent effects in polyatomic wave functions based on local eigenvectors of one particle density matrix. In NBO analysis, the second-order perturbation theory is used to study the interaction of acceptor non-Lewis NBOs and donor Lewis NBOs for which electron densities are used [23]. Table 5 shows the stabilization energy, energy difference of donor (i) and acceptor (j) NBO orbitals, Fock matrix element between orbitals of i and j NBO and the occupancy of donor and acceptor NBOs of BFMC molecule.

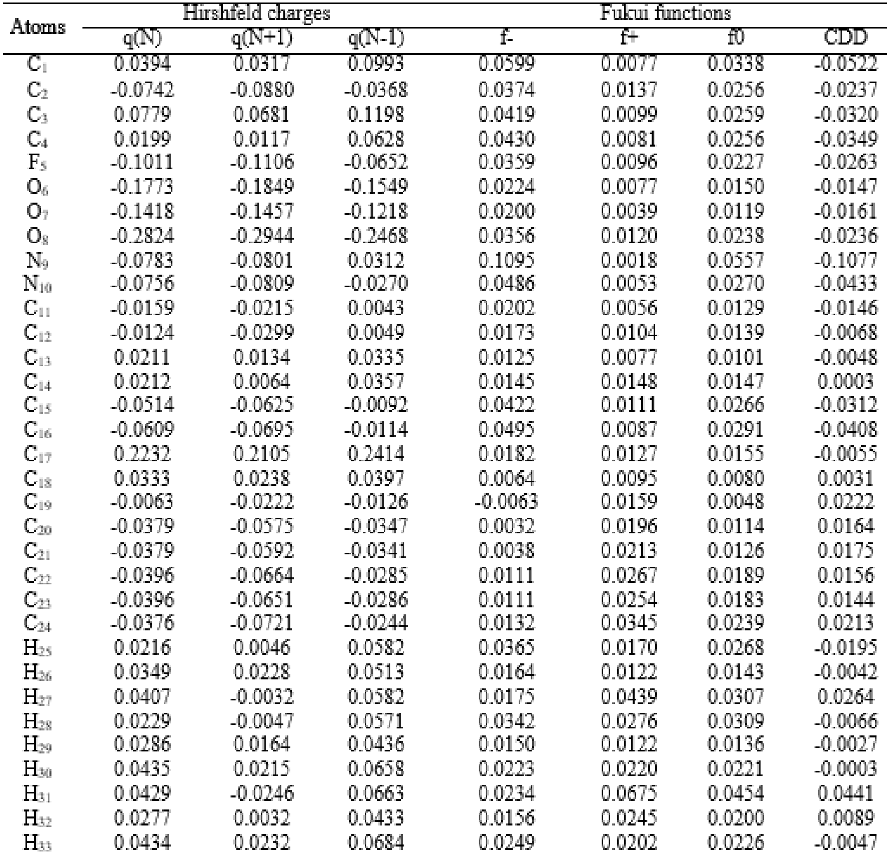
The interaction between donor NBO and acceptor NBO is the maximum for which the stabilization energy is large. For the lone pair interaction, the maximum calculated stabilization energy is 61.58 kcal/mol for LP(1) N10 corresponding to the σ*O7-C17 interaction. The second maximum stabilization energy of 41.59 kcal/mol corresponds to the interaction between LP(2) O7 and π*O8–C17. It can be seen from the table that the values of the stabilization energy between π-π* is more as compared to σ- σ* for most of the donor-acceptor NBO interactions.

Table 5: Second order perturbation theory of Fock matrix in NBO basis related to intra-molecular bonds of BFMC molecule computed at B3LYP/6-311++G (d,p) basis set [E(2) is stabilization energy; E(j)-E(i) is Energy difference of donor(i) and acceptor (j) NBO orbitals; F(i,j) is Fock matrix element between orbitals of i and j NBO, ED/e is occupancy].

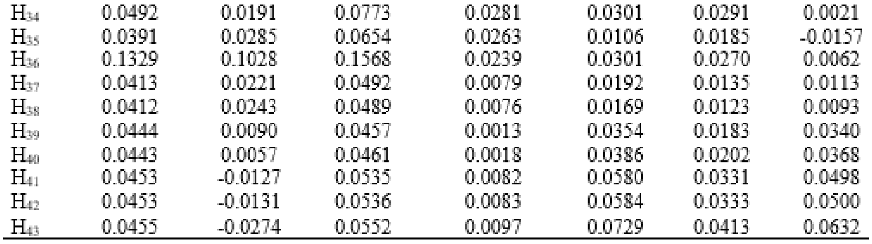
Donor NBO(i)	ED/e	Acceptor NBO(j)	ED/e	E(2)^{a} kcal/mol	E(j)-E(i)^{b} (a.u.)	F(i,j)^{c} (a.u.)
σ C1 – C2	1.96858	σ* C1– C16	0.71216	3.93	1.26	0.063
σ C1 – N10	1.98618	σ* C1 – C16	0.81699	1.66	1.33	0.043
σ C1 – C16	1.97111	σ* C1– C2	0.70818	4.19	1.26	0.065
π C1 – C16	1.65827	π* C4 – C15	0.26139	21.03	0.28	0.070
σ C2 – C3	1.97785	σ* C3 – C4	0.73257	4.53	1.27	0.068
π C2 – C3	1.72738	π* C1 – C16	0.28059	18.72	0.30	0.070
σ C2 – H34	1.97499	σ* C3 – C4	0.53955	4.19	1.08	0.060
σ C3 – C4	1.97381	σ* C2 – C3	0.71744	4.14	1.28	0.065
σ C3 – F5	1.99453	σ* C4 – C15	1.01277	1.45	1.57	0.043
σ C4 – N9	1.98248	σ* C4 – C15	0.77320	2.04	1.33	0.047
σ C4 – C15	1.96931	σ* C3 – C4	0.70667	3.29	1.25	0.057
π C5 – C15	1.67240	π* C2 – C3	0.026247	22.18	0.27	0.071
σ O6 – C13	1.99048	σ* C14 – H31	0.80061	0.97	1.20	0.030
σ O6 – C14	1.99051	σ* C12 – H27	0.80333	0.94	1.20	0.030
σ O7 – C17	1.98844	σ* C1 – N10	0.90954	2.63	1.32	0.053
σ O7 – C18	1.98481	σ* N10 – C17	0.81493	2.40	1.25	0.050
σ O8 – C17	1.99397	σ* N10 – C17	1.08663	1.94	1.52	0.049
π O8 – C17	1.99354	π* O8 – C17	0.39170	2.00	0.39	0.027
σ N9 – C11	1.97611	σ* C4 – C15	0.70088	1.89	1.26	0.044
π N9 – C11	1.97611	π* C4 – C15	0.70088	1.58	0.72	0.034
σ N9 – C12	1.98330	σ* C3 – C4	0.71553	2.41	1.26	0.049
σ N10 – C17	1.98531	σ* O7 – C18	0.84912	2.53	1.09	0.047
σ N10 – H36	1.98233	σ* O8 – C17	0.67403	5.02	1.27	0.071
σ C11 – C13	1.98713	σ* C4 – N9	0.62744	2.72	1.05	0.048
σ C11 – H25	1.98355	σ* C13 – H29	0.50552	2.47	0.89	0.042
σ C11 – H26	1.97742	σ* O6 – C13	0.51476	3.86	0.82	0.050
σ C12 – C14	1.98615	σ* C4 – N9	0.62876	2.84	1.06	0.049
σ C12 – H27	1.97734	σ* O6 – C14	0.51676	3.84	0.82	0.050
σ C12 – H28	1.98331	σ* C14 – H32	0.05116	2.43	0.89	0.042
σ C13 – H29	1.98512	σ* C11 – H25	0.50935	2.77	0.89	0.045

σ C13 – H30	1.98079	σ* N9 – C11	0.51272	3.19	0.85	0.046
σ C14 – C31	1.98113	σ* N9 – C12	0.51395	3.15	0.86	0.047
σ C14 – C32	1.98530	σ* C12 – H28	0.51078	2.71	0.89	0.044
σ C15 – C16	1.97202	σ* C1 – N10	0.69971	4.76	1.11	0.065
σ C15 – C33	1.97580	σ* C3 – C4	0.52280	3.74	1.06	0.056
σ C16 – H35	1.97636	σ* C1 – C2	0.51221	4.15	1.06	0.028
σ C18 – C19	1.97872	σ* C20 – C22	0.65170	2.33	1.22	0.048
σ C18 – H37	1.98533	σ* C19 – C20	0.52716	3.77	1.10	0.058
σ C18 – H38	1.98510	σ* C19 – C21	0.52708	3.66	1.10	0.057
σ C19 – C20	1.97400	σ* C19 – C21	0.70408	3.62	1.27	0.061
π C19 – C21	1.97406	σ* O7 – C18	0.70438	6.45	0.50	0.055
π C19 – C21	1.65207	π* C20 – C22	0.25825	20.25	0.28	0.068
σ C20 – C22	1.97873	σ* C18 – C19	0.70652	3.56	1.13	0.056
π C20 – C22	1.65994	π* C19 – C21	0.25953	20.63	0.29	0.069
σ C20 – H39	1.97947	σ* C19 – C21	0.52499	4.65	1.10	0.064
σ C21 – H23	1.97872	σ* C18 – C19	0.70636	3.62	1.12	0.057
π C21 – H40	1.97948	σ* C19 – C20	0.52509	4.65	1.09	0.064
σ C22 – H24	1.97963	π* C23 – C24	0.70620	1.74	1.07	0.042
σ C22 – H41	1.98047	σ* C23 – C24	0.70620	3.69	1.10	0.057
σ C23 – C24	1.97963	π* C23 – C24	0.70638	2.00	1.07	0.045
σ C23 – C24	1.65755	σ* C23 – H42	0.25883	10.13	3.62	0.171
σ C23 – H42	1.98047	σ* C22 – C24	0.52517	3.68	1.10	0.057
σ C24 – H43	1.98028	σ* C23 – H42	0.52222	11.63	3.43	0.179
LP (1) F5	1.98978	σ* C3 – C4	1.04528	1.08	1.59	0.037
LP (2) F5	1.97187	σ* C3 – C4	0.42428	5.82	0.96	0.067
LP (3) F5	1.93083	π* C2 – C3	0.42340	17.36	0.44	0.084
LP (1) O6	1.96469	σ* C14 – H31	0.56666	2.44	0.97	0.044
LP (2) O6	1.92047	σ* C14 – H32	0.29481	6.34	067	0.059
LP (1) O7	1.96518	σ* O8 – C17	0.59131	7.79	1.19	0.086
LP (2) O7	1.82926	π* O8 – C17	0.33532	41.59	0.33	0.110
LP (1) O8	1.97749	σ* N10 - C17	0.71006	2.36	1.14	0.047
LP (2) O8	1.83345	σ* O7 - C17	0.26921	31.19	0.61	0.125
LP (1) N9	1.82084	π* C4 – C15	0.27031	17.68	0.29	0.068
LP (1) N10	1.69620	π* O8 – C17	0.27808	61.58	0.27	0.117

Table 6: Computed values of the Fukui function using Hirshfeld charges.



Atoms	Hirshfeld charges			Fukui functions			
	q(N)	q(N+1)	q(N-1)	f-	f+	f0	CDD
C_1	0.0394	0.0317	0.0993	0.0599	0.0077	0.0338	-0.0522
C_2	-0.0742	-0.0880	-0.0368	0.0374	0.0137	0.0256	-0.0237
C_3	0.0779	0.0681	0.1198	0.0419	0.0099	0.0259	-0.0320
C_4	0.0199	0.0117	0.0628	0.0430	0.0081	0.0256	-0.0349
F_5	-0.1011	-0.1106	-0.0652	0.0359	0.0096	0.0227	-0.0263
O_6	-0.1773	-0.1849	-0.1549	0.0224	0.0077	0.0150	-0.0147
O_7	-0.1418	-0.1457	-0.1218	0.0200	0.0039	0.0119	-0.0161
O_8	-0.2824	-0.2944	-0.2468	0.0356	0.0120	0.0238	-0.0236
N_9	-0.0783	-0.0801	0.0312	0.1095	0.0018	0.0557	-0.1077
N_{10}	-0.0756	-0.0809	-0.0270	0.0486	0.0053	0.0270	-0.0433
C_{11}	-0.0159	-0.0215	0.0043	0.0202	0.0056	0.0129	-0.0146
C_{12}	-0.0124	-0.0299	0.0049	0.0173	0.0104	0.0139	-0.0068
C_{13}	0.0211	0.0134	0.0335	0.0125	0.0077	0.0101	-0.0048
C_{14}	0.0212	0.0064	0.0357	0.0145	0.0148	0.0147	0.0003
C_{15}	-0.0514	-0.0625	-0.0092	0.0422	0.0111	0.0266	-0.0312
C_{16}	-0.0609	-0.0695	-0.0114	0.0495	0.0087	0.0291	-0.0408
C_{17}	0.2232	0.2105	0.2414	0.0182	0.0127	0.0155	-0.0055
C_{18}	0.0333	0.0238	0.0397	0.0064	0.0095	0.0080	0.0031
C_{19}	-0.0063	-0.0222	-0.0126	-0.0063	0.0159	0.0048	0.0222
C_{20}	-0.0379	-0.0575	-0.0347	0.0032	0.0196	0.0114	0.0164
C_{21}	-0.0379	-0.0592	-0.0341	0.0038	0.0213	0.0126	0.0175
C_{22}	-0.0396	-0.0664	-0.0285	0.0111	0.0267	0.0189	0.0156
C_{23}	-0.0396	-0.0651	-0.0286	0.0111	0.0254	0.0183	0.0144
C_{24}	-0.0376	-0.0721	-0.0244	0.0132	0.0345	0.0239	0.0213
H_{25}	0.0216	0.0046	0.0582	0.0365	0.0170	0.0268	-0.0195
H_{26}	0.0349	0.0228	0.0513	0.0164	0.0122	0.0143	-0.0042
H_{27}	0.0407	-0.0032	0.0582	0.0175	0.0439	0.0307	0.0264
H_{28}	0.0229	-0.0047	0.0571	0.0342	0.0276	0.0309	-0.0066
H_{29}	0.0286	0.0164	0.0436	0.0150	0.0122	0.0136	-0.0027
H_{30}	0.0435	0.0215	0.0658	0.0223	0.0220	0.0221	-0.0003
H_{31}	0.0429	-0.0246	0.0663	0.0234	0.0675	0.0454	0.0441
H_{32}	0.0277	0.0032	0.0433	0.0156	0.0245	0.0200	0.0089
H_{33}	0.0434	0.0232	0.0684	0.0249	0.0202	0.0226	-0.0047



H_{34}	0.0492	0.0191	0.0773	0.0281	0.0301	0.0291	0.0021
H_{35}	0.0391	0.0285	0.0654	0.0263	0.0106	0.0185	-0.0157
H_{36}	0.1329	0.1028	0.1568	0.0239	0.0301	0.0270	0.0062
H_{37}	0.0413	0.0221	0.0492	0.0079	0.0192	0.0135	0.0113
H_{38}	0.0412	0.0243	0.0489	0.0076	0.0169	0.0123	0.0093
H_{39}	0.0444	0.0090	0.0457	0.0013	0.0354	0.0183	0.0340
H_{40}	0.0443	0.0057	0.0461	0.0018	0.0386	0.0202	0.0368
H_{41}	0.0453	-0.0127	0.0535	0.0082	0.0580	0.0331	0.0498
H_{42}	0.0453	-0.0131	0.0536	0.0083	0.0584	0.0333	0.0500
H_{43}	0.0455	-0.0274	0.0552	0.0097	0.0729	0.0413	0.0632

8. FUKUI FUNCTION

Fukui function is a local density functional descriptor to model chemical reactivity and site selectivity. Local reactivity descriptors indicate the preferred regions where a chemical species will change its density when the number of the electrons is modified [25]. It is possible to define the corresponding condensed or aromatic Fukui functions on the j th atom site as,

$$f_j^+ = q_j(N+1) - q_j(N)$$
$$f_j^- = q_j(N) - q_j(N-1)$$
$$f_j^0 = \frac{1}{2}[q_j(N+1) - q_j(N-1)$$

The electrophilic, nucleophilic, and free radical on the reference molecule is denoted by the symbols f_j^-, f_j^+, f_j^0 respectively. In the above equations, the electrons in neutral, anionic and cationic state of jth site of atom are denoted by N, N+1, N-1 chemical species. Chattaraj et al. [26] introduced the thought of generalized philicity. It contains the majority of information concerning well-known different global and local reactivity and selectivity descriptors and the data concerning electrophilic/nucleophilic attacking power at a given atomic site. Morell et al. [27] gave the concept of a dual descriptor ΔF(r), which is defined as the difference between the nucleophilic and electrophilic Fukui function and is given by the equation,

$$\Delta F(r) = q_j^+ - q_j^-$$

The sites favored for a nucleophilic attack and an electrophilic attack in terms of dual descriptor ΔF(r)>0 and ΔF(r) values of BFMC molecule at B3LYP/6-311++ G (d, p) level have been reported in Table 6. According to the condition for the dual descriptors, the nucleophilic sites having most positive values [ΔF(r)>0] in BFMC molecule are C_{14}, C_{18}, C_{19}, C_{20}, C_{21}, C_{22}, C_{23}, C_{24}, H_{27}, H_{31}, H_{32}, H_{34}, H_{36}, H_{37}, H_{38}, H_{39}, H_{40}, H_{41}, H_{42}, H_{43}. Similarly, the electrophilic site has the negative values [ΔF(r)] corresponding to C_1, C_2, C_3, C_4, F_5, O_6, O_7, O_8, N_9, N_{10}, C_{11}, C_{12}, C_{13}, C_{15}, C_{16}, C_{17}, H_{25}, H_{26}, H_{28}, H_{29}, H_{30}, H_{33}, H_{35}. The behaviour of the molecule as an electrophile and the nucleophile throughout the reaction depends on the local behaviour of the molecule. The table clearly indicates that in the titled compound the reactivity order for the probability of an attack by a nucleophile is $H_{43}>H_{42}>H_{41}>H_{31}>H_{40}>H_{39}>H_{27}>C_{19}>C_{24}> C_{21}>C_{20}> C_{22}>C_{23}>H_{37}$ with H_{43} being the most vulnerable to an attack by a nucleophile at 0.0632 and the electrophilic reactivity order is $N_9>C_1>N_{10}>C_{16}>C_4>C_3>C_{15}>F_5>C_2$ with N_9 being most electrophilic at -0.1077.

9. CONCLUSION

Some computational techniques like Density Functional Theory are methods to study the properties of a sample that give accurate results in a short time. In this work, DFT calculations are employed for which two basis sets B3LYP/6-311++G (d,p) and B3LYP/cc-pVDZ are used. The bond length and bond angle of the optimized Benzyl(3-Fluoro-4-morpholinophenyl)carbamate molecule is observed. The thermodynamic functions (Heat capacity, Entropy and Enthalpy) are calculated between the temperature range of 100 to 1000 Kelvin. Natural Bond Orbital (NBO) analysis of the molecule presents inter and intramolecular interactions. The large first-order hyperpolarizability of the molecule shows that the molecule can be used for Non-linear optical applications. The Fukui function analyzes the local density functional descriptor to model chemical reactivity and site selectivity within the molecule. All the theoretical calculations show that the molecule is a potential candidate for various applications.

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