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Density Functional Theory (DFT), Natural Band Orbital and Energy Studies of N-(2-Fluorophenyl)-2,6-dimethyl-1,3-dioxan-4-amine

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Abstract

In this paper ,*N-(2-Fluorophenyl)-2, 6-dimethyl-1, 3-dioxan-4- amine* ($C_{12}H_{16}FNO_2$) optimized geometries and frequencies of the stationary point and energies in the ground state using DFT (B3LYP) methods with 6-311Gbasis set. The calculated HOMO and LUMO energies also confirmed that the charge transfer occurred within the molecule. Bond length and bond angles values for$C_{12}H_{16}FNO_2$ were calculated by using B3LYP/ 6-311G.

Keywords: $C_{12}H_{16}FNO_2$, Dioxan, DFT, HOMO, LOMO.

Introduction

A major objective of the present course of discourses is the explanation of the reactivity of heteroaromatic compounds. Heteroaromatic compounds with 5- and 6-membered rings are best deliberated as modified benzenes. There are two quite separate ways in which benzene can be modified by the substitution of a heteroatom for one or more of the carbon atoms of the ring. The number of heteroatoms affects mainly the magnetic properties.

Dioxan is a general solvent that is often used in place of glacial acetic acid when mixtures of substance easer to be counted. It is also used [1] as stabilizer in chlorinated solvents and in many organic syntheses. There are only a very few [2–4] reports in the literature on oxidation of dioxan with other oxidants dioxan molecules, which had been used for crystallization, engaged the pocketin a similar way to that of the two leucine side chainsin the N-terminal arm bound structure. Dioxan is used as a solvent in chemical synthesis, as a fluid for scintillation calculating, and as a dehydrating agent in the research oftissue sections for histology.

1,3dioxans are cyclic acetals with a six-membered ring. The chemistry of 1,3dioxans is closely related to the protection of functional groups, therefor, the central application of 1,3 dioxans in organic synthesis is the security of ether carbonyl compounds. Many reviews dealing with the research and hydrolysis of 1,3dioxans or related cyclic acetals could be establish in works. [5-8] Since the first synthesis of a 1,3 dioxan for the protection of 4- and 6-hydroxy groups in pyranose carbohydrates,[9] the protection of carbonyl compounds or 1,3-diols as 1,3-dioxans has become a standard transformation in organic synthesis.

The studying of the structures and properties of the compound is interested. During this study we report the optimized geometries, assignments and electronic structure calculations for the compound. [10]

The crystal structure of the title compound ($C_{12}H_{16}FNO_2$) has been reported. [11] In recent years, computational chemistry is playing an important role in supporting and supplementing the experimental research, and explains the observed results. The present study considers$C_{12}H_{16}FNO_2$ whose include 1,3dioxan.The structure has been confirmed by neutron diffraction studies an disjustified by VSEPR theory.[12-13]

During this study, were report the optimized geometries, assignment sand electronic structural calculations for the compound. The main objective of the present study is to assess the performance of the hybrid density functional method B3LYP, with the6-311Gbasissets. The comparison between theory and calculation is made. In present work, density functional theory has been performed to study the electronic properties of $C_{12}H_{16}FNO_2$ to determine HOMO and LUMO of its IR, NMR and RAMAN spectrum. [14]

Computational Details

All computations were calculated by the Gaussian 09W [15] program. The molecular structure, frequencies and energy of N-(2-Fluorophenyl)-2,6-dimethyl-1,3-dioxan-4-aminein the ground state were computed by performing the DFT with the 6-311G basis set.

Results and Discussion

Molecular properties

The molecular structure and atom numbering of $C_{12}H_{16}FNO_2$ are shown in Figure1. Its figure shows three chiral centers in C_1, C_2, and C_4. All calculations were carried out using the computer program Gaussian 09W. The optimized structural parameters of $C_{12}H_{16}FNO_2$ were calculated by the DFT (B3LYP) levels with the 6-311G basis set are listed below in Table 1.

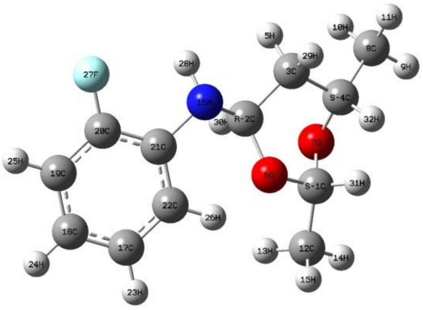


Fig 1.Molecular structure and atom numbering.

Table 1.Molecular properties for $C_{12}H_{16}FNO_2$ at DFT (B3LYP) levels with the 6-311G basis sets. A) Bond lengths B) Bond angle C) Dihedral angle.

A)

Bond lengths (Å)	**DFT(B3LYP)/6-311G**	**Experimentally**
C_1 —O_6	1.465	1.410
C_1— O_7	1.449	1.408
C_1—C_{12}	1.511	1.495
C_2 —O_6	1.492	1.444
C_2—C_3	1.535	1.508
C_4—O_7	1.474	1.437
C_4—C_8	1.518	1.506
C_2—N_{16}	1.420	1.422
N_{16}— C_{21}	1.393	1.382
C_{20}—C_{21}	1.402	1.396
C_{20}—F_{27}	1.414	1.356

B)

Bond angle (°)	**DFT(B3LYP)/6-311G**	**Experimentally**
O_6— C_1—O_7	110.23	110.36
O_7— C_1—C_{12}	107.90	108.61
C_4—O_6—C_2	113.89	111.98
C_1—O_7—C_4	112.15	111.59
O_6— C_2—N_{16}	108.90	109.35
C_2—N_{16}—C_{21}	124.91	122.05
N_{16}—C_{21}—C_{20}	118.84	118.92
C_{21}—C_{20}—F_{27}	116.61	117.05
C_3—C_4—O_7	108.55	108.78
O_7—C_4—C_8	106.78	107.55
C_3—C_4—C_8	114.07	113.66
N_{16}—C_{21}—C_{22}	124.81	124.81
C_{20}—C_{21}—C_{22}	116.42	116.24

C)

Dihedral angle(◦)	**DFT(B3LYP)/6-311G**
C_{12}—C_1—O_7—C_4	166.3998
C_{12}—C_1—O_6—C_2	-97.7943
O_6—C_2—C_3—C_4	35.6248
C_3—C_4—O_7—C_1	-68.4928
C_3—C_2—N_{16}—C_{21}	163.2197
N_{16}—C_{21}—C_{22}—F_{27}	-177.8838
N_{16}—C_{21}—C_{22}—H_{26}	3.8879
C_8—C_4—O_7—C_1	168.0993

Vibrational Analysis

Vibrational spectroscopy is extensively used in organic chemistry for the identification of functional groups of organic compounds (Raman spectra is used as a complementary IR spectrum). The calculated data of the vibrational spectrum of $C_{12}H_{16}FNO_2$ are given below in Table 2. The calculated infrared spectra and Raman spectra of N-(2-Fluorophenyl)-2,6-dimethyl-1,3-dioxan-4-amine are presented in Figure 2 and 3.

Table 2. DFT (B3LYP) with 6-311Glevel calculated vibrational frequencies of $C_{12}H_{16}FNO_2$.

DFT(B3LYP)/6-311G		
Frq(cm^{-1})	IR	Raman Activity
726.37	85.92	0.2867
805.29	6.7816	16.8468
1083.52	92.64	1.7561
1175.96	139.68	3.6930
1318.64	60.20	6.7189
1362.07	72.97	7.4319
1559.54	138.88	6.0809
3216.97	56.24	126.4306
3274.55	51.14	69.9264
3284.79	117.91	97.2259

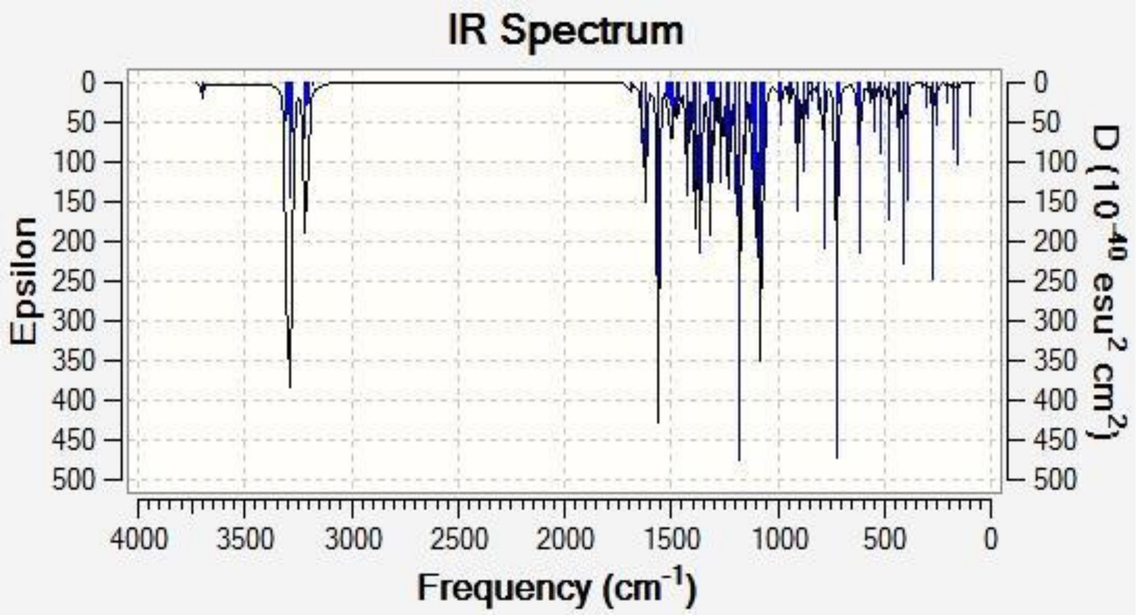


Fig 2. Calculated infrared spectra of N-(2-Fluorophenyl)-2,6-dimethyl-1,3-dioxan-4-mine by DFT (B3LYP) B) 6-311G.

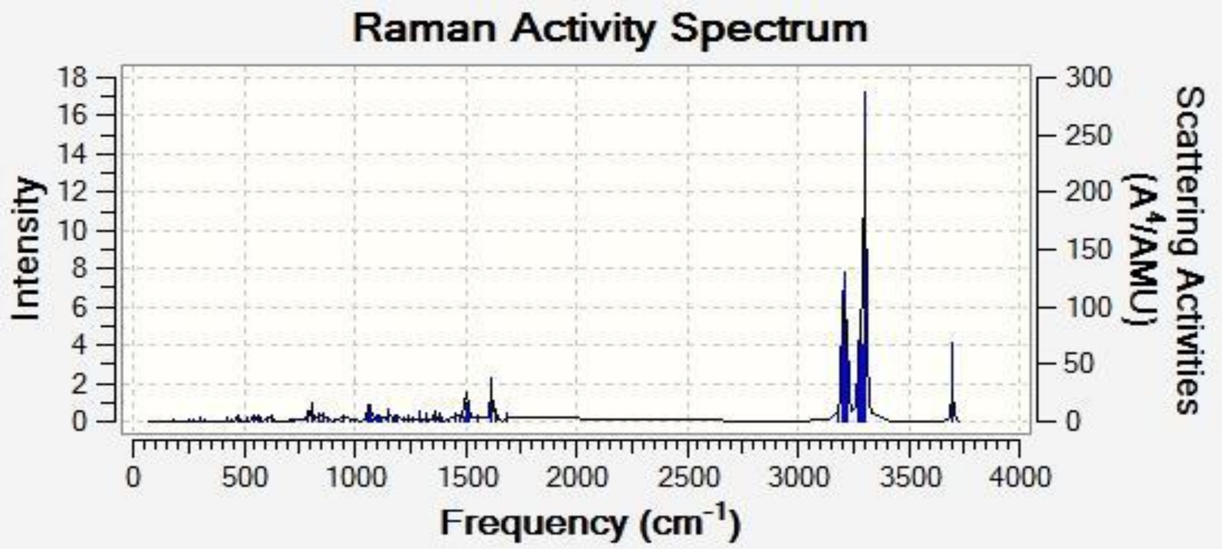


Fig 3. Calculated Raman spectra of N-(2-Fluorophenyl)-2,6-dimethyl-1,3-dioxan-4-amine by DFT (B3LYP)/6-311G.

NMR Analysis

NMR spectroscopy is a useful technique for identifying and analyzing organic compounds. In this paper, we have carried out computed chemical shift calculations of the present molecule. The NMR spectrum of N-(2-Fluorophenyl)-2,6-dimethyl-1,3-dioxan-4-amine is showed in Figure 4.

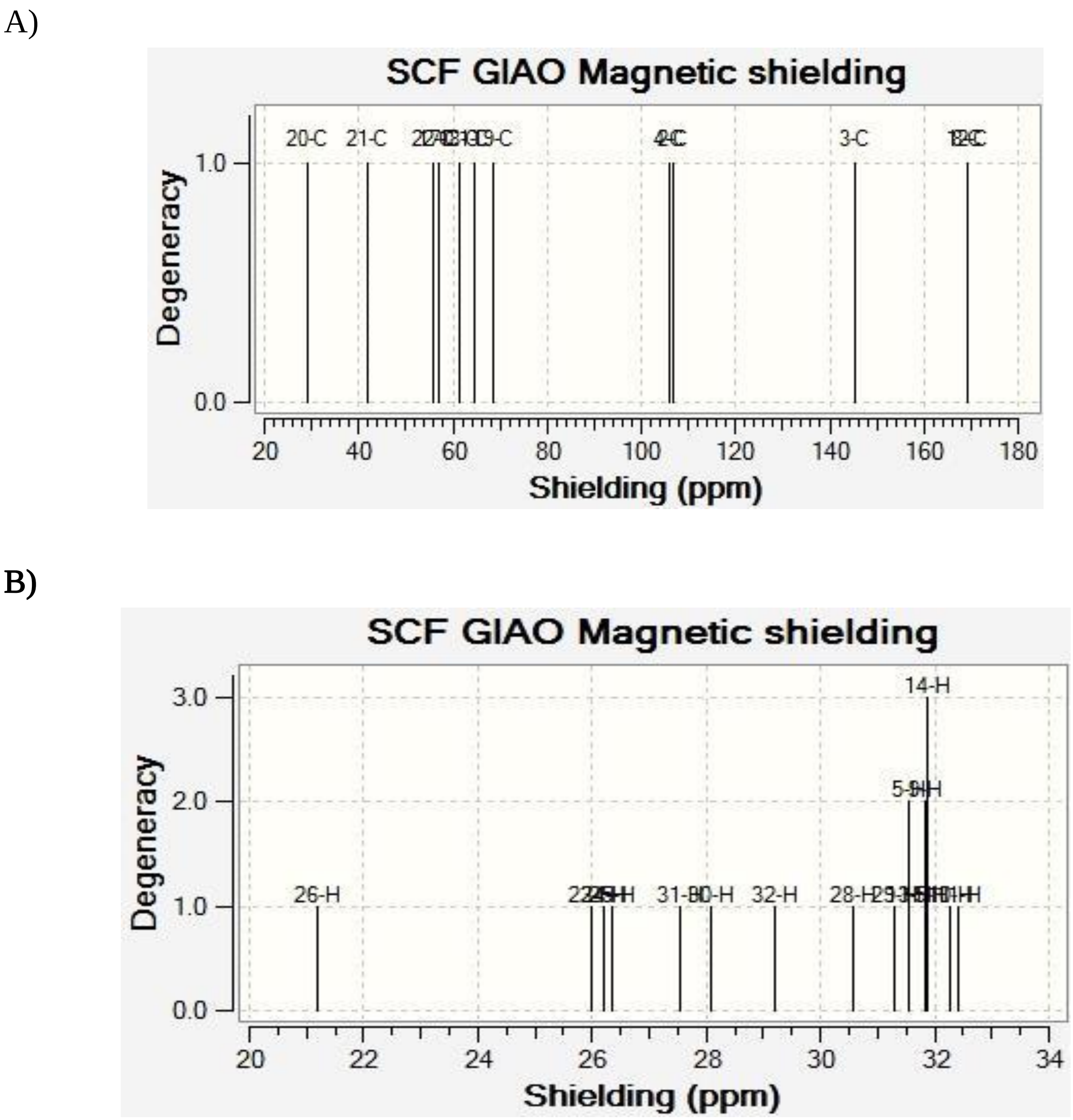
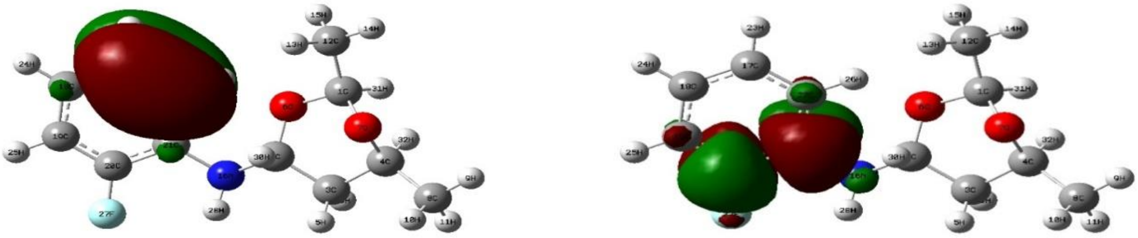


Fig 4. Calculated A) ^{13}CNMR B) ^{1}HNMR spectra of *N-(2-Fluorophenyl)-2,6-dimethyl-1,3-dioxan-4-amine* by DFT (B3LYP) 6-311G.

Orbital Analysis

The frontier orbitals are the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO). These two orbitals are highlighted because they are the closest in energy. 3D plots of HOMOs and LUMOs were obtained equivalent by DFT (B3LYP)/ 6-311G are showed in Figure 5.



E LUMO = 0.01190 a.u	ΔE = 0.25119 a.u	E HOMO = -0.23929 a.u

Fig 5. The atomic orbital compositions of the frontier molecular orbital for *N-(2-Fluorophenyl)-2,6-dimethyl-1,3-dioxan-4-amine* was obtained equivalent by DFT (B3LYP)/6-311G.

Electron Density Distribution

The total electron density distribution is a physical property of molecules. The electron density is typically showed as a comparison of the identified electron density with that predictable by spherical models of the atoms and is called deformation electron density. The total electron density was calculated by DFT (B3LYP)/ 6-311G. The maps of total electron density $C_{12}H_{16}FNO_2$ is shown in Figure 6 and also Table 3 show the Charge of $C_{12}H_{16}FNO_2$.

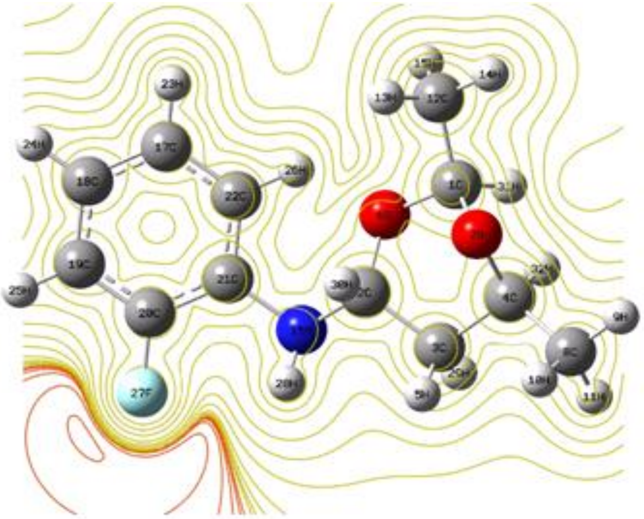


Fig 6. Contour maps of electron density for *N-(2-Fluorophenyl)-2,6-dimethyl-1,3-dioxan-4-amine* in the planes of the molecules. Electron density was calculated at the DFT (B3LYP)/6-311G.

Table 3. Charge of $C_{12}H_{16}FNO_2$.

Atom $_{NO}$	**Charge**	**Atom** $_{NO}$	**Charge**
C_1	0.293	N_{16}	-0.605
O_6	-0.518	C_{21}	0.043
O_7	-0.429	C_{20}	0.307
C_2	0.111	C_{19}	-0.214
C_3	-0.274	C_{18}	-0.115
C_4	-0.071	F_{27}	-0.320
C_8	-0.520	C_{17}	-0.204

Natural bond orbitals (NBO)

Natural Bond Orbitals (NBOs) are localized few-center orbitals that describe the Lewis-like molecular bonding pattern of electron pairs in optimally compact form .The NBO analysis involving hybridizations of selected bonds, σ and σ* energy are calculated by the DFT (B3LYP) levels with the 6-311G basis set shown in Table 4. The first bond in the Table is between carbon {atom 1} and oxygen {atom 6} and 31.77% of the bond is contributed from the C orbitals which have a hybridization of 21.7% s+ 78.23% p, while 68.23% of the bond comes from the O orbital which is 24.69% s and 75.31% p. Thus the C has formed essentially $sp^{3.59}$ hybrid orbitals, each interacting with the, $sp^{3.05}$ one carbon atom.

Table 4. The NBO Calculated Hybridizations for *N-(2-Fluorophenyl)-2,6-dimethyl-1,3-dioxan-4-amine.*

DFT(B3LYP)/6-311G				
Bond(BD)	**hybridization**	**E σ**	**E σ***	**ΔE**
C_1 —O_6	$sp^{3.59}$,$sp^{3.05}$	1.9846	0.0710	1.9136
C_1— O_7	$sp^{3.57}$,$sp^{3.69}$	1.9785	0.0492	1.9293
C_1—C_{12}	$sp^{2.36}$,$sp^{2.53}$	1.9854	0.0261	1.9593
C_2 —O_6	$sp^{3.67}$,$sp^{2.56}$	1.9873	0.0465	1.9408
C_2—C_3	$sp^{2.39}$,$sp^{2.74}$	1.9777	0.0275	1.9502
C_4—O_7	$sp^{3.9}$,$sp^{2.79}$	1.9842	0.0357	1.9485
C_4—C_8	$sp^{2.68}$,$sp^{2.48}$	1.9817	0.0248	1.9569
C_2—N_{16}	$sp^{3.07}$,$sp^{2.37}$	1.9812	0.0285	1.9527
N_{16}— C_{21}	$sp^{2.34}$,$sp^{2.77}$	1.9823	0.0267	1.9556
C_{20}—C_{21}	$sp^{1.00}$,$sp^{99.99}$	1.6608	0.0432	1.6176
C_{20}—F_{27}	$sp^{3.52}$,$sp^{2.42}$	1.9951	0.0244	1.9707

Thermodynamic parameters

Some thermodynamic parameters frequencies for N-(2-Fluorophenyl)-2,6-dimethyl-1,3-dioxan-4-amineis calculated by using the DFT (B3LYP) methods with 6-311G basis sets and was showed in Table 5.

Table 5. Some thermodynamic parameters Frequencies for $C_{12}H_{16}FNO_2$. Zero-point energy, correction energy, enthalpy lengths, Gibbs free energy.

Thermodynamic parameters	$C_{15}H_{11}OF$
Zero-point correction	0.222704 (Hartree/Particle)
Thermal correction to Energy	0.231245 (Hartree/Particle)
Thermal correction to Enthalpy	0.232190 (Hartree/Particle)
Thermal correction to Gibbs Free Energy	0.188985 (Hartree/Particle)
Sum of electronic and zero-point Energies	-572.778135 (Hartree/Particle)
Sum of electronic and thermal Energies	-572.769594 (Hartree/Particle)
Sum of electronic and thermal Enthalpies	-572.768650 (Hartree/Particle)
Sum of electronic and thermal Free Energies	-572.811854 (Hartree/Particle)

Conclusions

In this research, we are interested in investigating N-(2-Fluorophenyl)-2,6-dimethyl-1,3-dioxan-4-amine which was chosen for theoretical studies. The optimized geometries and frequencies of the stationary point and the minimum-energy paths were calculated using the DFT (B3LYP) methods with 6-311G basis set. In general,B3LYP/6-311G calculations indicated some selected bond length and bond angles values for the $C_{12}H_{16}FNO_2$.

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