DFT, FT-IR, Fukui Function and MESP analyses of 2-ethoxy-4-{(E)-[(3 nitrophenyl)imino]methyl}phenol

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Abstract

The theoretical analyses of 2-ethoxy-4-{(E)-[(3-nitrophenyl)imino]methyl}phenol have been carried out using the density functional theory (DFT) based on B3LYP level at 6-311++ G (d, p) by Gaussian program. . The molecular geometry shows good agreement with the experimental and theoretical bond lengths and bond angles. With the use of the basis set, the charge analysis and vibrational wavenumbers of the FTIR for 2-ethoxy-4-{(E)-[(3-nitrophenyl)imino]methyl}phenol were made. The molecular electrostatic surface potential (MESP) and local reactivity descriptors (fukui functions) have been studied for the title compound at the same level of theory.

Keywords: Density Functional Theory, Molecular Electrostatic Surface Potential and Fukui Function.

1. Introduction

The growth of technology and research is facilitated by the Schiff base materials, which enables an analysis of a compound's characterization with new and more advantageous methods. Theoretical investigations are reliable to characterize the molecule due to their effectiveness and accuracy relates to the evaluation of a number of molecular properties. They were made to support the experimental evidences. In the present study, the optimization of the molecular structure was calculated using B3LYP exchange correlation functional[1]. The vibrational spectral studies have been analysed on the basis of calculated potential energy distribution (PED) [2]. The Molecular electrostatic Surface Potential (MESP) is used to identify the intramolecular interactions of a molecule. A Fukui function reveals the electrophilic and nucleophilic nature of the compound.

2. Computational Details

Gaussian 09 W program [3] was used to perform the DFT calculations for the 2-ethoxy-4-{(E)-[(3-nitrophenyl)imino]methyl}phenol. The optimized geometry, vibrational wavenumbers of FT-IR, were calculated at the B3LYP level with the standard 6-311++G(d,p) basis set. The charge analysis, molecular electrostatic surface potential (MESP) and the Fukui analysis were also investigated.

3. Results and Discussion

3.1 Optimized geometry

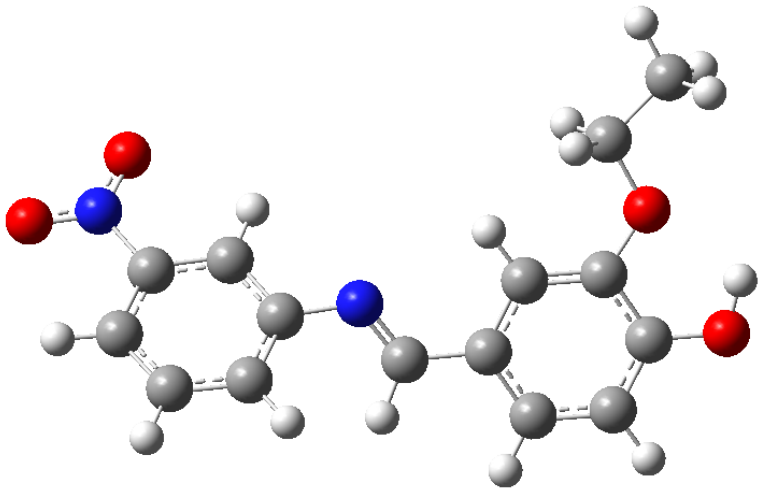

Fig.1 Optimized structure of 2-ethoxy-4-{(E)-[(3-nitrophenyl)imino]methyl}phenol

The bond length C_4-N_2 increases while that of C_{11}-N_{14} decreases because of the attachment of NO_2 group and intramolecular hydrogen bonding. Due to the hydroxyl and ethoxy groups being attached, the bond angle increases in C_{18}-C_{20}-O_{28} when compared with C_{21}-C_{20}-O_{28}. The dihedral angle C_{11}-N_{14}-C_{15}-C_{17} shows the non-planar nature of the compound and it is shown in Table 1.

Table 1

Optimized geometry of 2-ethoxy-4-(E)-[(3-nitrophenyl)imino]methylphenol at B3LYP/6-311G(d,p) level

Parameters	Experimental values (Å)	Calculated Values (Å)
C_4-N_2	1.457(6)	1.470
C_{11}-N_{14}	1.418(5)	1.408
C_{18}-C_{20}-O_{28}	126.8(4)	126.5
C_{21}-C_{20}-O_{28}	113.4(5)	114.2
C_{11}-N_{14}-C_{15}-C_{17}	180.0(4)	178.5

3.2 Charge analysis

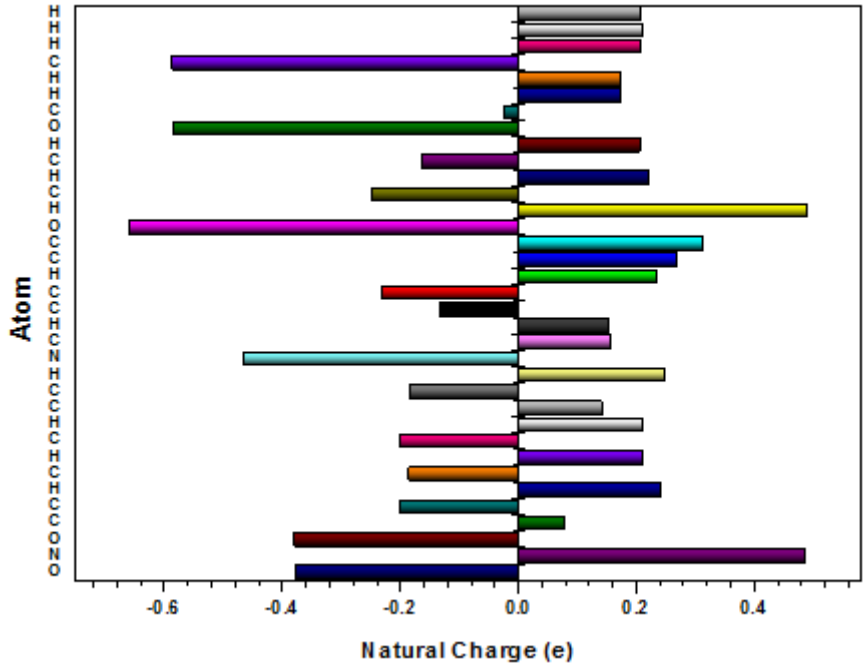

Fig.2 Natural Charge plot of 2-ethoxy-4-{(E)-[(3-nitrophenyl)imino]methyl}phenol

The natural charge of 2-ethoxy-4-{(E)-[(3-nitrophenyl)imino]methyl}phenol was calculated by using B3LYP/6-311G++(d,p) basis set. The calculated natural atomic charges were shown in Table 2. The graphical representation shows a charge disposal of a molecule is illustrated in Fig. 2

The charge at C_{11} shows positive charge due to the presence of intramolecular hydrogen bonding and C_4 shows the positive charge in benzene ring and the other carbon atoms in the benzene ring shows the negative charge due to the attachment of nitro group and the influence of steric effect between H_6 and H_8. The charge at C_{20} and C_{21} shows the positive charge and all other carbon atoms shows negative charge. In C_{20} shows positive due to the presence of ethoxy group and the influence of steric effect between H_{19} and H_{31} and C_{21} is positive due to the attachment of O_{22}-H_{23} group and also the influence of steric effect between H_{25} and H_{27}. The charge at H_{13} increases when comparing to all the other hydrogen atoms in benzene ring is due to the attachment of NO_2 group. The highest positive charge occurs at H_{23} atom and the highest negative charge occurs at O_{22} atom due to the presence of intramolecular hydrogen bonding. This is supported by optimized geometry.

3.3 Vibrational analysis

The C-H stretching vibrations normally lie between 3100 and 3000 cm^{-1}[4]. In this region the bands are not affected appreciably by the nature of substituents. The C-H symmetric stretching is observed at 3093cm^{-1}. The C-C stretching vibration is expected in the region between 1628-1570 cm^{-1}[5]. The peak observed at 1626 cm^{-1}. The carbonyl C=O stretching vibration is expected in the region of 1715-680 cm^{-1} and in the present study it is observed at 1707 cm^{-1} in theoretical calculation. The C-N stretching mode of vibration observed nearly 1300 cm^{-1}[6]. The peak observed in IR at 1320 cm^{-1}. The range between 1550-1475 cm^{-1} corresponds to N-O asymmetric stretching group of vibration. In FT-IR the band occurs at 1481 cm^{-1}.

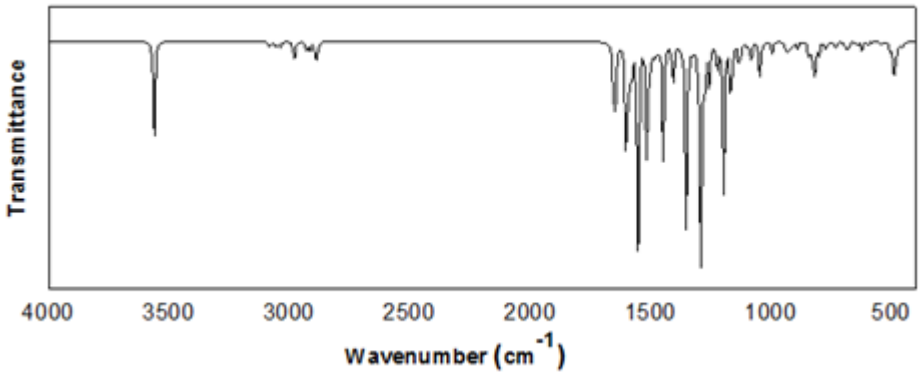

Fig. 3 FTIR spectrum of 2-ethoxy-4-{(E)-[(3-nitrophenyl)imino]methyl}phenol

3.4 Molecular electrostatic surface potential analysis (MESP):

The MESP (Molecular Electrostatic Surface Potential) map of 2-ethoxy-4-{(E)-[(3-nitrophenyl)imino]methyl}phenol was calculated using B3LYP / 6-311++G(d,p) level of theory. The charge distributions of MESP are very helpful in the visualization of the molecular interaction represents the molecular shape and size [7] are shown in Fig.4. Various colours identifies in the mapping reflects the total electrons in atomic sites. Red colour indicates more negative and white indicates more positive. The red region exhibits a greater electronegative electrostatic potential, blue region displays more electropositive electrostatic potential and green region denotes a zero potential zone. In the present study, it is well defined from the map that shows that the electrons are richly situated on Nitrogen atoms and the electrons are positioned insufficiently on hydrogen atoms.

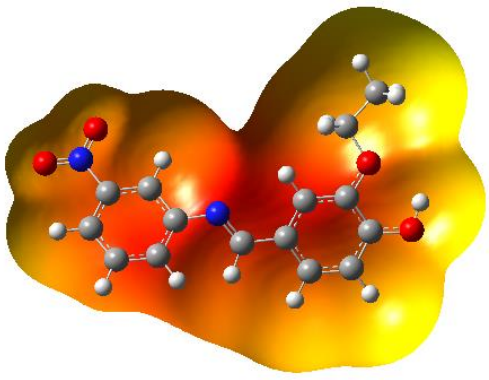

Fig. 4 MESP plot for 2-ethoxy-4-{(E)-[(3-nitrophenyl)imino]methyl}phenol

3.6 Fukui function

The Fukui function is the most basic and commonly used reactivity indicators. Fukui function indicates these reactive sites in electrophilic or nucleophilic processes within a molecule [8]. The following equations are used to calculate the Fukui functions for electrophilic, nucleophilic, and free radical attacks on the basis of the B3LYP/6-311++G(d,p) level of theory.

$$f_k^{-} = q_j(\mathrm{N}) - q_j(\mathrm{N}-1)$$

$$f_k^{+} = q_j(\mathrm{N}+1) - q_j(\mathrm{N})$$

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

For an electrophillic f_k^-, nucleophillic f_k^+ or free radical attack f_k^0 of the molecule. In these equations q_j is the atomic charge at the j^{th} atomic site in the neutral (N), anionic (N+1) or cationic (N-1) chemical species. The values of the Fukui function were obtained from the NBO charges are shown in Table 2. Adding an electron to a molecule causes the electron density to decrease in some places, as indicated by the negative Fukui function, alternatively removing an electron from a molecule causes the electron density to be increased.. Equation gives the difference between electrophilic and nucleophilic Fukui function is given by,

$$\Delta f(\mathrm{r}) = [f^{+}(\mathrm{r}) - f^{-}(\mathrm{r})]$$

When Δf(r)>0, then the position specifies a electrophilic attack, however when Δf(r)<0, its position specifies an nucleophilic attack. From the calculated values the order of the electrophilic position at Δf(r)>0 for the 2-ethoxy-4-{(E)-[(3-nitrophenyl)imino]methyl}phenol is 35H>22O>32C>28O>14N>3O>1O>24C>7C>18C>12C>26C>17C>5C>9C>29C, while the nucleophilic position Δf(r) <0 is 4C>16H>11C>30H>31H>27H>33H>34H>10H>25H>8H>19H>6H>15C>13H>20C>21C>23H>2N are ordered in descending order. Reactive nucleophilic and electrophilic sites are positioned in accordance with the surface of the total electron density and chemical activity.

Table 2
Fukui Analysis of 2-ethoxy-4-{(E)-[(3-nitrophenyl)imino]methyl}phenol

Atoms	Anion	Cation	Neutral	f_k^-	f_k^+	f_k^0	Δf(r)
	q_{N-1}	q_{N+1}	N				
1O	-0.31581	-0.17313	-0.37848	-0.06267	0.20535	0.07134	0.26802
2N	0.13705	0.2387	0.48659	0.34954	-0.24789	0.050825	-0.59743
3O	-0.30391	-0.17494	-0.38001	-0.0761	0.20507	0.064485	0.28117
4C	0.02227	0.05767	0.07767	0.0554	-0.02	0.0177	-0.0754
5C	-0.22367	-0.1246	-0.20225	0.02142	0.07765	0.049535	0.05623
6H	0.11503	0.13219	0.24219	0.12716	-0.11	0.00858	-0.23716
7C	-0.07143	-0.07379	-0.18647	-0.11504	0.11268	-0.00118	0.22772
8H	0.09152	0.11649	0.21242	0.1209	-0.09593	0.012485	-0.21683
9C	-0.24439	-0.11832	-0.20156	0.04283	0.08324	0.063035	0.04041
10H	0.09783	0.11215	0.21203	0.1142	-0.09988	0.00716	-0.21408
11C	0.06481	0.05983	0.14296	0.07815	-0.08313	-0.00249	-0.16128
12C	-0.09983	-0.11604	-0.18509	-0.08526	0.06905	-0.00811	0.15431
13H	0.11787	0.1325	0.24925	0.13138	-0.11675	0.007315	-0.24813
14N	-0.27586	-0.27235	-0.46707	-0.19121	0.19472	0.001755	0.38593
15C	-0.0241	0.09878	0.15709	0.18119	-0.05831	0.06144	-0.2395
16H	0.07149	0.08744	0.15408	0.08259	-0.06664	0.007975	-0.14923
17C	-0.06053	-0.09576	-0.13365	-0.07312	0.03789	-0.01762	0.11101
18C	-0.16849	-0.09111	-0.23376	-0.06527	0.14265	0.03869	0.20792
19H	0.11537	0.12572	0.2334	0.11803	-0.10768	0.005175	-0.22571
20C	0.14343	0.12162	0.26913	0.1257	-0.14751	-0.01091	-0.27321
21C	0.08757	0.11286	0.31283	0.22526	-0.19997	0.012645	-0.42523
22O	-0.35108	-0.34369	-0.66081	-0.30973	0.31712	0.003695	0.62685
23H	0.24014	0.25441	0.48911	0.24897	-0.2347	0.007135	-0.48367
24C	-0.11988	-0.1126	-0.24933	-0.12945	0.13673	0.00364	0.26618
25H	0.10137	0.1262	0.22184	0.12047	-0.09564	0.012415	-0.21611
26C	-0.11907	-0.09766	-0.16521	-0.04614	0.06755	0.010705	0.11369
27H	0.09853	0.11684	0.20619	0.10766	-0.08935	0.009155	-0.19701
28O	-0.29694	-0.30011	-0.58337	-0.28643	0.28326	-0.00159	0.56969
29C	-0.01157	-0.01501	-0.02365	-0.01208	0.00864	-0.00172	0.02072
30H	0.0865	0.09102	0.17366	0.08716	-0.08264	0.00226	-0.1698
31H	0.0873	0.09138	0.17433	0.08703	-0.08295	0.00204	-0.16998
32C	-0.29262	-0.29668	-0.58773	-0.29511	0.29105	-0.00203	0.58616
33H	0.0996	0.1077	0.2061	0.1065	-0.0984	0.00405	-0.2049
34H	0.10158	0.11442	0.21111	0.10953	-0.09669	0.00642	-0.20622
35H	0.9993	0.10786	0.20643	-0.79287	-0.09857	-0.44572	0.6943

Conclusion

The compound 2-ethoxy-4-(E)-[(3-nitrophenyl)imino)methylphenol was identified and analyzed at the DFT level. The geometrical parameters of 2-ethoxy-4-(E)-[(3-nitrophenyl)imino)methylphenol were found to be in good agreement with the experimental results. The presence of functional groups has been identified by FT-IR spectral analysis. MESP map confirms the intramolecular interactions which justifies the presence of hydrogen bonding. Fukui calculations were also performed with variable charge and multiplicity, and the electrophilic and nucleophilic sites were also investigated.

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