Molecular Structure, Optimized Geometry, HOMO-LUMO Energy and Mulliken Charges of a New Schiff Base 2-(Naphthalen-2-yliminomethyl) Phenol by *ab Initio* and Density Functional Theory Calculations

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ABSTRACT   The molecular structure, optimized geometry, HOMO-LUMO energy and Mulliken charges of 2-(naphthalen-2-yliminomethyl) phenol (2-NAS) are calculated using ab initio and density functional theory methods employing the 6-311+G(d,p) basis set. The optimized geometrical parameters obtained by B3LYP method show good agreement with experimental X-ray data. The HOMO and LUMO energies show that charge transfer occurs in the molecule. The Mulliken charges are computed. The intra-molecular hydrogen bonding interaction was identified between nitrogen (aminonaphthalene moiety) and hydroxyl group of methyl phenol (H-O...N).

1. Introduction
Naphthalene used as an insecticide and also used in the synthesis of 2-naphthol, a precursor for various dyestuffs- azo dyes, eosin, indigo, pigments, rubber processing chemicals and other miscellaneous chemicals and pharmaceuticals [1]. Schiff base complexes have been studied extensively, due to their interesting structures and broad applications [2,3]. Studies of these compounds are of great interest in various aspects of chemistry, such as functional coordinated complex, photo electric materials, catalytic materials [4,5] etc. The presence of the amino group in this compound leads to condensation with aldehyde, thus enlarging the number of functional groups. Schiff bases with azomethine linkage were used as anti infectious agents. Recently, the synthesis and crystal structure of a new Schiff base 4-[(2-hydroxy-benzylidene)-amino-N-(5-methyl-isoxazol-3-yl)-benzene sulfonamide [6], synthesis of metal complexes chelated with N-naphthalenyl aminomethyl phenol and their application to OELD [7] have already been reported. In our previous work, we have studied synthesis and crystal structure of a new Schiff base 2-(naphthalen-2-ylimino methyl) phenol [8]. Density functional theory (DFT) and ab initio (HF) have become very popular recently as a general approach to molecular properties. In this present study, the molecular structure, optimized geometry, HOMO-LUMO energy and Mulliken charges have been performed.

2. Computational details
To provide complete information regarding the structural characteristics of 2-NAS the HF and DFT-B3LYP with 6-311+G(d,p) basis set correlation functional calculations have been carried out. The calculations of geometrical parameters in the ground state were performed using the Gaussian 09W program [9], invoking gradient geometry optimisation [10]. Moreover, no constrains for symmetry, bonds and angles, were employed in the geometry optimization calculations. The optimized geometrical parameters, HOMO, LUMO, dipole moment, the first-order hyperpolarizability and the Mulliken charges were calculated.

3. Experimental Details
The title compound was synthesized by the condensation of 2-naphthylamine (NA) and 2-hydroxy benzaldehyde (salicylaldehyde-SA) [11]. A mixture of NA(0.25m) was mixed with SA(0.25m) and the contents were refluxed for 4 hours. The reaction mixture was kept for crystallization. After three days yellow prisms of compound (2-NAS) were obtained (scheme a). A crystal with dimensions of 0.04 × 0.05 × 0.05 mm³ was used for X-ray data collection.

4. Results and Discussion
Arunagiri et al. [8] already reported the crystal structure of the title compound [2-(naphthalen-2-ylimino methyl) phenol], $C_{17}H_{13}NO$. The 2-NAS is of orthorhombic crystal system, space group $Pca2_1$, with dimension, a = 13.6460(3) Å, b = 5.8732(1) Å, c = 15.8729(3) Å, α =β = γ = 90° and Z=4.

4.1. Molecular geometry
The optimized geometrical parameters, namely, bond lenths and angles calculated by HF/6-311+G(d,p) and B3LYP/6-311+G(d,p) methods listed in Table 1 are in accordance with atom numbering scheme shown in Fig.1. The correlation between the experimental and calculated geometric parameters obtained by both methods. Owing to our calculations, B3LYP method correlates well for bond lenths and angles when it is compared with HF method.

From the experimental data (XRD), the bond length of N12 = C19 is found to be 1.281 Å. Similarly the calculated N12 = C19 bond length is 1.278 (HF) and 1.268 Å (B3LYP) respectively. The bond length and bond angle of N12 = C19 and C2−N12−C19, the smallest difference between the experimental and calculated B3LYP value is found to be 0.013 Å and 1.287°. The deviation is not much. The formation of double bond between carbon and nitrogen (C=N) confirms the condensation.

The calculated bond length of C22−O27 is 1.411 Å (HF) and 1.379Å (B3LYP) values are compared with expermental value of 1.356 Å. The hydroxy group of salicylate (O27−H32), bond lengh is 0.974Å (HF) and 0.949Å (B3LYP) respectively. Experimentally the bond length is found to be 0.930 Å. It agrees well with calculated B3LYP value. The very slight deviation is due to hydrogen bonding between the hydroxyl group and azomethine nitrogen.

5. HOMO-LUMO energy
Highest Occupied Molecular Orbital (HOMO) and Lowest

Unoccupied Molecular Orbital (LUMO) are very important parameters for quantum chemistry [12]. HOMO represents the ability to donate an electron; LUMO represents the ability to accept an electron. The LUMO–HOMO energy gap of 2-NAS shows that the energy gap reflects the chemical reactivity and the level of conductivity of the molecule [13]. That is, the smaller value of energy gap, the easier electron transfers from HOMO to LUMO. Relatively large LUMO–HOMO energy gap of the studied molecule indicates that it would not be kinetically stable [14]. Molecular orbitals provide insight into the nature of reactivity, conjugation, aromaticity, lone pairs and some of the structural and physical properties of molecules. The region of HOMO spread over the entire molecule while in the LUMO the ring part has more overlapping. The energy gap between HOMO and LUMO is a critical parameter in determining electrical transport properties [15]. The atomic compositions of the frontier molecular orbital of 2-NAS are shown in Fig.2. The HOMO and LUMO orbitals are distributed not only on the conjugated molecular backbones, but also as a substituent.

HOMO energy = −7.5826238 eV
LUMO energy = 1.6030589 eV

The frontier orbital energy gap (HOMO- LUMO) is found to be – 5.9795649 eV for B3LYP/6-311+G(d,p) method. The HOMO and LUMO energy gap explains the fact that eventual charge transfer interaction is taking place within the molecule. The corresponding global minimum energy obtained by the HF and B3LYP/6-311+G(d,p) methods are −785.57910042 Hartrees and −780.37385651 Hartrees.

The value of dipole moment for 2-NAS was also calculated. Dipole moment (μ) is a measure of the molecular charge distribution and is given as a vector in three dimensions. According to B3LYP and HF calculations, the higher dipole moment was observed 3.6594 Debye for HF/6-311+G(d,p) basis set whereas the smaller one was observed 2.9758 Debye for B3LYP/6-311+G(d,p) basis set.

6. Mulliken charges

Atomic charge has been used to describe the processes of electronegativity equalization and charge transfer in chemical reactions [16] and to model the electrostatic potential outside molecular surfaces [17]. Effective atomic charge calculations have an important role in the application of quantum chemical calculation to molecular system because of atomic charges effect dipole moment, molecular polarizability, electronic structure, acidity–basicity behavior and a lot of properties of molecular systems. Our interest here is the comparison of the B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) methods to describe the electron distribution of the 2-NAS. Mulliken charge distributions were calculated by determining the electron population of each atom as defined by the basis set. The calculated Mulliken charge values using B3LYP and HF levels of theory and basis set is listed in Table 2. The better represented graphical forms of the results were depicted in Fig. 3.

The results of Table 2 and related figure indicate that the change of the charge distribution occurs by a changing the basis set. The charge changes with basis set are changed due to polarization [18,19]. As seen from Table 2 that C1, C3, C5, C6, C7, C8, C9, C22, C24, C25 and C26 atoms exhibit a substantional negative charge (Except C2, C4, C19 and C23), which are donor atoms of both methods. C10 and C21 atoms exhibits a positive charge, which is an acceptor atoms of both methods. By using both methods, all the H atoms have positive charges. N12 and O27 atoms also exhibit a negative charge, which are donor atoms. These atoms may also play an important role in the biological activity of 2-NAS.

7. Hyperpolarizability calculations

Before calculating the hyperpolarizability of the investigated compound, the geometry taken from the starting structure, based on its crystallogrphic data was optimized in the B3LYP level. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. All optimized structures were confirmed to be minimum energy conformations [20]. The polarizability and hyperpolarizability characterize the response of a system in an applied electric field [21]. The first-order hyperpolarizability (β) of this novel molecular system and the related properties (β0, α0 and Δα) of 2-NAS are calculated using B3LYP with 6-311+G(d,p) basis set, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first hyperpolarizability is a third - rank tensor that can be described by a 3 × 3 × 3 matrix. The 27 components of the 30 matrix can be reduced to 10 components due to the Kleinman symmetry [22,23]. The components of β0 are defined as the coefficients in the Taylor series exponents the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes:

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma + \quad \dots (1)$$

where E^0 is the energy of the unperturbed molecules, F_α is the field at the origin and μ_α, $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first-order hyperpolarizability respectively. The total static dipole moment (μ), the mean polarizability (α_0) and the mean first-order hyperpolarizability (β_0), using the x, y, z components they are defined as follows:

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_x^2\right)^{\frac{1}{2}} \quad \dots (2)$$

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

$$\beta_0 = \sqrt{(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2} \quad \dots\dots(3)$$

The α_0 and β_0 components of Gaussian output are reported in atomic units and therefore the calculated values are converted into e.s.u. units (α_0 : 1 a.u = 0.1482 × 10^{-24} e.s.u ; β_0 : 1 a.u. = 8.3693 × 10^{-33} e.s.u) [24].

According to the present calculations, polarizability (α) is 27.99290× 10^{-24} e.s.u. and the first-order hyperpolarizability (β_0) is 2.373314 × 10^{-30} e.s.u. for 2-NAS molecule, which is comparable with the reported values of similar derivatives [25]. The calculated polarizability (α_0) and first order hyperpolarizability (β_0) is collected in Table 3 and 4. The theoretical calculation seems to be more helpful in determination of particular components of β_0 tensor than in establishing the real values of β_0. Domination of particular components indicates the substantial delocalization of charges in those directions. The maximum β_0 was due to the behavior of non-zero μ value.

8. Conclusion

The results of experimental and the HF and DFT/B3LYP level of theory with 6-311++G(d,p) basis set is reported here. Computed and experimental geometric parameters of the title compound has been compared with each other. Results with multiplied factors seemed to be in good agreement with experimental ones. The B3LYP level, which have electron correlation component, shown better fit to the experimental ones than those of HF level in terms of evaluate bond angles. It is very useful for understanding molecular structure analysis. The first order hyperpolarizability of 2-NAS was found to be 2.373314 × 10^{-30} e.s.u. The Mulliken charges, HOMO and LUMO calculations were performed for the title molecule.

Table 1.

Optimized geomentrical parameters of 2-NAS with 6-311+G(d,p) basis set, bond lengths (Å), bond angles (°)

Parameters	HF	B3LYP	XRD value[8]	Parameters	HF	B3LYP	XRD value[8]
C1-C2	1.378	1.366	1.369	C2-C1-C9	120.786	121.325	122.112
C1-C9	1.423	1.417	1.411	C2-C1-H11	120.296	118.773	119.00
C1-H11	1.082	1.072	0.930	C9-C1-H11	118.914	119.902	119.00
C2-C3	1.424	1.423	1.408	C1-C2-C3	120.101	119.370	118.702
C2-N12	1.431	1.413	1.420	C1-C2-N12	122.351	123.239	124.392
C3-C4	1.371	1.362	1.365	C3-C2-N12	117.207	117.371	116.902
C3-H13	1.080	1.072	0.930	C2-C3-C4	120.363	120.415	120.612
C4-C10	1.426	1.420	1.412	C2-C3-H13	118.361	119.891	120.00
C4-H14	1.083	1.074	0.930	C4-C3-H13	121.275	119.673	120.00
C5-C6	1.379	1.364	1.357	C3-C4-C10	121.085	121.153	121.52
C5-C10	1.422	1.419	1.420	C6-C7-H17	119.554	119.453	120.00
C5-H15	1.083	1.074	0.930	C8-C7-H17	120.095	120.219	120.00
C6-C7	1.418	1.416	1.400	C7-C8-C9	120.899	120.753	121.502
C6-H16	1.082	1.073	0.930	C7-C8-H18	120.356	120.431	119.00
C7-C8	1.378	1.364	1.360	C9-C8-H18	118.744	118.816	119.00
C7-H17	1.082	1.073	0.930	C1-C9-C8	122.174	121.973	122.572
C8-C9	1.424	1.421	1.407	C1-C9-C10	119.109	119.167	118.802
C8-H18	1.083	1.074	0.930	C8-C9-C10	118.717	118.859	118.622
C9-C10	1.436	1.413	1.413	C4-C10-C5	122.566	122.295	123.122
N12-C19	1.278	1.268	1.281	C4-C10-C9	118.522	118.543	118.262
C19-H20	1.090	1.076	0.930	C5-C10-C9	118.909	119.159	118.632
C19-C21	1.488	1.469	1.450	C2-N12-C19	124.576	123.369	122.082
C21-C22	1.404	1.393	1.405	N12-C19-H20	115.181	122.751	119.00
C21-C26	1.407	1.394	1.390	N12-C19-C21	130.091	121.525	121.952
C22-C23	1.394	1.387	1.392	H20-C19-C21	114.711	115.717	119.00
C22-O27	1.411	1.379	1.356	C19-C21-C22	123.548	120.258	121.952
C23-C24	1.396	1.386	1.375	C19-C21-C26	118.389	121.561	119.432
C23-H28	1.081	1.074	0.930	C22-C21-C26	117.991	118.180	118.592
C24-C25	1.397	1.390	1.382	C21-C22-C23	121.053	121.235	119.692
C24-H29	1.082	1.073	0.930	C21-C22-O27	119.741	117.225	121.512
C25-C26	1.395	1.385	1.376	C23-C22-O27	119.165	121.539	118.802
C25-H30	1.081	1.072	1.020	C22-C23-C24	120.050	119.598	120.102
C26-H31	1.083	1.071	1.020	C22-C23-H28	118.695	120.099	120.00
O27-H32	0.974	0.949	0.930	C24-C23-H28	121.254	120.333	120.00
				C23-C24-C25	119.870	120.188	120.802
				C23-C24-H29	119.883	119.552	120.00
				C25-C24-H29	120.247	120.259	120.00
				C24-C25-C26	119.731	119.584	119.302
				C24-C25-H30	120.269	120.263	120.00
				C26-C25-H30	120.00	120.154	120.00
				C21-C26-C25	121.239	121.214	121.502
				C21-C26-H31	118.987	117.874	119.00
				C25-C26-H31	119.765	120.912	119.00
				C22-O27-H32	113.288	115.311	107.102

Table 2.
Mulliken charges for optimized geometry of 2-NAS at HF and B3LYP methods with 6-311+G(d,p) basis set

Atom	HF	B3LYP	Atom	HF	B3LYP
C1	-0.320373	-0.174767	H17	0.188542	0.232984
C2	0.488423	-0.275369	H18	0.206995	0.246592
C3	-0.123917	-0.381078	C19	-1.046802	0.283550
C4	-0.319000	0.079654	H20	0.222558	0.244104
C5	-0.379556	-0.267397	C21	2.014791	0.915857
C6	-0.313188	-0.235923	C22	-1.226612	-1.157727
C7	-0.458368	-0.345581	C23	-0.129921	0.157120
C8	-0.559097	-0.434410	C24	-0.124726	-0.432444
C9	-0.362931	-0.059114	C25	-0.189158	-0.377562
C10	1.118040	0.414619	C26	-0.239421	-0.269054
H11	0.233973	0.261150	O27	-0.539689	-0.776595
N12	-0.172145	-0.124272	H28	0.218312	0.233335
H13	0.200747	0.238667	H29	0.201495	0.240382
H14	0.206990	0.246716	H30	0.200293	0.239485
H15	0.209285	0.243815	H31	0.213952	0.292310
H16	0.188798	0.233277	H32	0.391711	0.507675

Table 3.
**The Polarizability (α_0) of 2-NAS derived from B3LYP/6-311+G(d,p) calculation.**

α_0 Component	Values (a.u.)
α_{xx}	154.23497
α_{xy}	95.69365
α_{yy}	301.01981
α_{xz}	11.32001
α_{yz}	−14.35770
α_{zz}	185.88597
$\alpha_{0\ Total}$	188.88597 a.u.
$\alpha_{0\ Total}$	27.99290×10^{-24} e.s.u.

Table 4.
**The first order hyperpolarizability (β_0) of 2-NAS derived from B3LYP/6-311+G(d,p) calculation**

| β_0 Component	Values (a.u.)
β_{xxx}	−12.97555
β_{xxy}	−40.37055
β_{xyy}	−100.89516
β_{yyy}	−242.74165
β_{xxz}	2.82011
β_{xyz}	−65.40514
β_{yyz}	−70.58959
β_{xzz}	19.00856
β_{yzz}	25.10198
β_{zzz}	137.38278
$\beta_{0\ Total}$	283.57382 a.u.
$\beta_{0\ Total}$	2.373314×10^{-30} e.s.u

Figure caption
Scheme (a). Schematic representation of synthesis of Schiff base
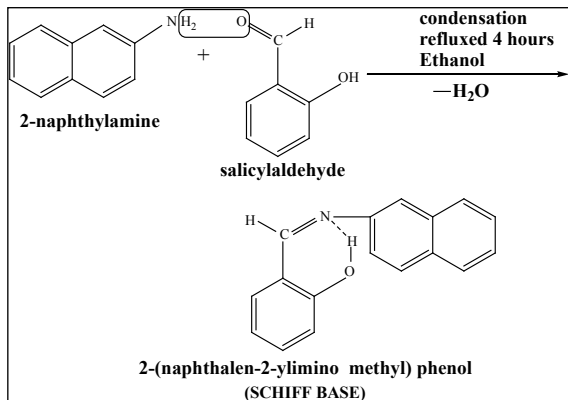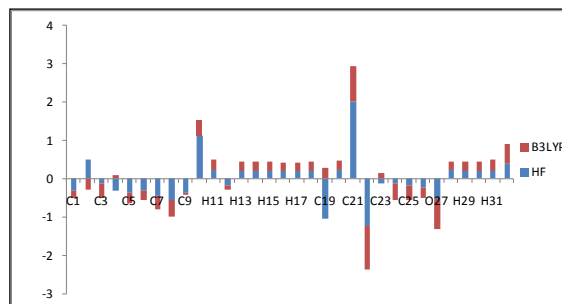

Fig.1. Optimized molecular structure of 2-(naphthalen-2-yliminomethyl) phenol along with numbering of atoms.
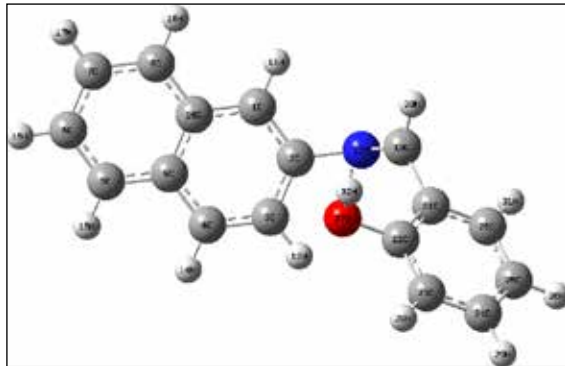
Fig.2. The atomic orbital compositions of the frontier molecular orbital for 2-(naphthalen-2-yliminomethyl) phenol.
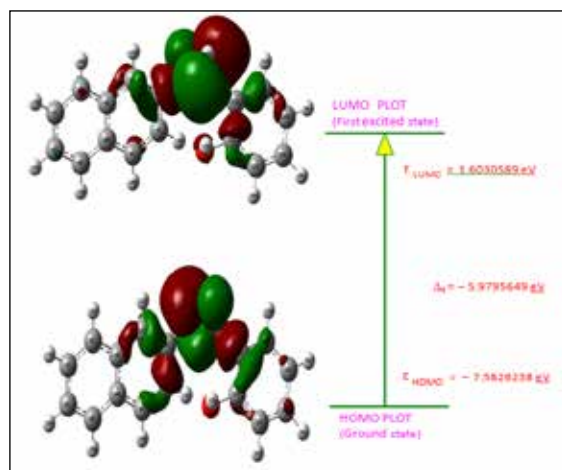
Fig.3. Comparative of Mulliken's plot by HF/6-311+G(d,p) and B3LYP/6-311+G(d,p) of of 2- (naphthalen-2-ylimino methyl) phenol.

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