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Synthesis, FT-IR, ^{1}H and ^{13}C NMR spectroscopic and computational investigation of a new (*E*)-*N*^{1}-(2-(4-isobutylphenyl)propylidene)benzene-1,2-diamine

E. Dhinesh Kumar[1], A. Prabhakaran[2] and M. Arockia Doss[3]
[1]Department of Chemistry, Annamalai University, Annamalainagar 608 002, India.
[2]Department of Chemistry, CK College of Engineering and Technology, Cuddalore, 607003.
[3]Department of Chemistry, St. Joseph University, Nagaland 797 115, India.

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ABSTRACT

(*E*)-*N*^{1}-(2-(4-isobutylphenyl)propylidene)benzene-1,2-diamine, an organic material has been synthesized and their chemical structure was confirmed by means of elemental analysis, FT-IR, ^{1}H and ^{13}C NMR spectral techniques. The molecular geometry has been interpreted with the aid of structure optimization based on DFT/B3LYP and HF methods with 6-31G(d,p) level theory. The SXRD data were compared with the optimized parameter. Optimized geometry parameters are very well agrees with the reported one. FT-IR spectrum is recorded at room temperature. Functional group assignment was discussed on the B3LYP and HF level theories. The chemical reactivity and charge density of the compounds was obtained by Mulliken and MEP surface analyses. The energy gap, electronic properties were measured and discussed. The intramolecular charge transfer interaction and π-electron cloud movement in title molecule must be responsible for the NLO properties.

Introduction

Schiff bases are products of the reaction taking place between primary amines and ketone or carbonyl compounds [1,2]. Synthesis of privileged Schiff base an economical and environment friendly method is always desirable because Schiff base moieties are of paramount interest in medicinal chemistry due to their antifungal, antimicrobial, antitumor and anticancer properties [3-12]. The Schiff base structural motif is also a building block of pharmaceutics and functional materials. Schiff bases have fun a important role in progress of coordination chemistry [13,14] as they eagerly form stable complexes. Furthermore, their effective role as therapeutic agents [15] and their remarkable catalytic activity [16,17] have added to their significance. In addition, Schiff bases are used as intermediates in synthesis of organic compounds, pigments, dyes, stabilizers and corrosion inhibitors [18,19]. From this review it makes clear that there are a large number of systems that can be studied by employing a variety of experimental techniques. It is, therefore, quite important to select such systems that can serve as useful prototypes of important and unique properties. During the last years, computational chemical models are playing an ever increasing role in chemical research [20-22]. The quantum chemical computations have been recently used as a successful method in the vibrational analysis of natural products, drug and biological compounds [23-25]. Nonlinear optics deal with the interaction of electromagnetic fields applied in different materials to generate new electromagnetic fields, modified in wavenumber, phase or other physical properties [26].Organic molecules capable of efficiently processing optical signals are important in such techniques as optical communication, optical computing and dynamic image processing [27,28]. Phenyl substituents can increase molecular hyperpolarizability,[29] a result described as surprising. Many organic molecules containing conjugated π electrons and first order hyperpolarizabilities have been analysed by means of vibrational spectroscopy [30]. Despite the great interest on optical properties of Schiff bases, we have found only a marginal theoretic background in the field of rational colour design of Schiff base-based materials. This work deals with the synthesis, spectral characterization of (*E*)-*N*^{1}-(2-(4-isobutylphenyl)propylidene)benzene-1,2-diamineand also quantum chemical calculations are used to elucidate the molecular structure, HOMO–LUMO, dipole moment, polarizability, first order hyperpolarizability, Mulliken population along with the molecular electrostatic potential surface.

Experimental details

Synthesis of the (*E*)-*N*^{1}-(2-(4- isobutylphenyl)propylidene) benzene-1,2-diamine (IBPBD)

After mixing the methanolic solution (50 ml) of benzene-1,2-diamine with 2-(4-isobutylphenyl)propanal in methanol (50 ml), the **IBPBD** was easily synthesized by refluxing the solution. At water bath temperature, reflux was continued for ca. 2 h. The crystalline solid formed was collected by vacuum filtration and washed in absolute ethanol. The product was dried at room temperature. **Fig. 1** shows a schematic picture representing the synthesis of molecule.

All solvents and chemicals were purchased from commercial sources (Sigma–Aldrich and Fisher Scientific) and were used without additional purification. The melting point of **IBPBD** was calculated in open capillaries and is uncorrected. FT-IR spectrum was obtained by using an AVATAR-330 Fourier transformed infrared (FT-IR)

Tele:
E-mail address: arockia91@gmail.com

spectrometer using KBr (pellet form). The NMR spectra were measured on a Bruker instrument in DMSO-*d*$_6$ solution. The chemical shifts were measured relative to TMS.

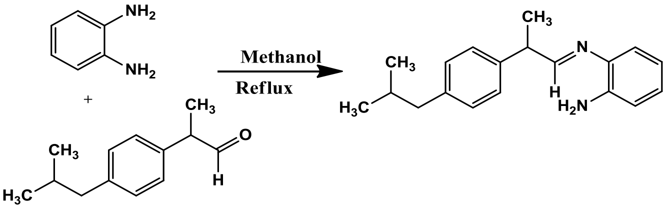


Fig. 1. Representation of the synthesis of the Schiff base.

White solid; Yield 85%., M.P: 190-192°C, MF: $C_{19}H_{24}N_2$; elemental analysis: Calcd (%): C, 81.38; H, 8.63; N,9.99; found (%):C,81.30 ;H, 8.58; N, 9.87; IR (KBr, cm^{-1}): 2953 ($\nu_{ArC\ -H}$), 2922 ($\nu_{C–H}$), 1608 ($\nu_{C=N}$); 1560-1381 ($\nu_{C=C}$); 1266-1076 (β_{C-H}); 1013-699 (Γ_{C-H}); ^{1}H-NMR (DMSO-*d*$_{6,}$ppm) 6.22-7.97 (Ar-H), 6.47 (s, 1H, -C**H**=N), 1.95 (-CH-), 0.92 (-CH_3), ^{13}C-NMR (DMSO-*d*$_{6,}$ppm) 158.58 (-C=N), 112.26-149.02 (Ar-C), 26.23, 27.79 (-**C**H-),18.12, 24.24(-**C**H_3).

Theoretical background

Using the Gaussian 03 program [31], quantum chemical calculations of **IBPBD** were performed. The synthesized compound has been optimized using DFT/ B3LYP and HF methods using 6-31G(d,p) basis set [32]. The simulated IR spectrum was obtained at DFT/B3LYP and HF methods with a basis set of 6-31G(d,p). DFT hybrid B3LYP and HF methods tend to overestimate fundamental modes and hence the scaling factors 0.9608 and 0.9051 [33] have been uniformly applied to the B3LYP and HF methods, respectively. The reactive sites of the title molecule were evaluated. In addition, the dipole moment, polarizability and first order hyperpolarizability have been obtained from same level of theories.

Results and discussion

Conformational analysis

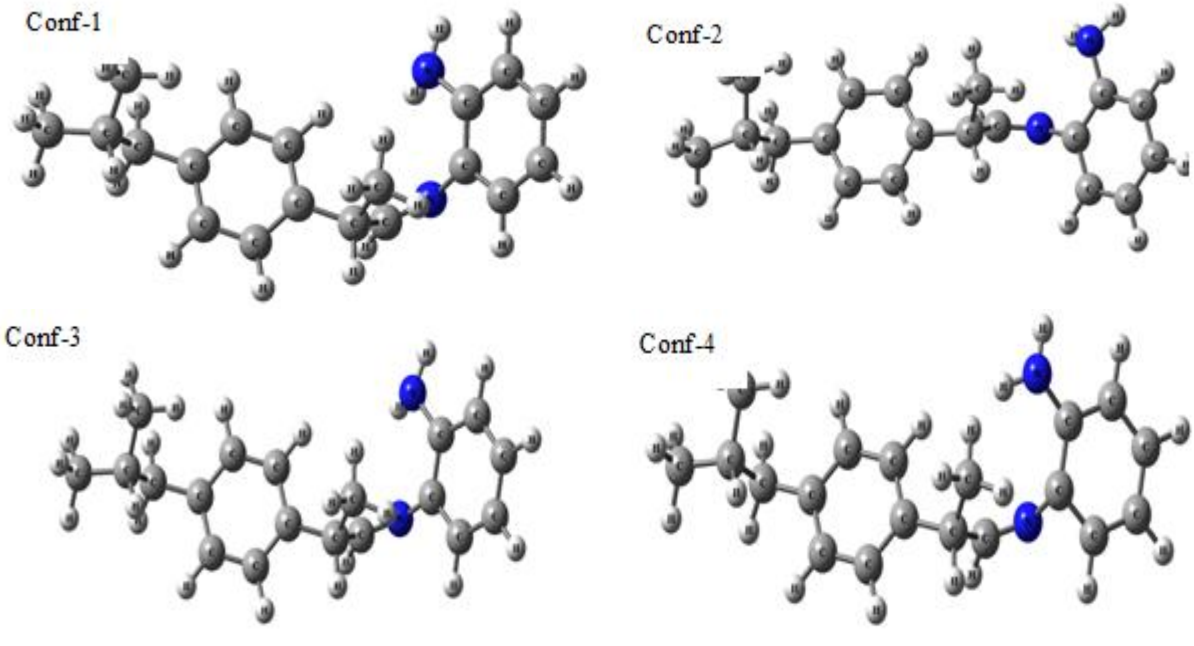


Fig. 2. The possible optimized geometrical conformations for IBPBD.

Table. 1. Calculated energies and energy differences of possible conformers of the IBPBD by DFT (B3LYP/6-31G(d, p)). method.

Conformers	Energy		Energy differences		Dipole moment (Debye)
	(Hartree)	(kcal/mol)	(Hartree)	(kcal/mol)	
Conf-1	-847.751187	-531972.347	0	0	1.62
Conf-2	-847.751204	-531972.358	0.0000174	0.01088102	1.68
Conf-3	-847.747829	-531970.24	-0.0033575	-2.1068397	1.63
Conf-4	-847.631071	-531896.973	-0.1201162	-75.374085	2.54

The stability of the stable conformer is in the order I > II > III> IV. The energy difference shows that the conformer 1 is most stable. The most stable conformer I is slightly out of planar, where the methyl group in imine linkage and amine group in phenyl ring are above and below the plane.

Table 2. Selected bond lengths, bond angles and dihedral angles of Schiff base.

Bond length (Å)	DFT	HF	XRD[a]	Bond angle (°)	DFT	HF	XRD[a]
C1-C2	1.400	1.398	1.395	C1-C2-C3	120.5	120.5	120.1
C2-C3	1.393	1.392	1.372	C1-C6-C5	120.5	120.5	
C2-H7	1.100	1.100	1	C6-C1-C2	119.0	119.0	119.6
C3-C4	1.400	1.397	1.372	C1-C11-C14	112.4	112.4	112.67
C3-H8	1.102	1.101	1	C3-C4-C5	119.2	119.2	
C4-C5	1.399	1.378	1.374	C4-C24-C30	109.0	109.0	
C5-C6	1.393	1.390	1.394	C11-C14-C20	110.4	110.4	
C5-H9	1.100	1.100	0.95	C24-C30-N31	134.1	134.1	123.5
C1-C6	1.400	1.396	1.395	N31-C32-C33	120.4	120.4	124.7

C6-H10	1.100	1.100	0.95	C32-C33-N42	120.3	120.3	
C24-C30	1.517	1.506	1.524	C34-C33-N42	121.2	121.2	
C30-N31	1.312	1.287	1.285	C35-C33-N42	120.1	120.1	
N31-C32	1.472	1.412	1.47	Dihedral angle (°)			
C32-C33	1.433	1.430	1.395	C2-C1-C11-C14	-103.4	-103.4	
C33-C35	1.412	1.379	1.372	C6-C1-C11-C14	77.1	77.1	
C34-H37	1.101	1.120	1	C3-C4-C24-C26	63.2	63.2	
C34-C36	1.390	1.392	1.395	C5-C4-C24-C26	-116.4	-116.4	
C36-H40	1.099	1.098	1	N31-C30-C24-C26	4.3	4.3	
C36-C38	1.392	1.382	1.372	N31-C32-C33-N42	12.4	12.4	
C38-H41	1.100	1.100	1	C34-C32-C33-N42	-175.2	-175.2	
C38-C35	1.389	1.382	1.372	C38-C35-C33-N42	175.2	175.2	
C35-H39	1.101	1.101	1				
C32-C35	1.412	1.401	1.374				

a-values are taken from Ref. [34,35]

The molecular structure and stable conformation of IBPBD have been determined by gas-phase calculations. Conformational analysis of the IBPBD was carried. All the possible geometry of the conformers was optimized to find out the energetically and thermodynamically most stable configuration of the compound. All possible conformations of the compound IBPBD under investigation are shown in Fig. 2. The ground state energy, energy difference and dipole moment of conformers are presented in Table 1**.**

Optimization geometry

Now a days DFT calculation has gained immense importance in getting refined results on molecular geometry and optical behavior of systems, in the absence of single crystal XRD data. The gas phase geometry of compound was fully optimized with respect to the energy using the B3LYP/6-31G (d,p) basis set. All selected compounds had C1 point group. For these compounds, only the ground state geometries are optimized. The results are summarized in Table 2. The optimized structure of compound is shown in Fig. 3. Relevant bond distances and angles are reported in Table 2 and are in good agreement with those reported in similar Schiff base compounds [34,35].

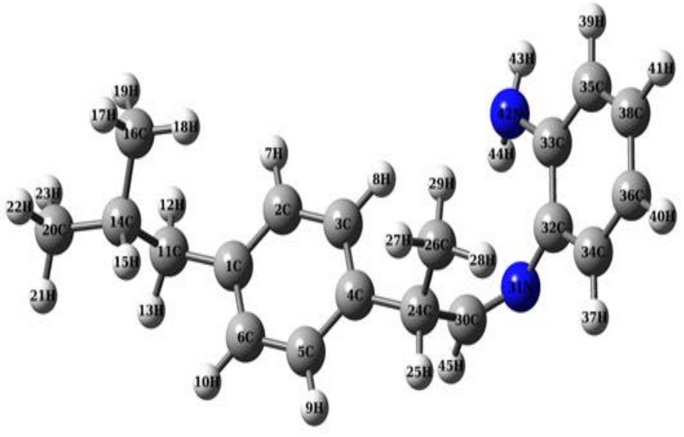


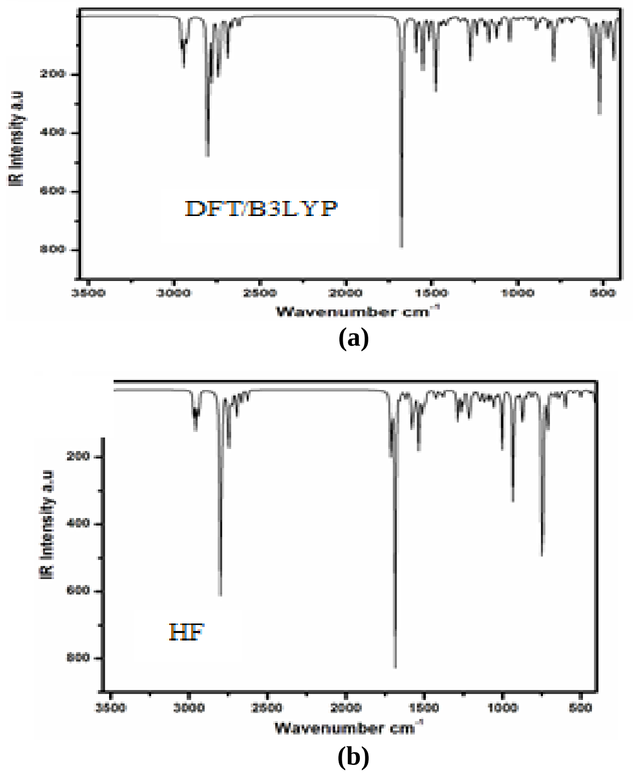
Fig.3. Optimized geometry of Schiff base with atoms numbering.

The optimized C30=N31 bond length is calculated as 1.312 and 1.287 Å by B3LYP and HF methods with 6-31G (d, p) basis set, respectively.The molecule corresponds to the C=N and N-C bond distances being 1.285 and 1.470 A˚, respectively. In which case, HF value is in line with literature value [34,35]. Closer examination of the bond lengths and angles of title compound in **Table 2** relative to the XRD values shows the larger deviations in the bond lengths of N-H and C-H only. The calculated C-C bond distances in the phenyl ring is in the range 1.393-1.433 and 1.378-1.430 Å by B3LYP and HF methods, respectively, which compared favourably with experimental values (1.372–1.395 Å) [34,35].

FT-IR spectral analysis

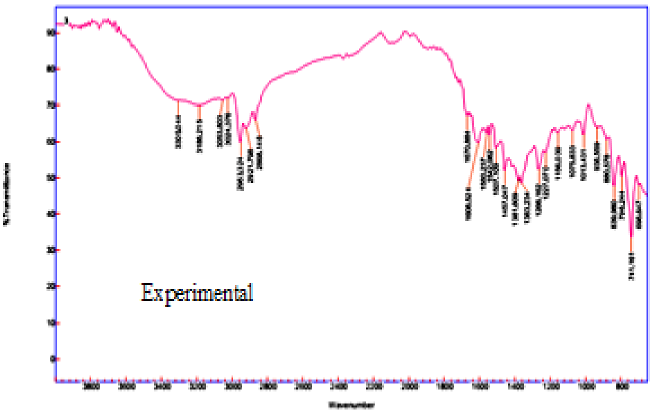
The observed FTIR spectrum of **IBPBD** along with the simulated infrared spectrum is shown in **Figs. 4(a-c)**. The theoretical spectra were obtained from the DFT-B3LYP and HF methods using 6-31G(d,p) level theory. In infrared spectra, most aromatic compounds have peaks in the region 3100-2950 cm^{-1}, these are because of the stretching vibrations of the ring C-H bands. In the present study, the FT-IR band identified at 2953 cm^{-1} is assigned to C-H stretching vibrations. In B3LYP and HF methods the value lies at 2957 and 2971 cm^{-1}, respectively.

The C-H stretching occurs at lower frequencies than those of aromatic ring. The CH$_3$ stretching is expected at 2950-2870 cm $^{-1}$ [36,37] and usually the bands are weak. The title molecule possesses methylene and methyl groups. Methyl group symmetric stretching appeared at 2922 cm $^{-1}$ and the corresponding calculated values are 2925 and 2947 cm $^{-1}$ in B3LYP and HF level theories, respectively. The C=N stretching vibration calculated as 1609 cm $^{-1}$ (B3LYP) agreed well with recorded value of 1608 cm $^{-1}$ by FT-IR spectrum, while the HF value is positively deviated.



(a)

(b)



(c)

Figs.4. (a-c) The simulated IR and experimental FT-IR spectra of IBPBD.

Table.3. Experimental and calculated IR frequencies of compound IBPBD.

Assignments	FT-IR	DFT	intensity	HF	intensity
$\nu_{ar\cdot C\text{-}H}$	2953	2957	31.29	2971	20.8
$\nu_{ali\cdot C\text{-}H}$	2922	2925	37.16	2947	6.47
$\nu_{C=N}$	1608	1609	232.4	1642	269.66
$\nu_{C=C}$	1560	1567	34.65	1590	10.38
	1542	1550	0.17	1555	3.31
	1507	1515	6.35	1514	9.23
	1457	1475	56.91	1461	0.78
	1381	1402	1.33	1399	6.48
$\beta_{C\text{-}H}$	1266	1273	6.8	1296	2.65
	1227	1237	48.92	1221	4.5
	1156	1170	10.59	1167	0.78
	1076	1083	19.32	1095	8.44
$\Gamma_{C\text{-}H}$	1013	1023	6.66	1046	29.51
	937	964	5.2	947	131.16
	881	882	2.44	880	16.03
	840	845	6.23	858	2.4
	796	810	54.64	824	7.47
	741	752	8.12	756	14.23
	699	710	3.88	723	39.93

The bands observed in the region 1560-1381 cm $^{-1}$ in FT-IR have been intended to C=C stretching modes. The calculated bending modes are found in the region 1567-1402 and 1590-1399 cm $^{-1}$ in B3LYP and HF, respectively. The calculated bending modes are found in the region 1273-1083 and 1296-1095 cm^{-1} in B3LYP and HF, respectively. These experimental frequencies are in agreement with the theoretical values. The other in-plane and out of plane bending modes have also been assigned and reported in the **Table 3**.

Mulliken charge analysis

The Mulliken atomic charge account's computation plays an important role in quantum chemical prediction for the molecular structure due to atomic charges effect dipole moment, molecular polarizability, electronic structure and more a lot of properties of molecular systems [38]. The charge distributions over the atoms suggest the formation of donations and acceptable pairs involving the charge transfer in the IBPBD.

The calculated Mulliken charges of IBPBD at B3LYP and HF with the 6-31G (d, p) basis set is listed in **Table 4**.The charge distribution of the title compound shows that the carbon atom attached with hydrogen atoms is negative. The nitrogen atoms (N31 and N42) have maximum negative Mulliken charges in all methods. The charge distribution of the title molecule shows that the carbon atoms C1, C4, C14,C26, C30, C32 and C33 are positive charges, while carbon atoms C30 and C33 are more positive due to the presence of electronegative nitrogen atoms.

Table .4. Mulliken atomic charges of compound IBPBD.

Atom	DFT	HF	Atom	DFT	HF
C1	0.1145	0.0068	C26	0.0450	0.0776
C2	-0.0315	-0.0045	C30	0.1955	0.3327
C3	-0.0049	-0.0421	N31	-0.3903	-0.5510
C4	0.1163	0.0008	C32	0.1384	0.1564
C5	-0.0422	-0.0040	C33	0.2317	0.2686
C6	-0.0237	-0.0033	C34	-0.0035	-0.0258
C11	-0.0677	-0.0110	C35	-0.0341	-0.0207
C14	0.0392	0.0060	C36	-0.0188	-0.0162
C16	-0.0058	-0.0166	C38	-0.0132	0.0035
C20	-0.0117	-0.0054	N42	-0.1412	-0.2091
C24	-0.0925	-0.1170			

Molecular electrical potential surfaces

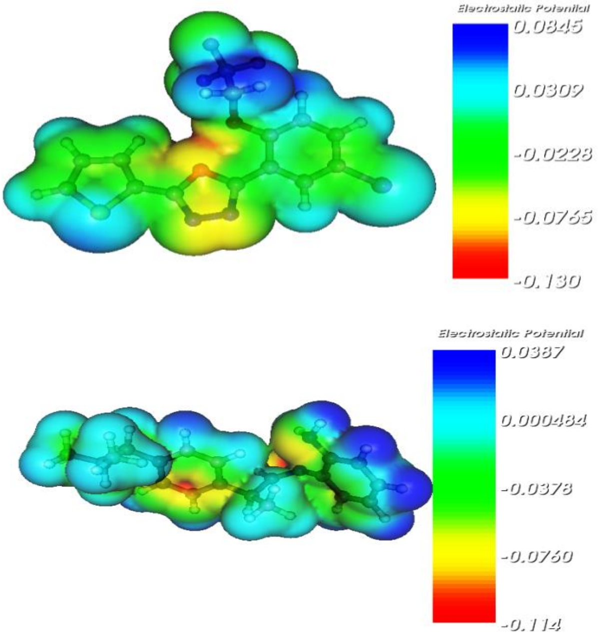


Fig. 5. Molecular electrostatic potential diagram of Schiff base.

Electrostatic potential maps illustrate the charge distributions of molecules three dimensionally. The purpose of finding the electrostatic potential is to find the reactive site of a molecule.

These maps can view variably charged regions of a molecule. Knowledge of the charge supplements can be used to determine how molecules interact with each other [38].

The MEP of **IBPBD** clearly indicates the electron rich centres of nitrogen N31 and N42 atoms. The contour map of **IBPBD** has been and is shown in **Fig. 5**.The hydrogen atoms attached to the nitrogen and phenyl ring posses the maximum bang of positive charge (blue).

Analysis of frontier molecular orbitals (FMOs)

In principle, there are several ways to calculate the excitation energies. The first, and the simplest one, involves the difference between the HOMO and the LUMO of a neutral system. Examining molecular orbitals and the spatial distribution of other molecular properties is useful for nature of reactivity, structural and physical properties of molecules. This method is very practical, particularly for calculating large systems; however, the use of DFT and HF one-electron energy differences to estimate excitation energies is still a matter of debate [39]. To understand this phenomenon in the context of the molecular orbital picture, the molecular HOMOs and molecular LUMOs were generated and plots are given in **Fig. 6**.

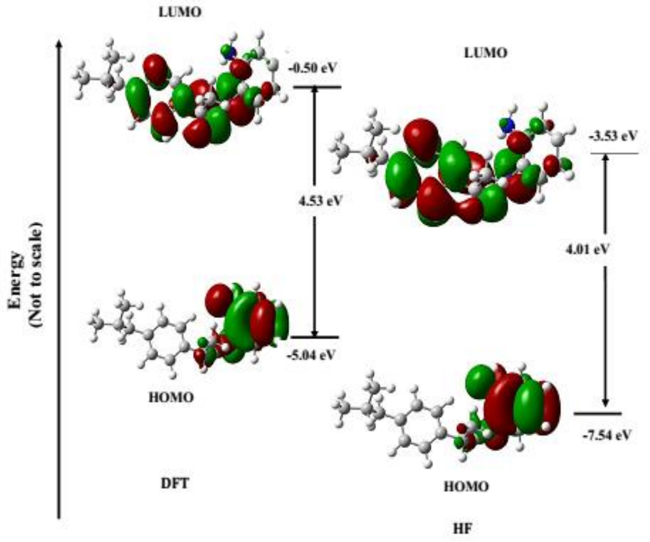


Fig. 6. Molecular orbitals and energies for the HOMO and LUMO.

It is shown that the HOMO of **IBPBD** is fully delocalized on the *ortho*-substituted aniline ring through the π, σ bond and LUMO occupied in imine linkage. The calculated energy value of HOMO is -5.04 eV in B3LYP and -7.52 eV in HF and LUMO is -0.50 and -3.53 eV in B3LYP and HF, respectively. The frontier orbital energy gap in case of title compound is found to be 4.53 and 4.01 eV in B3LYP and HF, respectively. The obtained small energy gap in HF method is still an indicator that the complex can be easily polarized and molecular charge transfer interactions occur within the compound. The chemical reactivity and site selectivity of the molecular systems have been determined on the basis of Koopman's theorem [40].

Chemical hardness is related with the stability and reactivity of a chemical compounds, it measures the resistance to change in the electron distribution or charge transfer. In this point of view, the larger the energy gap, the harder and less reactive the molecule. As seen from **Table 5**, the title compound in DFT method behave hard, while HF method somewhat soft material. This is mainly because of bad gap. The electrophilicity index describes the electron accepting ability of the systems.

High values of electrophilicity index increases electron accepting abilities of the molecules. Thus, electron accepting abilities of compound are arranged in following order: HF > DFT.

Table. 5. Calculated energy values (eV) of compounds IBPBD in gas phase.

Energies	DFT	HF
E_{HOMO}	-5.04	-7.54
E_{LUOMO}	-0.50	-3.53
$E_{LUMO\text{-}HOMO}$ (ΔE)	4.53	4.01
Electronegativity(χ)	-2.77	-5.54
Hardness(η)	2.27	2.01
Electrophilicity index(ψ)	1.69	7.64
Softness(s)	163.29	184.47

Non-linear optical effects

Schiff base crystal has emerged as a promising NLO crystal recently, owing to its large non linear optical (NLO) activity. NLO effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields [38,39].The total static dipole moment (μ), the polarizabilty (α_0) and the first order hyperpolarizability (β_0) using the x, y, z components are calculated using the following equations.

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

$$\alpha_{tot} = \frac{1}{3}\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$$

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

$$\beta_0 = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

Nonlinear optical susceptibility of vanillin using the related properties of IBPBD were calculated using the B3LYP and HF method with 6-31G (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 dipole moment in a molecule is an important property that is mainly used to study the intermolecular interactions involving the non-bonded type dipole-dipole interactions. The title molecule has the highest dipole moment, in that, it has the highest charge distribution among the other molecules. Polarizability is proportional with molecular volume. The bigger molecular polarizability means the more interaction with the electric field of light. The calculated polarizability (α_o) values are 1.85 and 1.88 x10^{-23} in B3LYP and HF levels theories, respectively.As seen from **Table 6**, the value of first order hyperpolarizability (β_0) of **IBPBD** is found to be 0.38 and 0.44x x10^{-30} in B3LYP and HF levels theories respectively, which is greater that of urea [42].

Table. 6. Dipole moment, polarisability, first order hyperpolarizability of Schiff base.

Parameter	Dipolemoment (Debye)		Parameter	Hyperpolarisability (a.u)	
	DFT	**HF**		**DFT**	**HF**
μ_x	-1.5365	-1.3672	β_{xxx}	-34.0075	-17.4327
μ_y	0.5032	0.335	β_{yyy}	10.7153	9.0768
μ_z	-0.0315	0.445	β_{zzz}	-6.0567	-4.3129
μ_{total}	1.62	1.48	β_{xyy}	23.1338	25.2808
	Polarisability (a.u)		β_{xxy}	16.4727	
α_{xx}	128.7096	129.42	β_{xxz}	27.2622	38.7591
α_{yy}	116.082	117.52	β_{xzz}	-0.8538	-2.2956
α_{zz}	128.985	132.99	β_{yzz}	13.3974	14.2271
α_{xy}	5.473	6.10	β_{yyz}	-9.0151	-7.9717
α_{xz}	3.3962	5.86	β_{xyz}	-13.012	-12.782
α_{yz}	-7.2816	-7.78	β_0 (esu) x10^{-30}	0.38	0.44
α_o (esu) x10^{-23}	1.85	1.88			
Δα (esu) x10^{-24}	2.84	3.41			

Conclusion

A new (*E*)-N^1-(2-(4-isobutylphenyl)propylidene) benzene-1,2-diamine has been synthesized successfully in appreciable yield and was characterized by elemental analysis, FT-IR, ^{1}H and ^{13}C NMR spectral techniques. The ground-state molecular geometry was ascertained by using the density DFT/B3LYP and HF methods using 6-31G(d,p) as a basis set. FT-IR was recorded in the solid phase and analyses the vibrational behaviour of chemical bonds and its functional groups. Vibrational spectrum has also been discussed on the basis of DFT/B3LYP and HF methods with 6-31G(d,p) basis set. The obtained theoretical vibrational frequencies are in good agreement with calculated data. Information regarding the charge allocation and site of high electro negativity of **IBPBD** were obtained by Mulliken and MEP surfaces. Molecular properties and energy gap like electron affinity, ionization potential, hardness, electrophilicity and chemical potential were calculated. The calculated dipole moment and hyperpolarizability results indicate that the **IBPBD** has a plausibly good nonlinear optical behaviour.

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