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Single crystal, spectral and electronic transition studies on (E)-N-(3-Methoxy-4hydroxybenzylidene)-4-nitrobenzohydrazide monohydrate

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Abstract

The single crystal of (E)-N-(3-MMethoxy-4-hydroxybenzylidene)-4-nitrobenzohydrazide monohydrate (MHBNB) was grown by a slow evaporation method. The crystal structure was determined by single crystal X-ray diffraction method. The electron density, Hirshfeld surface and fingerprint analysis reveals that the crystal packing is governed by several weak O-H...C, O-H...O and O-H...N intermolecular interactions. The analysis of bond critical points (BCP) and topology of the crystalline form of MHBNB were analyzed. The intrusion of H₂O molecule does not affect the aromaticity of the pheyl rings but marginally distrurbs the aromaticity of hydrazide link. The FT-IR (4000-400cm⁻¹) and FT-Raman (3500-50 cm⁻¹) spectra were recorded to study the vibrational behavior of MHBNB molecule. To explore the electronic transition of MHBNB, the UV absorbance spectrum was recorded in the range of 200-800nm. Furthermore, the Density functional theory (DFT) and Time-dependent DFT (TD-DFT) calculations were performed to investigate the molecular geometry, vibrational behavior, electronic excitation and interintramolecular charge transfers within the molecule. The singlet (S) and Triplet (T) electronic excited states (n state=6) of MHBNB were examined, in which, the electron spin density (s), excitation energy (Δ E1-6), oscillator strength (f) and electric dipole moment (μ) were examined. The frontier molecular orbitals (FMOs) were studied to find the band gap of FMOs. The natural atomic orbitals (NAO) and natural localized molecular orbitals (NLMO) of MHBNB were analyzed. The density of states (DOS) and Total density of states (TDOS) of functional groups in MHBNB molecule were also evaluated. This compound has very good first order hyperpolarizability (β_0) coefficient.

Keywords: FT-IR; FT-Raman; FMOs; NAO; TD-DFT; *corresponding author: <u>sscbphysics@gmail.com</u> +91 9976853476

1. Introduction

Investigation of organic optical materials is playing a major role in recent research. Organic optical materials (OM) are widely used in optoelectronics, photonics, optical switching, telecommunications, modulator, optical computing and integrated optical circuit applications [1-2] since most of the OM materials constituted by weak Van der Waals and hydrogen bonds with conjugated π -electrons [3]. The compounds having hydrazide (CH-N-C=O) and π -electrons possess enhanced optical activity [4]. Moreover, the organic single crystals exhibiting photoconductive, photovoltaic and photocatalytic activities [5]. The conjugative electron systems in the compound display extremely larger second-order optical nonlinearities [6]. The aim of the present study is, obtain the single crystal structure and study the vibrational and electronic spectra; in addition, Density Functional Theory (DFT) and Time Dependant-DFT calculations were performed to investigate the molecular orbitals, excited electronic states and natural atomic-orbitals of the title compound. The novelty of this compound is it has lesser frontier molecular orbital band gap and very good β_0 coefficient.

2. Computational details

The quantum chemical calculations of MHBNB were performed using the B3LYP level of theory supplemented with 6-31G(d,p) basis set, using Gaussian 09 program package invoking geometry optimization [7]. Initial geometry generated from geometrical parameters was minimized without any constraint in the potential energy surface at DFT level. The optimized minimum structure parameters were used in the vibrational wavenumber calculations at the DFT level to characterize all stationary points as minima. The Raman activities were transformed into Raman intensities using Raint program [8] by the expression:

$$I_{i} = 10^{-12} \times (v_{0} - v_{i})^{4} \times \frac{1}{v_{i}} \times RA_{i}$$
(1)

Where I_i is the Raman intensity, A_i is the Raman scattering activities, v_i is the wavenumber of the normal modes and v_0 denotes the wavenumber of the excitation laser [9]. Hirshfeld surface maps and fingerprint plots were generated from the crystallographic data using the CrystalExplorer 3.1 [10].

3. Experimental details

3.1 Synthesis of (E)-N-(3-methoxy-4-hydroxybenzylidene)-4-nitrobenzohydrazide (MHBNB)



The reaction scheme of (E)-N-(3-Methoxy-4-hydroxybenzylidene)-4-nitrobenzohydrazide

The ethanol solution of 3-methoxy-4-hydroxybenzaldehyde was added to the ethanol solution of 4nitrobenzohydrazide. The mixture was refluxed for 4hrs in a heating mantle. The resulting solution was allowed to cool slowly at room temperature. After few days the suitable crystalline of the title compound were separated. Finally the single crystals of the synthesized compound were grown by slow evaporation technique using ethanol as solvent. The block like single crystals are harvested after two weeks (yield = 90%, Melting point = 195° C).

3.2 Characterization techniques

The single crystal X-ray diffraction structural analysis of MHBNB was carried out using Bruker kappa Apex II CCD diffractometer. The FT-IR spectrum of the synthesized MHBNB was measured in the 4000–400 cm⁻¹ region at the spectral resolution of 4 cm⁻¹ using Shimadzu FT-IR affinity spectrophotometer (KBr pellet technique). The FT-Raman spectrum was recorded using Bruker RFS 27 spectrometer operating at laser 100mW in the spectral range of 4000–50 cm⁻¹.

4. Results and Discussion

4.1 Crystal Structure and geometry

Crystal of MHBNB was grown at room temperature and single crystal X-ray data were collected on a Bruker AXS Kappa Apex II CCD diffraction with graphite monochromatic Mo K α radiation (λ =0.71073 Å). The crystals were coated with inert oil, mounted on a glass capillary, and crystal data were collected at 298 K. The reflections with I>2 σ (I) were employed for structure solution and refinement. The shelxl program was used to solve the structure by direct methods. The structure refined using full-matrix least squares refinement on |F|2 using the SHELXL97 [11] software. Fourier synthesis led to the location of all of the non-hydrogen atoms. For the refinement, all data were used including negative intensities. The criterion of F2>2 σ (F2) was employed for calculating R1, R factor based on F2 (wR2) are statistically

about twice as large as based on F, and R factors based on all data will be even larger. Non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms in the MHBNB structure could be located in the difference Fourier map. However, the hydrogen atoms were geometrically relocated at chemically meaningful positions and were given riding model refinement. The refinement data are listed in Table 1.

The MHBNB crystal structure belongs to a monoclinic and P21/n space group. The lattice cell parameters are a=7.9566, b=21.3735, c=9.7681(Å) and the symmetry code of the molecule in the crystal unit is (i) x-1/2, -y+1/2, z+3/2; (ii) x+1/2, -y+1/2, z-1/2; (iii) x+1, y, z-1; (y) x-1, y, z+1; The bond parameter such as the bond length (Å), bond angle (°), dihedral angle (°) and hydrogen bonding interactions were measured. This water also involves in hydrogen bonding interaction, but it does not change the symmetry, there was observed a negligible influence due to the water present. The determined structure was optimized by Density functional theory (DFT) calculation. The structure parameters were calculated and compared with X-ray diffraction bond parameters, for example, the carbonyl (C=O) bond length has observed as about 1.229Å, whereas the calculated value is about 1.23Å. Similarly, the observed C=N (1.276Å), C-N (1.337Å), C-O (1.367Å) and C-C in ring (~1.41 & ~1.37Å) bond lengths are matches well with the computed bond parameters. The hydrogen bonding (HB) interactions have been observed like D-H, H...A, D...A, and D-H...A. among the closest molecule, The donor nitrogen (N1-H2...O25ii) makes the intermolecular hydrogen bonding with closest neighboring oxygen (O25ii) in hydroxybenzylidene (in ring 2), its D...A hydrogen bonding distance is about 3.078 Å and bonding angle is about 151°. Similarly, HB at the terminal like C10-H11...O25i and C10-H11...O26ii is about 3.281 and 3.080 Å (D...A), respectively, its corresponding angles are 154° and 129°(D-H...A). The determined crystal structure and optimized gases phase structure are shown in Figure 1 (a-b). The comparison of experimental and computed bond parameters are listed in Table S1 (Supporting information).

4.2 Vibrational analysis:

The vibrational analysis for MHBNB has carried out using FT-IR (4000-400 cm-1) and FT-Raman (3500-50 cm-1) spectra (as shown in Figure 2a and Figure 2b). In addition to that, the DFT calculation was also performed to explore the characteristic vibration in BCOP. The calculated wavenumbers were scaled down by the appropriate scale factor [12] to bring closer with observed wavenumbers. This molecule consists of 39 atoms and possesses 111 normal modes of vibrations but experimentally unable to observe all those modes however the observed wavenumbers have compared with the simulated wavenumbers.

The hydroxyl (OH) stretching is very sensitive to hydrogen bonding and this vibration usually appears at 3500-3700cm-1 [13]. In the present investigation, the O-H stretching vibration appears at 3673 cm-1 as a weak band, it indicates that there is no hydrogen bonding interaction at this OH (since the peak appeared

weak and no broad). The N-H stretching vibration in heterocyclic molecule appears in the range of 3500-3300cm-1 [14], the N-H stretching in ENBNB observed at 3458 cm-1 as a medium band in FT-IR spectrum. The aromatic CH stretching vibration normally occur in the characteristic region of 3100-3000 cm-1[15], this molecule indicates the C-H peak at 3057cm-1 as a medium band in FT-Raman. The vibrational modes of methoxyl groups are highly influenced by interactions such as electronic effects, Fermi resonance and intermolecular hydrogen bonding [12]. The symmetric and asymmetric stretching vibration of aryl methoxyl groups often appears at 3000 and 2925 cm-1 [16] whereas, in the present work, the -OCH3 stretching vibration appears at 3001 cm-1 as weak band in FT-IR. The C=O stretching vibration is an important class of vibration in a molecule, which is generally expected in the region 1710-1600 cm-1, herein the C=O stretching has observed as strong band at 1788 cm-1 in FT-Raman, here seems a positive deviation from the literature, this positive deviation is due to a short-range hydrogen bonding interaction with the neighboring H2O. The above mentioned observed wavenumber agrees well the computed wavenumber as well as literature. The recorded and computed results are listed in Table 2.

4.3 Molecular orbital (MO) theory:

MO theory calculation was performed using the TD-DFT method, the results presented in Table 3(a-b), in which the singlet and triplet excited states were interested (n states=6). The first excited lays between HOMO (H) and LUMO (L), its energy gap has calculated about 2.62 eV, whereas, in the triplet state, the first excited state lays over 86 - 89th MO, its calculated band gap is about 0.835eV. By comparing the first singlet and triplet excited states, the band gap difference is 1.79eV. In addition to that, the electric dipole moment is four times higher the first excited triplet state (7.926 Debye) than singlet excited state (2.107 Debye). In second excited singlet state, the 86-88th (H-1-L) MO involves, its band gap is about 3.399 eV, whereas the oscillator strength (f) and electric dipole moment (μ) are very weak in S state. Similarly, the f and μ are very weak at ES3, ES5 and ES6 it is due to the lesser x, y and z components and weak transitions among the frontier H-L. On the other hand, at singlet ES4, the f and μ are higher than triplet ES4 due to positive μ_x (2.557a.u) component.

The frontier HOMO and LUMO play an important role in optical and electronic applications; in the present investigation, the band gap has calculated about 2.982 eV (462nm). The HOMO majorly locates over the 2pz, 3py, 3pz, 4pz, 5s orbitals of hydrazine and hydroxybenzylidene ring, whereas, the LUMO locates over the 4pz, 5s, 5px, 5py, and 5pz orbitals of the nitrobenzohydrazide ring. The details of the molecular orbital coefficient have shown in Figure S1 (a-b) and Figure S2 (a-c) (Supporting information).

4.4 NBO analysis:

Natural atomic orbital (NAO) and Natural bond orbital (NBO) analysis were performed using Gaussian NBO version 3.1. The obtained results are presented in Table 4. In which, the core level atomic orbital population has calculated about 47.98e, and valence orbital population has calculated about 125.47e, whereas the total minimal basis is about 173.46e and Rydberg basis (Non-Lewis- NL) has calculated about 0.539e. In the natural bond orbital analysis, shows the core electrons as about 47.98e, valence Lewis electrons 121.40e and total Lewis electrons is about 169.39e. In NBO investigation, we mainly concentrate on Pi (π) bond (donor (i) \rightarrow Pi* (π *) acceptor (j)) interactions. The bond N3=C10 (σ/π) has an inequivalent bond like σ N3-C10 (NBO4) and π N3-C10 (NBO5) having occupancy about 1.986e and 1.928e respectively. The stabilization energy over $\pi N3-C10 \rightarrow \pi^*C9-C29$ has calculated about ~8.34kcal/mol. In the 3-Methoxy-4-hydroxybenzylidene ring, the maximum stabilization energy (21.57, 17.94 and 18.28 kcal/mol) appears due to π C9-C29 \rightarrow π *N3-C10, C5-C7, C6-C13 (NBO19 \rightarrow NBO590, 595, 598) delocalization. Similarly, in the 4-nitrobenzohydrazide ring, the strong stabilization appears at π C12-C16, π C18-C19 and π C21-C23 valence Lewis orbitals with corresponding valence non-Lewis orbitals. The significant contribution also revealed from lone pair (n) oxygen atoms, in which nO25 yields more stabilization due to $nO25 \rightarrow \pi^*C6$ -C13 overlap. On the whole, the dominant stabilization energy (303.86 and 208.84kcal/mol) obtained at the valence non-Lewis interaction due to π *C6-C13 \rightarrow π *C9-C29 and π *C12-C16 \rightarrow π *C21-C23 stabilization.

4.5 Hirshfeld surface analysis

Hirshfeld surface (HSs) and 2D fingerprint plot were generated using Crystal Explorer 3.1 based on the results of single crystal X-ray diffraction studies, in which the crystal packing builds through the O...H-C (2.15Å) and O...H-N (2.35Å) hydrogen bonding interactions (between hydrazine and neighboring methoxy benzohydroxyl). This packing unit is like a zigzag crystal building by means of square-shaped intermolecular hydrogen bonding interactions as shown in Figure S3 (a-j) (Supporting information). The function of dnorm is a ratio encompassing the distances of any surface point to the nearest interior (d_i) atom and exterior (d_e) atom and the van der Waals radii of the atoms [17]. The negative value of d_{norm} indicates the sum of d_i and de is shorter than the sum of the relevant van der Waals radii, which is considered to be the closest contact and is visualized as red colored in the HSs. The white color denotes intermolecular distances close to van der Waals contacts with d_{norm} equal to zero whereas contacts longer than the sum of van der Waals radii with positive dnorm values are colored with blue. A plot of d_i versus d_e is 2D fingerprint plots which recognize the existence of different types of intermolecular interactions. For this crystal structure, the D-H...A hydrogen bonding interactions when the H...A distance is shorter

than the sum of the van der Waals radii more than 0.13Å is observed, the intermolecular hydrogen bonding appears between hydrazine link and Methoxy benzohydroxyl of neighbor like O-H...N (0.5%),O-H...C (34.7%) and O-H...O (34.7%) as shown in the Figure S3 (e-h) (Supporting information). In the shape index, the highlighted red and blue triangles shown by purple color ellipse indicate the $\pi^{\bullet\bullet\bullet\pi}$ interactions identically present in the crystal structure and its 2D fingerprint shows the C···C contact contributes 5.2% of the Hirshfeld surface. Red and blue triangles pattern explicitly how the molecules overlap and contact with one another. Red triangle represents the carbon atoms present in the benzene ring of the molecule outside the surface, while blue represents the carbon atoms of benzene ring inside the surface. The curvedness surface indicates the electron density surface curves around the molecular interactions [18]. Moreover, the flat green region separated by the blue edges in curvedness surface is another characteristic of $\pi^{\bullet\bullet\bullet\pi}$ stacking. The deep red color spots in the de surface are responsible for strong interaction of O···H (16.2%) and the red spots in di surface correspond to H···O (18.5%) interactions.

4.6 Density of States

Using Multiwfn 3.4.1 version [19], the topology of MHBNB has as shown in Figure S4 (Supporting information) and also the density of states of MHBNB were studied using the same software. Density of states is an important concept of solid state physics, which represents the number of states in unit energy interval. In an isolated system, the energy levels are discrete, though the concept of DOS valueless, if the discrete energy levels are broadened to curve artificially, the DOS graph can be used as a valuable tool for analyzing the nature of electron structure. The original total DOS (TDOS) of isolated system can be written as

$$TDOS(E) = \sum_{i} \delta(E - \varepsilon_i)$$

(2)

Where $\{\varepsilon\}$ is eigenvalue set of single-particle Hamilton, δ is Dirac delta function. If δ is replaced by broadening function F(x), such as Gaussian, Lorentzian and pseudo-Voigt function, we get broadened TDOS [19].

The title molecule under B3LYP/6-31G(d,p) wave function is ground state, the orbitals canonical MOs, fragments 1-5 are defined as functional groups as shown in Figure 4. The vertical dashed line indicates the position of the HOMO level. The original DOS graph (as shown in Figure 4) is discrete comb-like lines and it is difficult to distinguish the discrete lines. However the discrete lines are broadened, the black curve is TDOS, and it reveals the dense of energy levels are distributed. Besides that PDOS is separated as fragments (f1-f5), in which, f1 (red curve) belongs to -C=O-N-N=C-group, it has the considerable contribution in the HOMO level, and maximum contribution is by ring carbons (f5) denoted

as the green line in DOS spectrum. Also, a meager contribution found by means of –OCH3 (blue line-f2) and NO2 (pink line-f3) in HOMO level. Moreover, the fragments f1 and f5 also considerably contribute to the LUMO level. The OPDOS magnitude is much smaller than TDOS and PDOS.

4.7 Nonlinear property analysis

Theoretical investigation plays a substantial role in understanding the quantitative structure– property relationship (QSPR), which is able to assist in designing novel NLO materials. For a molecule to be NLO active, it is important to have high hyperpolarizability (β_0) values. The calculated values of β_0 by finite field approach method are given in Table 5, along with the corresponding components.

The first-order hyperpolarizability β_0 is given by,

$$\beta_{0} = \left(\beta_{x}^{2} + \beta_{y}^{2} + \beta_{z}^{2}\right)^{1/2}$$

(3)

For MHBNB, we have obtained the high value of βxxx , βxxy and βxyy components (Table 5) thus indicating that there is a charge imbalance along the y-axis which is due to the high electronegative oxygen atoms lying in the X–Y plane. The $\beta 0$ value (78.65x10-30esu) also indicates that the compound has very good nonlinear optical property. This compound has greater $\beta 0$ coefficient than that of urea. Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore, it was used frequently as a threshold value for comparative purposes [20].

5 Conclusions

The MHBNB crystallizes in monoclinic and P21/n space group with lattice parameters a=7.9561, b=21.3735, and c=9.781. The packing of molecules in the crystal is governed by weak O-H...N, O-H...C and O-H...O interactions. The simulated geometries of the compound agree well with the geometrical parameters obtained through single crystal X-ray diffraction technique. The functional groups vibrational assignments were made using experimental and computational data. In TD-DFT calculations, S and T excited states were computed; the S first excited state denotes the H-L band gap of 2.62eV. On comparing the S first excited state with the T first excited the f and μ are very weak in S states. The HOMO majorly locates over the 2pz, 3py, 3pz, 4pz, 5s orbitals of hydrazine and hydroxybenzylidene ring atoms, whereas, the LUMO locates over the 4pz, 5s, 5px, 5py, and 5pz orbitals of nitrobenzohydrazide ring atoms. The more hyperconjugative energy (303.86 and 208.84kcal/mol) obtained at the Lewis and non-Lewis interaction due to π *C6-C13 \rightarrow π *C9-C29 and π *C12-C16 \rightarrow π *C21-C23. DOS graph is discrete comblike lines are broadened, the black curve is TDOS. This reveals the dense of energy levels. Among the fragments, ring carbon, has considerable distributed electron density. An appreciable First-order hyperpolarizability of the molecule makes it an active NLO compound.

Supporting information's

CCDC 1821369 contains the supplementary crystallography data for this title molecule. These data can be obtained free of charge from the Cambridge Crystallography Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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Ctill Alla

Chemical formula	$C_{15}H_{15}N_3O_6$
$M_{ m r}$	333.30
Crystal system	Monoclinic, $P2_1/n$
Space group	$P2_1/n$
Temperatue (K)	296
<i>a, b, c</i> (Å)	7.9566(4), 21.3735(14), 9.7681(7)
β (°)	107.269 (2)
$V(\text{\AA}^3)$	1586.28 (17)
Ζ	4
Radiation Type	ΜοΚα
$\mu (\mathrm{mm}^{-1})$	0.11
Crystal size (mm)	$0.15 \times 0.15 \times 0.10$
Diffractometer	Bruker kappa Apex II CCD Diffractometer
Absorption correction	Multi-scan' SADABS (Sheldrick, 1996)
Reflections $[I > 2\sigma(I)]$	28649, 3070, 2077
R _{int}	0.041
$(\sin\theta/\lambda)_{\rm max}$ (Å ⁻¹)	0.615
Refinement $R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.170, 0.81
No. of reflections	3070
No. of parameters	228
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and
	constrained refinement
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	0.33, -0.26

Table 1 Crystallographic data and structure refinement parameters of MHBNB

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Mode no.	Unscaled cm ⁻¹	Scaled cm ⁻¹	FT-IR cm ⁻¹	FT- Raman cm ⁻¹	Intensity KM/Mole	Vibrational Assignments
110	3819	3674		3673w	96.6417	vO ₂₅ -H ₂₆
109	3706	3565		3524w	287.1698	$vO_{25}-H_{26}$
108	3515	3381	3458ms		18.4295	νN_1 -H ₂
107	3248	3124	3276m		1.6564	νC_{19} -H ₂₀ R2
102	3183	3062		3057m	64.737	vC19-H20 R2
97	3022	2908	3001w		37.1952	vCH ₃ (C33-H43,35,36)
96	1765	1698		1788w	344.9814	vC=O
94	1689	1625			70.2102	vC3=N ₁₀
92	1655	1592	1597vs	1591vs	120.4776	vC-C R1
88	1577	1517	1519vs	1517w	41.5001	vC-C R2
79	1399	1346	1345ms	1344ms	314.3328	vC ₁₀ -NO ₂
71	1235	1188		1199w	55.8104	ωCH3
68	1192	1147		1141w	104.4462	β COH, β CCH in R1
62	1094	1052		1059w	28.3654	vN1-N3
61	1069	1029	1035ms		33.6426	Trigonal bending R1
55	920	885		895w	24.9959	βΝ-C=Ο
52	894	860	850ms		10.6079	γCCH opb R1
45	733	705	713ms		26.9112	γCCH opb R2
41	646	622	625w		61.6307	Water opb
31	472	454		463w	0.5175	Ring 1 floating
14	189	182		179w	8.2426	τCH3 rocking
8	90	87		81w	1.1157	R1 opb

Table 2 FT-IR, FT-Raman and simulated Vibrational assignments on MHBNB using B3LYP/6-31G(d,p) level of basis set.

v-stretching; β -in-plane bending; τ -rocking; ω -wagging; γ -out-of plane bending; R-Ring; w-weak; ms-medium strong; vs-very strong;

S.No.	Singlet excited electronic transitions	Band gap (eV/nm)	Oscillator strength
1	H→L	2.6232 /472.65	0.1354
2	$H_{-1} \rightarrow L$	3.3986 /364.81	0.0320
3	$H_{-7} \rightarrow L, H_{-7} \rightarrow L_{+1}, H_{-7} \rightarrow L_{+3}$	3.6508 /339.61	0.0005
4	$H_{-2} \rightarrow L, H_{-1} + L$	3.8183 /324.71	0.6265
5	$H_{-6} \rightarrow L, H_{-2} \rightarrow L, H_{-2} \rightarrow L_{+1}, H \rightarrow L_{+1}$	3.9212 /316.19	0.0018
6	$\mathrm{H}_{\text{-9}} {\rightarrow} \mathrm{L}, \mathrm{H}_{\text{-9}} {\rightarrow} \mathrm{L}_{+1}, \mathrm{H}_{\text{-6}} {\rightarrow} \mathrm{L}, \mathrm{H}_{\text{-4}} {\rightarrow} \mathrm{L}$	4.1550 /298.40	0.0014

Table 3a Singlet (S) state transitions, Band gap and oscillator strength between HOMO and LUMO MO of MHBNB

Table 3b Triplet (T) state transitions, Band gap and oscillator strength between HOMO and LUMO MO of MHBNB

S.No.	Triplet excited state transitions	Band gap	Oscillator strength
1	$L \rightarrow L_{1,} H_{-1} \rightarrow H, L \rightarrow L_{1,}$	0.8352 eV/ 1484.46 nm	0.1622
2	$L \rightarrow L_{1,} L \rightarrow L_{3,} L \rightarrow L_{7,} H_{-6} \rightarrow H, H_{-1} \rightarrow H$	1.0255 eV /1209.01 nm	0.1232
3	$L \rightarrow L_{1,} L \rightarrow L_{+2,} L \rightarrow L_{+7,} H_{-6} \rightarrow H, H_{-2} \rightarrow H, H_{-1} \rightarrow H,$	1.4906 eV /831.76 nm	0.0385
4	$\begin{array}{c} L \rightarrow L_{+2}, L \rightarrow L_{3}, H_{-10} \rightarrow H, H_{-7} \rightarrow H, H_{-4} \rightarrow H, \\ H_{-3} \rightarrow H, H_{-2} \rightarrow H, \end{array}$	1.6255 eV /762.73 nm	0.0004
5	$\begin{array}{c} L \rightarrow L_{1,} L \rightarrow L_{+2,} L \rightarrow L_{3,} L \rightarrow L_{5,} L \rightarrow L_{7,} H_{-7,} H_{-7,}$	1.7323 eV /715.72 nm	0.0474
6	$\begin{array}{c} H_{-10} \rightarrow H, H_{-7} \rightarrow H, H_{-4} \rightarrow H, H_{-3} \rightarrow H, H_{-2} \rightarrow H \end{array}$	1.9252 eV /644.02 nm	0.0130

Table 3c Singlet and Triplet excited state (n states=6) energy, oscillator strength and electric dipole moment of MHBNB using TD-DFT calculation.

Excited	Singlet excited state (S, E ₁₋₆)			Triplet excited state (T, E ₁₋₆)			
Energy states (E ₁₋₆)	S, Energy, eV	f	μ, D	T, Energy, eV	f	μ, D	$\Delta \mathbf{E}_{(S-T)}, \mathbf{eV}$
E_1	2.62	0.1354	2.1071	0.84	0.1622	7.9260	1.79
E_2	3.40	0.0320	0.3840	1.03	0.1232	4.9042	2.37
E_3	3.65	0.0005	0.0059	1.49	0.0385	1.0547	2.16
E_4	3.82	0.6265	6.6974	1.63	0.0004	0.0093	2.19
E_5	3.92	0.0018	0.0191	1.73	0.0474	1.1158	2.19
E ₆	4.16	0.0014	0.0135	1.93	0.0130	0.2764	2.23

f-oscillator strength, μ -electric dipole moment, D-Debye

Туре	Occupancy	Donor NBO (i)	Occupancy	Acceptor NBO (j)	^a E ⁽²⁾ kcal/mol	${}^{b}\epsilon(j)$ - $\epsilon(i)$	^c f(i,j)
π-π*	1.92848	$\pi_{\rm N3-C10}$	0.39869	π^{*}_{C9-C29}	8.34	0.37	0.054
π-π*	1.98098	π_{O4-C15}	0.36646	$\pi^{*}_{C12-C16}$	3.17	0.42	0.036
π-π*	1.70452	π_{C5-C7}	0.37200	π^{*}_{C6-C13}	18.49	0.28	0.066
			0.39869	π^{*}_{C9-C29}	18.25	0.29	0.067
π-π*	1.68589	π_{C6-C13}	0.34018	π^{*}_{C5-C7}	15.9	0.3	0.062
			0.39869	π^{*}_{C9-C29}	10.21	0.3	0.071
π-π*	1.66880	π_{C9-C29}	0.20089	π^{*}_{N3-C10}	21.57	0.26	0.069
			0.34018	π^*_{C5-C7}	17.94	0.28	0.064
			0.37200	π^{*}_{C6-C13}	18.28	0.27	0.064
π-π*	1.63825	$\pi_{C12-C16}$	0.30037	π^{*}_{O4-C15}	14.95	0.31	0.061
			0.37497	$\pi^{*}_{C18-C19}$	22.03	0.28	0.07
			0.26437	$\pi^{*}_{C21-C23}$	17.34	0.3	0.065
π-π*	1.63748	$\pi_{C18-C19}$	0.36646	$\pi^{*}_{C12-C16}$	18.57	0.29	0.066
			0.26437	$\pi^{*}_{C21-C23}$	18.74	0.3	0.069
			0.61942	$\pi^{*}{}_{N27-O31}$	27.64	0.14	0.06
π-π*	1.61419	$\pi_{C21-C23}$	0.36646	$\pi^{*}_{C12-C16}$	21.99	0.27	0.069
			0.37497	$\pi^{*}_{C18-C19}$	22.28	0.27	0.069
π-π*	1.86482	n _{O4}	0.07626	$\pi^*_{\mathrm{N1-C15}}$	26.18	0.69	0.122
			0.06462	$\pi^{*}_{C12-C15}$	16.96	0.67	0.097
π-π*	1.86286	n _{O25}	0.37200	π^{*}_{C6-C13}	29.46	0.35	0.096
	1.83509	n _{O28}	0.34018	π^{*}_{C5-C7}	30.78	0.34	0.095
π-σ*		· · · ·	0.01831	$\sigma^*_{C33-H34}$	5.5	0.69	0.057
			0.01833	$\sigma^*_{C33-H36}$	5.49	0.69	0.057
π-σ*	1.90001	n _{O31}	0.10396	$\sigma^*_{C18-N27}$	11.92	0.56	0.073
			0.05544	$\sigma *_{N27-O32}$	18.87	0.71	0.105
	1.90085	n _{O32}	0.10396	$\sigma^*_{C18-N27}$	11.81	0.57	0.073
			0.05466	$\sigma^*_{N27-O31}$	18.69	0.72	0.104
π - π^*			0.61942	$\pi^{*}_{N27-O31}$	161.21	0.14	0.137
π-π*	0.20089	π^*_{N3-C10}	0.39869	π^{*}_{C9-C29}	63.94	0.03	0.068
π-σ*	0.30037	π^{*}_{O4-C15}	0.02733	σ^* _{O4-C15}	6.77	0.52	0.131
π - π^*	0.37200	π^{*}_{C6-C13}	0.39869	π^{*}_{C9-C29}	303.86	0.01	0.079
π-π*	0.36646	$\pi^{*}_{C12-C16}$	0.30037	π^{*}_{O4-C15}	80.67	0.02	0.069
		$\pi^{*}_{C12-C16}$	0.26437	$\pi^{*}_{C21-C23}$	208.84	0.01	0.082
π-π*	0.37497	$\pi^{*}_{C18-C19}$	0.26437	$\pi^{*}_{C21-C23}$	161.83	0.02	0.081
π-π*	0.61942	$\pi^*_{N27-O31}$	0.37497	$\pi^{*}_{C18-C19}$	14.9	0.14	0.058

Table 4 Second order perturbation theory analysis of fock matrix in NBO basis for MHBNB

^a $E^{(2)}$ means energy of hyper conjugative interaction (stabilization energy). ^bEnergy difference between donor(i) and acceptor(j) NBO orbitals. ^cF(i,j) is the fork matrix element between i and j NBO orbitals.

Parameter	Values
β_{xxx}	8924.07
β_{xxy}	676.38
β_{xyy}	171.02
eta_{yyy}	-199.61
β_{xxz}	150.75
β_{xyz}	36.78
β_{yyz}	-58.36
β_{xzz}	-4.12
β_{yzz}	3.12
β_{zzz}	2.48
β ₀	78.653x10 ⁻³⁰ esu

Table 5 The $\,\beta_0$ components of MHBNB molecule.

*Standard Urea = 0.3728×10^{-30} esu.



Figure 1a Ortep diagram of (E)-N'-(3-methoxy-4-hydroxybenzylidene)-4-nitrobenzohydrazide (MHBNB)



Figure 1b (E)-N'-(3-methoxy-4-hydroxybenzylidene)-4-nitrobenzohydrazide (MHBNB)



Figure 2a The recorded FT-IR and computed IR spectrum of MHBNB



Figure 2b The observed FT-Raman and computed Raman spectra of MHBNB

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Figure 4 Density of states in MHBNB with respect to functional groups.

Highlights

- ✓ Spectral (IR / Raman, UV) and Single crystal structure determination
- \checkmark Singlet and Triplet state transitions
- ✓ Contribution of $2P_{xyz}$ orbitals in occupied MOs.
- ✓ Density of states of functional groups
- ✓ Natural atomic orbital (NAO) analysis
- ✓ Bond critical points and topology analysis