



# Solvent-induced modulation of electronic absorption, fluorescence and third-order nonlinear optical properties in a tailored Schiff-base chromophore: Experimental and computational insights

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## ABSTRACT

A novel Schiff-base chromophore, ((*E*)-*N'*-(2,6-dimethoxybenzylidene)-3-hydroxy-2-naphthohydrazide) (DHN), was synthesized via a reflux-assisted route and structurally confirmed using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy along with single-crystal X-ray diffraction (SCXRD). The solvent-dependent linear optical properties were investigated through UV-Vis absorption and fluorescence measurements, revealing pronounced solvatochromic shifts and strong intramolecular charge-transfer (ICT) bands, highlighting the impact of solvent polarity on electronic structure. NLO response via solvatochromic analysis indicated that polar solvent such as DMSO exhibit the highest  $\alpha_{\text{CT}}$ ,  $\beta_{\text{CT}}$ , and  $\gamma_{\text{CT}}$  values, while less polar solvents produce lower NLO responses, demonstrating tunable optical properties. Thermal analysis (TG-DTA) demonstrated stability up to 222.5 °C, with no significant transitions prior to decomposition. The third-order nonlinear optical (NLO) behaviour was evaluated using open and closed-aperture Z-scan measurements (532 nm CW laser), revealing reverse saturable absorption, a negative nonlinear refractive index ( $n_2 = 2.032 \times 10^{-7} \text{ cm}^2/\text{W}$ ), high third-order susceptibility ( $\chi^{(3)}$ ), and efficient optical-limiting performance. Complementary time-dependent DFT (B3LYP/6-311++G(d,p), PCM-IEFPCM) calculations accurately reproduced the experimental UV-Vis absorption (340 nm) and identified the dominant HOMO  $\rightarrow$  LUMO transition as a delocalized charge-transfer process. Frontier molecular orbital mapping and molecular electrostatic potential analysis elucidated donor-acceptor pathways and active sites governing NLO activity. NBO analysis revealed significant  $\sigma \rightarrow \sigma^*$  and  $\pi \rightarrow \pi^*$  donor-acceptor interactions, along with notable lone-pair contributions, confirming extensive intramolecular charge delocalization across the DHN chromophore. Collectively, these results establish DHN as a solvent-tunable chromophore with strong third-order NLO response, suitable for optical limiters, photonic devices, and advanced optoelectronic applications.

## 1. Introduction

Organic chromophores with pronounced nonlinear optical (NLO) properties have received significant attention due to their potential applications in photonic devices, optical limiters, and telecommunication technologies [1–3]. Schiff-base derivatives are particularly appealing due to the azomethine ( $-\text{C}=\text{N}-$ ) linkage, which enables tunable electronic and optical properties through targeted molecular design by facilitating  $\pi$ -conjugation and intramolecular charge transfer (ICT).  $\pi$ -Conjugated donor- $\pi$ -acceptor (D- $\pi$ -A) Schiff-base systems are promising candidates for third-order NLO applications due to their extended conjugation, strong dipolar character, and high molecular polarizability, which result in enhanced first and second-order

hyperpolarizabilities [4,5].

The behaviour of these chromophores in solution is strongly influenced by the surrounding solvent environment. Electron density distribution, excited state stabilization or destabilization, and pronounced solvatochromic shifts in absorption and emission spectra can be significantly influenced by solvent polarity, hydrogen-bonding ability, dielectric constant, and specific solute-solvent interactions. These shifts serve as a sensitive probe for ICT efficiency, variations in dipole moments, and charge-transfer dynamics [6,7]. For instance, Ghosh et al. [8] demonstrated that coumarin-based Schiff bases produce significant Stokes shifts and red-shifted fluorescence in polar solvents, which suggests that they have efficient ICT and enhanced excited-state dipole moments. Bhattacharya et al. [9] demonstrated that solvent-dependent

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spectral shifts are influenced by structural relaxation around donor–acceptor bonds, whereas Herzfeld et al. [10] asserted that hydrogen-bonding solvents can significantly affect the photophysics of thiosemicarbazone derivatives. All together, these studies show how important solvation is for changing the electronic structure and photophysical responses of Schiff-base chromophores.

Reverse saturable absorption (RSA) and strong frequency-dependent optical responses are examples of measurable third-order nonlinear effects that have been reported in recent experimental and theoretical studies on Schiff-base systems, especially in carefully designed donor–acceptor frameworks [11]. The results demonstrate that when conjugation and intramolecular charge transfer pathways are properly optimized, Schiff-base chromophores can be very competitive with traditional NLO materials. However, the nonlinear behaviour described in the literature varies greatly based on the solvent environment, excitation conditions, substituent pattern, molecular architecture, and even aggregation state. This variability emphasizes the need for systematic research that establishes a clear link between the resulting nonlinear optical performance and environment-dependent photophysical properties, electronic structure, and molecular design. These findings are corroborated by numerous recent studies. Strong third-order responses have been observed for Schiff bases based on pyrrole and 1,4-phenylenediamine, highlighting the significance of donor-rich frameworks for optical limiting applications [12–14]. Thiazole–furan Schiff bases show clear solvent and intensity-dependent nonlinear behaviour, as shown by Aswathy et al. [15], underscoring the significance of environmental influences. Munusamy et al. [16] reported that the presence of strong electron-accepting groups in quinoline-functionalized Schiff bases results in enhanced nonlinear activity. Khalid et al. [17] confirmed that substituent modification allows for effective tuning of the molecular response. Moreover, Muhammad Tahir et al. [13] demonstrated that strong donor–acceptor conjugation enhances 1,4-phenylenediamine-based systems, leading to notable third-order nonlinear effects. Collectively, these investigations indicate that the NLO performance of Schiff-base chromophores is optimized through the combination of rational molecular engineering and appropriate solvent modulation.

Despite these advances, hydrazide-based Schiff-base systems remain relatively underexplored. The presence of additional –NH– groups can enhance dipole moments, strengthen ICT pathways, and improve molecular stability, all of which are essential for high-performance NLO behaviour. Nevertheless, there are only a handful of studies that have systematically integrated solvatochromic analysis, solution-phase Z-scan experiments, and theoretical calculations to comprehend the impact of solvation on the properties of third-order NLOs. The creation of solvent-tunable organic NLO materials with consistent photonic performance depends on closing this gap.

In this study, we report the synthesis of a novel hydrazide-based Schiff-base chromophore, ((*E*)-*N'*-(2,6-dimethoxybenzylidene)-3-hydroxy-2-naphthohydrazide) (DHN), prepared via a reflux-assisted route. The molecular structure was confirmed using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, as well as single-crystal X-ray diffraction (SCXRD). The compound was further characterized by thermal analysis, solvatochromic studies, photoluminescence (PL) spectroscopy, and UV–Vis–NIR absorption. Solute–solvent interactions, excited-state relaxation pathways, and ICT strength were investigated by linear optical measurements in solvents with different polarities. The third-order NLO response was evaluated using open- and closed-aperture Z-scan experiments (532 nm, CW) to determine the nonlinear refractive index ( $n_2$ ), nonlinear absorption coefficient ( $\beta$ ), optical limiting threshold, and third-order susceptibility ( $\chi^{(3)}$ ). Complementary DFT and TD-DFT calculations were employed to investigate frontier molecular orbitals, hyperpolarizability parameters, and electronic structure. The combined experimental and theoretical results have shown that DHN is a solvent-tunable chromophore that is suitable for optical limiters, photonics, and advanced optoelectronic applications. This is evidenced by pronounced ICT, significant solvent-dependent spectral shifts, and strong third-order NLO

activity.

## 2. Materials and methods

### 2.1. Material synthesis

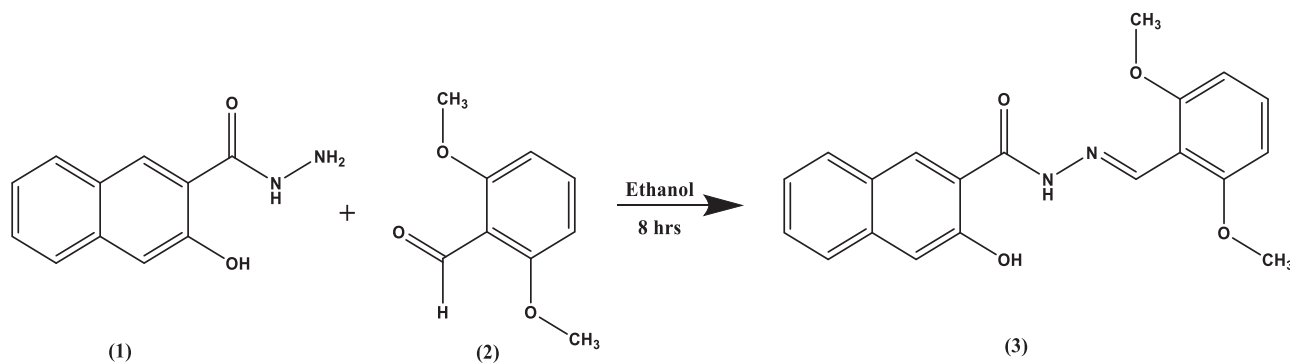
Analytical grade 2,6-dimethoxybenzaldehyde, 3-hydroxy-2-naphthohydrazide, and glacial acetic acid were purchased from Sigma Aldrich and used without further purification. The target compound, (*E*)-*N'*-(2,6-dimethoxybenzylidene)-3-hydroxy-2-naphthohydrazide, was prepared via an acid-catalyzed condensation reaction under reflux conditions. Equimolar quantities of 2,6-dimethoxybenzaldehyde and 3-hydroxy-2-naphthohydrazide were accurately weighed and dissolved in 20 mL of ethanol in a 50 mL round-bottom flask, resulting in a clear homogeneous solution. A few drops (2–6) of glacial acetic acid were added to act as a proton donor, which facilitated the nucleophilic attack of the hydrazide nitrogen on the aldehyde carbonyl group. The reaction mixture was then heated under reflux for 8 h to ensure complete condensation. After completion of the reaction, the mixture was allowed to cool to room temperature. Any insoluble impurities were removed by filtration, and the clear filtrate was transferred to a clean beaker. The beaker was covered with perforated parafilm to permit slow solvent evaporation under undisturbed conditions. Over approximately 15 days, yellow crystalline solids formed gradually. The crude product was collected and further purified through recrystallization from ethanol, yielding well-defined crystals with improved purity and crystallinity. A single crystal, measuring 0.235 mm × 0.349 mm × 0.502 mm, was carefully selected for SCXRD studies to determine the precise molecular structure of the synthesized compound. The synthetic route for the DHN compound is illustrated in Scheme 1, and the corresponding  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are provided in the supporting Information.

### 2.2. Instrumentation details

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the DHN compound were acquired in DMSO using an Agilent 600MR DD2 NMR spectrometer to confirm the molecular framework. The DHN single crystal XRD data were recorded at room temperature using a Bruker D8 Venture diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Optical absorption measurements were carried out on a Beckman Coulter DU-73 spectrophotometer in the range 240–600 nm, and solvatochromic behaviour was examined in different solvents. Photoluminescence spectra were obtained between 375 and 900 nm using a Hitachi F-7000 spectrofluorometer. Thermal properties were examined by simultaneous TGA/DTA using a NETZSCH STA 2500 system under a nitrogen atmosphere from 30 to 1200 °C at a heating rate of 10 °C min $^{-1}$ . The third-order nonlinear optical response was assessed by the single-beam Z-scan technique using a HOLMARC Z-scan system (Model HOEDLOE-03), from which the NLO parameters were extracted.

### 2.3. Quantum chemical calculations

Theoretical calculations were carried out with the *Gaussian 09* software [18]. The molecular structure of the DHN compound was fully optimized using DFT at the B3LYP level with the 6-311++G(d,p) basis set [19] applied to all C, H, N, and O atoms. The choice of the 6-311++G(d,p) basis set ensures a reliable description of the electronic structure of the conjugated DHN chromophore, as the inclusion of triple zeta valence functions together with polarization and diffuse functions is important for accurately describing charge distribution and electronic excitation in donor–acceptor systems. Electronic absorption spectra were simulated using time-dependent DFT and analyzed with *GaussView 6* [20]. TD-DFT calculations were performed by computing the lowest six singlet excited states (TD (NStates = 6)) to ensure that all relevant low-energy electronic excitations were adequately described. Solvent effects were taken into account in the TD-DFT calculations using the polarizable continuum model (PCM) to describe solvent polarization effects on the electronic



Scheme 1. Synthesis pathway of DHN compound

excitation energies. The crystal structure obtained from SCXRD was further analyzed by Hirshfeld surface analysis using *CrystalExplorer* 17.5 [21];  $d_{\text{norm}}$  surfaces and two-dimensional fingerprint plots were generated to quantify and visualize intermolecular contacts. Natural Bond Orbital analysis was carried out to investigate intramolecular charge redistribution and donor-acceptor interactions at the B3LYP/6-311++G(d,p) level of theory on the optimized molecular geometry. Frontier molecular orbital (FMO) analysis was performed at the same level of theory to evaluate the electronic structure and intramolecular charge-transfer characteristics of the DHN compound. The HOMO and LUMO energies and their energy gap ( $E_g$ ) were calculated to assess molecular stability, polarizability, and electronic transition behaviour. Additionally, the frequency-dependent nonlinear optical parameters, including dipole moment, linear polarizability, and first- and second-order hyperpolarizabilities, were evaluated within the TD-HF method using the GAMESS [22] at various frequencies. Total dipole moment ( $\mu$ ), isotropic and anisotropic polarizabilities ( $\alpha_{\text{tot}}$ ,  $\Delta\alpha$ ), first hyperpolarizability ( $\beta_{\text{tot}}$ ), and second hyperpolarizability ( $\gamma_{\text{tot}}$ ) were obtained using the following relations:

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

$$\alpha_{\text{tot}} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}} \left[ (\alpha_{xx} + \alpha_{yy})^2 + (\alpha_{yy} + \alpha_{zz})^2 + (\alpha_{zz} + \alpha_{xx})^2 + 6 (\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2) \right]^{1/2} \quad (3)$$

$$\beta_{\text{tot}} = \left[ (\beta_{xxx} + \beta_{yyy} + \beta_{zzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{1/2} \quad (4)$$

$$\gamma_{\text{tot}} = \frac{1}{5} \left[ (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz}) + 2 (\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz}) \right] \quad (5)$$

All tensor components were converted from atomic units (a.u.) to electrostatic units (esu) using standard conversion factors: 1 a.u. of  $\alpha = 0.15 \times 10^{-24}$  esu, 1 a.u. of  $\beta = 8.64 \times 10^{-33}$  esu, and 1 a.u. of  $\gamma = 5.04 \times 10^{-40}$  esu.

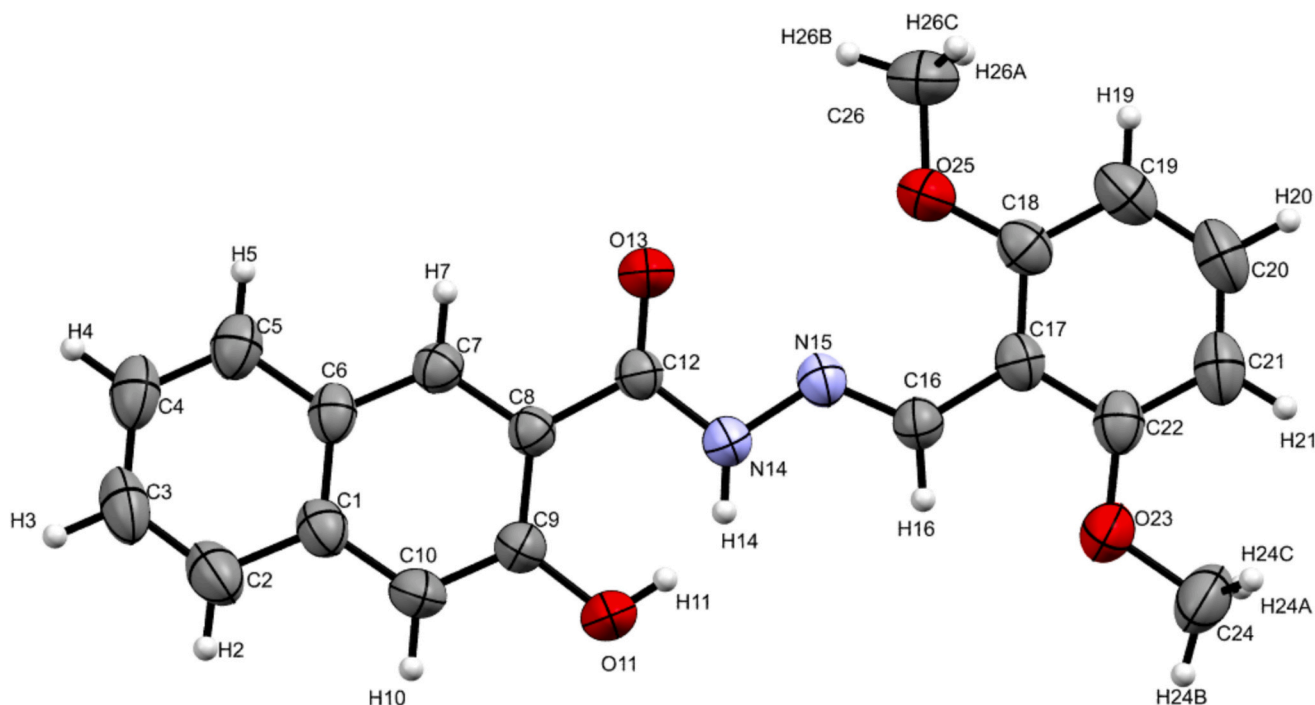


Fig. 1. ORTEP diagram of DHN drawn at 50% probability.

### 3. Result and discussion

#### 3.1. Structural characterization

##### 3.1.1. Structure determination by single-crystal XRD

Single-Crystal XRD analysis shows that the DHN adopts an orthorhombic crystal system and belongs to the *Pbca* space group, with eight molecules per unit cell. The refined lattice constants are  $a = 14.5550(8)$  Å,  $b = 13.4881(7)$  Å, and  $c = 17.7495(8)$  Å, with all angles equal to  $90^\circ$ . Fig. 1 depicts the molecular structure of DHN as an ORTEP diagram at a 50% probability level, and Table 1 provides a comprehensive summary of the crystallographic parameters and refinement details. The molecule contains three aromatic rings: ring A (C1–C2–C3–C4–C5–C6), ring B (C1–C10–C9–C8–C7–C6), which is fused to ring A, and a methoxy-substituted aromatic ring (C17–C18–C19–C20–C21–C22). All rings are essentially planar with  $sp^2$ -hybridized carbon atoms, as evidenced by least-squares plane deviations of 0.0056 Å for ring A, 0.0057 Å for ring B, and 0.0026 Å for the methoxy-substituted ring. The overall molecular conformation is nearly planar, with a dihedral angle of  $2.95^\circ$  between the fused phenyl system and the methoxy-phenyl ring.

The methoxy-phenyl ring and the fused phenyl rings are connected by a conjugated acyl-hydrazone fragment (O13=C12–N14–N15=C16), which exhibits unique bonding characteristics as evidenced by XRD data. The C12–N14 and N14–N15 linkages show single-bond behaviour, with bond distances of 1.351 Å and 1.377 Å, respectively. In contrast, the O13=C12 and N15=C16 connections display double-bond character, as indicated by their measured distances of 1.240 Å and 1.290 Å. These values are consistent with similar structural reports in the literatures [23,24]. Within the methoxy-phenyl moiety, the bond angles C20–C21–C22 ( $119.2^\circ$ ) and C18–C19–C20 ( $118.7^\circ$ ) indicate an almost planar trigonal arrangement. The methoxy substituents attached to this ring (C18–O25–C26 and C22–O23–C24) exhibit slightly bent geometries, with bond angles of  $119.8^\circ$  and  $118.5^\circ$ , respectively. These groups adopt a *–anti periplanar* orientation relative to the methoxy-phenyl ring,

as reflected by torsion angles of  $-179.8^\circ$  (C26–O25–C18–C17) and  $-178.8^\circ$  (C20–C21–C22–O23). In addition, the torsion angles for C6–C7–C8–C9 ( $-0.7^\circ$ ) and C10–C1–C6–C7 ( $-1.1^\circ$ ) suggest that this fragment is in a *–syn periplanar* configuration. The DHN crystal's torsional angles, bond lengths, and bond angles are all summarized in Tables S1–S3.

The molecules are organized into extended chains by C–H...O and C–H...C intermolecular interactions, which stabilize the crystal packing (see Fig. 2). Among these, the C3–H3...O13 (3.316 Å) and C4–H4...O13 (3.299 Å) contacts connect adjacent molecules, while the nearly linear C24–H24...O13 interaction ( $175.83^\circ$ ) acts as a strong stabilizing link within the lattice. Additional C–H...C contacts, such as C16–H16...C4 (3.499 Å) and C26–H26...C4 (3.670 Å), further consolidate the packing arrangement. Detailed parameters of these hydrogen-bonding interactions are provided in Table 2. Intramolecular interactions, including C7–H7...O13 and C16–H16...O23, help to maintain the molecular geometry, facilitating close packing. Beyond hydrogen bonding, aromatic  $\pi$ – $\pi$  stacking occurs between rings Cg2 and Cg3, with a centroid–centroid separation of 3.8305 Å, resulting in a parallel arrangement of neighboring aromatic systems. The aromatic (phenyl) ring centroids are defined as follows: Cg1 corresponds to phenyl ring A (C1–C2–C3–C4–C5–C6), Cg2 corresponds to phenyl ring B (C1–C10–C9–C8–C7–C6), and Cg3 corresponds to the methoxy-substituted phenyl ring (C17–C18–C19–C20–C21–C22). Additionally, a C–H... $\pi$  contact is observed between C24–H24B and Cg1, with a centroid distance of 3.454 Å and a symmetry operation of  $(2 - x, -y, 1 - z)$ . These C–H... $\pi$  interactions function as auxiliary connections, connecting hydrogen-bonded chains with the  $\pi$ – $\pi$  stacked framework and thereby improving the stability and cohesion of the three-dimensional crystal network (see Fig. S3). Overall, the lattice's structural integrity is maintained by the combined effects of weak dispersive forces (van der Waals forces), directional hydrogen bonds, and interactions between aromatic rings ( $\pi$ – $\pi$  stacking), which all affect the crystal packing.

##### 3.1.2. Geometry optimization and theoretical structural analysis

The molecular structure of DHN was optimized at the B3LYP/6-311++G(d,p) level using DFT to ensure a dependable ground-state geometry for subsequent electronic and optical analyses. The fully optimized coordinates of the DHN molecule are provided in the Supporting Information (see table S4). Geometry optimization was carried out in the gas phase, which is generally acceptable for rigid  $\pi$ -conjugated organic chromophores. To evaluate the influence of solvent on the molecular structure, the ground-state geometry of DHN was additionally optimized in ethanol using the polarizable continuum model (PCM). A comparison of the optimized geometrical parameters reveals only minor variations in bond lengths and bond angles between the gas-phase and solvent-phase structures, indicating that solvent inclusion does not significantly alter the overall geometry or planarity of DHN. The optimized structure (see Fig. 3) reveals a well-defined, conjugated framework in which the hydrazone linkage, naphthyl ring, and aromatic substituents form an extended  $\pi$ -system. The computed bond lengths for the methoxy and phenolic groups are within the usual range for  $sp^2$  hybridized C–O environments, whereas the C–N distances for the hydrazide and imine units show the anticipated partial double-bond behaviour. Delocalized electron density throughout the ring system is consistent with the uniform distribution of aromatic C–C bonds between  $\sim 1.37$  and  $1.42$  Å.

There is very little steric distortion in the molecular structure, as evidenced by the optimized bond angles' slight variation around ideal  $sp^2$  geometries. The torsional parameters, in particular, show that DHN takes on a primarily planar or nearly planar conformation. The presence of a stiff, conjugated backbone is confirmed by the dihedral angles that approach  $0^\circ$  or  $180^\circ$  for the imine bridge, naphthalene core, and nearby aromatic fragments. This planarity is expected to improve intramolecular charge-transfer efficiency and is crucial for stabilizing continuous  $\pi$ -electron delocalization. Overall, the optimized geometry makes DHN a rigid, planar chromophore that supports extended

**Table 1**  
Crystal data and structure refinement details of DHN crystal.

|                                      |                                                                                                                                    |
|--------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|
| Empirical formula                    | C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>                                                                      |
| Formula weight                       | 350.36                                                                                                                             |
| Temperature                          | 293                                                                                                                                |
| Wavelength                           | 0.71073 Å                                                                                                                          |
| Refns. for cell determination        | 9415                                                                                                                               |
| $\theta$ range for above             | $2.80^\circ$ to $27.07^\circ$                                                                                                      |
| Crystal system                       | orthorhombic                                                                                                                       |
| Space group                          | <i>Pbca</i>                                                                                                                        |
| Cell dimensions                      | $a = 14.5550(8)$ Å<br>$b = 13.4881(7)$ Å<br>$c = 17.7495(8)$ Å<br>$\alpha = 90^\circ$<br>$\beta = 90^\circ$<br>$\gamma = 90^\circ$ |
| Volume                               | 3484.6(3) Å <sup>3</sup>                                                                                                           |
| Z                                    | 8                                                                                                                                  |
| Density(calculated)                  | 1.336 Mg m <sup>−3</sup>                                                                                                           |
| Absorption coefficient               | 0.094 mm <sup>−1</sup>                                                                                                             |
| F <sub>000</sub>                     | 1472                                                                                                                               |
| Crystal size                         | 0.235 mm × 0.349 mm × 0.502 mm                                                                                                     |
| $\theta$ range for data collection   | $2.69^\circ$ to $27.11^\circ$                                                                                                      |
| Index ranges                         | $-18 \leq h \leq 18$<br>$-17 \leq k \leq 17$<br>$-22 \leq l \leq 22$                                                               |
| Reflections collected                | 102,460                                                                                                                            |
| Independent reflections              | 3848 [Rint = 0.0747]                                                                                                               |
| Absorption correction                | Multi-scan                                                                                                                         |
| Refinement method                    | full matrix least-squares on F <sup>2</sup>                                                                                        |
| Data/restraints/parameters           | 3848/0/238                                                                                                                         |
| Goodness-of-fit on F <sup>2</sup>    | 1.057                                                                                                                              |
| Final R indices [I > 2 $\sigma$ (I)] | R1 = 0.0747, wR2 = 0.2130                                                                                                          |
| R indices (all data)                 | R1 = 0.0973, wR2 = 0.2588                                                                                                          |
| Extinction coefficient               | 0.0065(18)                                                                                                                         |
| Largest diff. peak and hole          | 0.631; −0.531 e Å <sup>−3</sup>                                                                                                    |

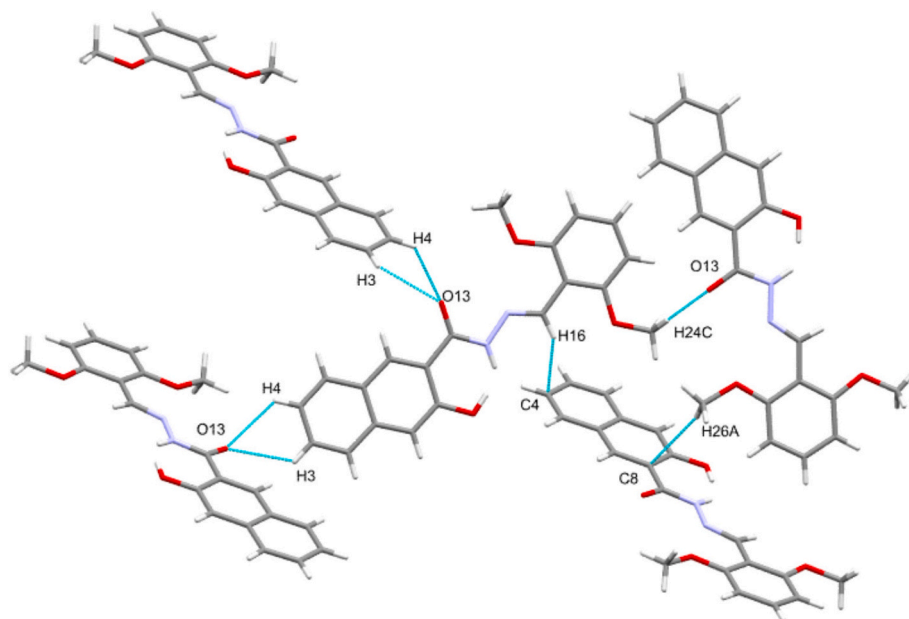


**Fig. 2.** The crystal packing interactions representation when viewed down b axis: C-H...O and C-H...C interactions (shown in blue dotted lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 2**

Intra and intermolecular hydrogen bonding geometry (Å, deg.) for the DHN.

| D-H...A                      | D-H   | H...A | D...A | D-H...A |
|------------------------------|-------|-------|-------|---------|
| C3-H3...O13 <sup>a</sup>     | 0.930 | 2.713 | 3.316 | 123.32  |
| C4-H4...O13 <sup>a</sup>     | 0.930 | 2.693 | 3.299 | 123.57  |
| C16-H16...C4 <sup>a</sup>    | 0.930 | 2.771 | 3.499 | 135.81  |
| C24-H24...O13 <sup>a</sup>   | 0.960 | 2.605 | 3.435 | 175.83  |
| C26-H26...C4 <sup>a</sup>    | 0.960 | 2.818 | 3.670 | 148.24  |
| C7-H7...O13 <sup>b</sup>     | 0.930 | 2.460 | 2.787 | 100.71  |
| C16...H16...O23 <sup>b</sup> | 0.930 | 2.281 | 2.659 | 103.66  |

<sup>a</sup> Intermolecular interaction.

<sup>b</sup> Intramolecular interaction.

conjugation and is structurally stable. This structural arrangement serves as the foundation for the molecule's anticipated electronic behaviour and establishes a dependable support for subsequent HOMO–LUMO, NBO, and nonlinear optical evaluations.

### 3.2. Optical studies

#### 3.2.1. UV–visible absorption studies

The optical characteristics of the DHN Schiff-base compound were explored to determine its suitability for optoelectronic and nonlinear optical applications [25]. The electronic transitions and absorption behaviour of organic chromophores were clearly depicted by UV–Vis measurements, which were implemented for this investigation [26]. From the recorded spectra, parameters such as transmittance, optical band gap, and refractive index behaviour were evaluated to establish the fundamental electronic features of the material. These findings are particularly important for optimizing the optical performance of advanced photonic devices [27].

In this study, the linear optical characteristics of the DHN Schiff base were examined using UV–Vis absorption spectroscopy over the 400–900 nm wavelength range at room temperature. The transmittance spectrum (Fig. 4(a)) reveals that the compound is highly transparent across the visible region, with a maximum transmittance of 98.54%. The sharp absorption edge and the high transparency suggest that there is minimal defect-related absorption and negligible scattering losses, which are essential for optoelectronic and nonlinear optical applications. Using the

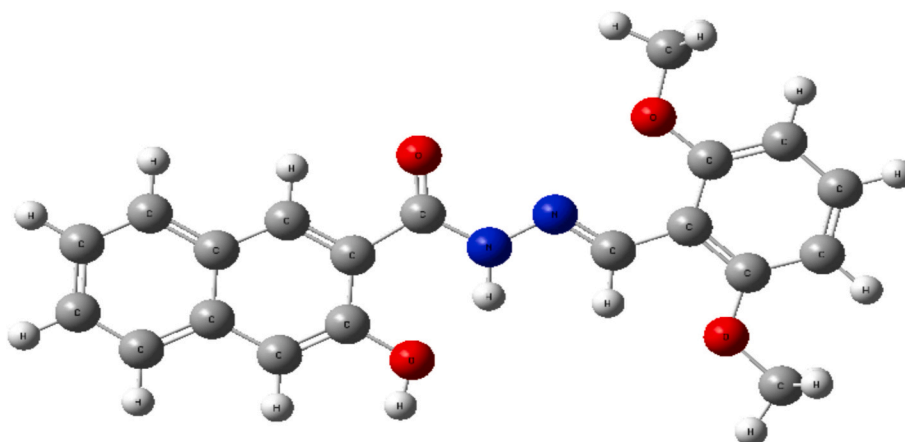


**Fig. 3.** Optimized structure of DHN compound.

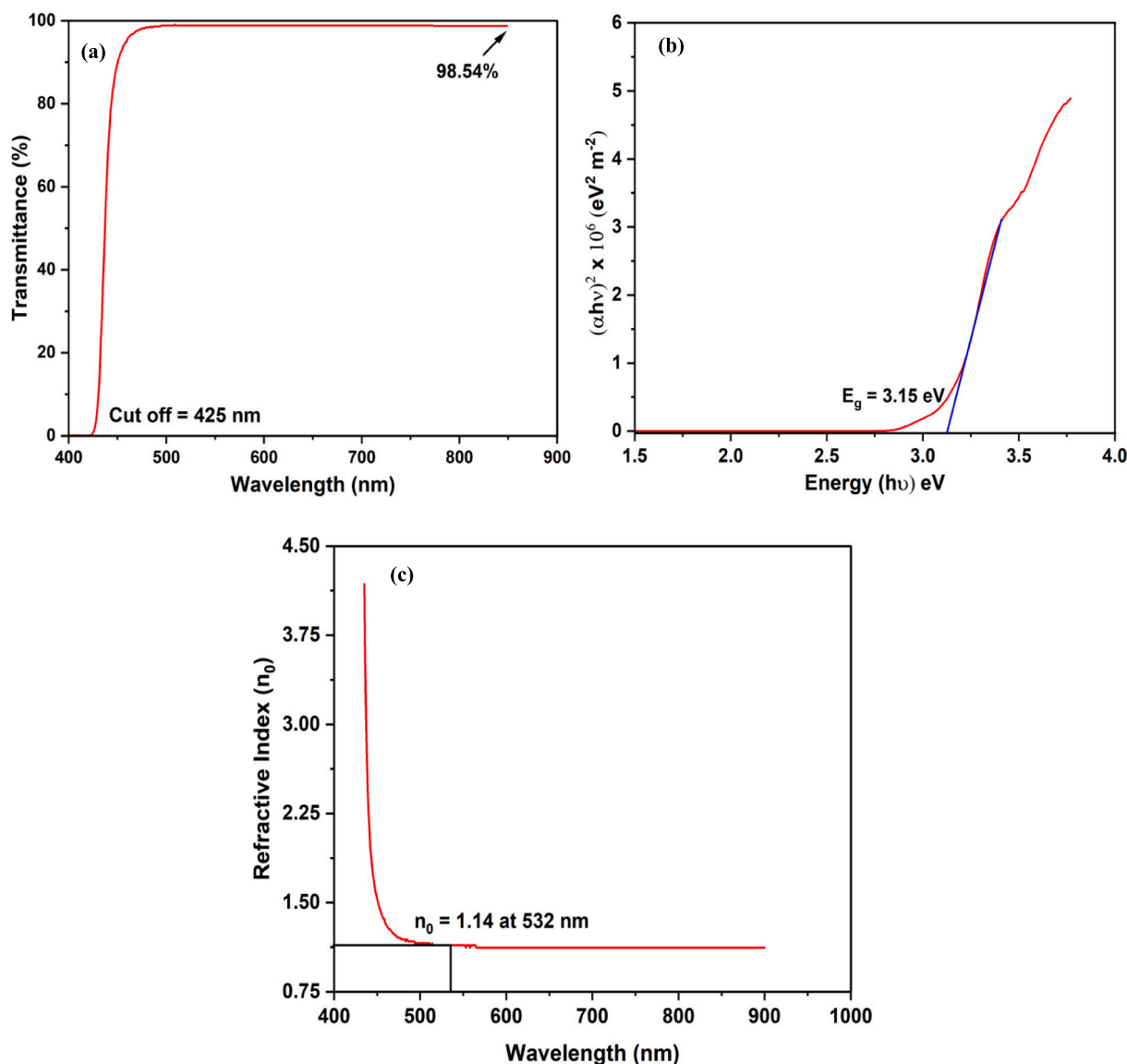


Fig. 4. (a) UV-Vis-NIR transmission spectrum, (b) Tauc's plot of the DHN, and (c) Variation of  $n_0$  with  $\lambda$ .

Tauc method [28] for direct allowed transitions, the optical band gap ( $E_g$ ) was calculated and is represented as  $\alpha h\nu = C(h\nu - E_g)^n$ . A band gap of 3.15 eV was realized by extrapolating the linear portion of the  $(\alpha h\nu)^2$  versus  $h\nu$  plot to the energy axis (Fig. 4(b)). At room temperature, this relatively wide band gap suggests that the material is suitable for high-frequency optoelectronic devices, UV-blocking coatings, and applications that require visible-range transparency with absorption limited to the near-UV region, as well as minimal thermal excitation.

The refractive index of the DHN compound was calculated using Fresnel's relation, based on the experimentally obtained reflectance and extinction coefficient. From the absorption edge toward the transparent region, the refractive index progressively drops, as shown in Fig. 4(c), reaching a value of 1.14 at 532 nm. This relatively low refractive index in the visible range is beneficial for minimizing reflection losses and improving optical transmission [29]. These measurements also served as the foundation for estimating the third-order nonlinear optical susceptibility, which provides valuable insight into the material's NLO performance [30]. DHN is a promising candidate for applications such as antireflection coatings, optical waveguides, and multilayer photonic structures, where precise management of light propagation is essential, from an engineering perspective, due to its combination of high optical

transparency and low refractive index [31]. The mathematical expressions applied for calculating the absorption coefficient, reflectance, and refractive index follow the methodology described in literature [23]. Overall, the optical characterization confirms that the DHN Schiff base has a low refractive index of 1.14, an exceptional visible-range transmittance exceeding 98%, and a wide band gap of 3.15 eV. These characteristics together highlight its potential for transparent photonic components, nonlinear optical devices, and optical switching that require controlled photon-matter interaction and effective light transmission.

### 3.2.2. Photoluminescence (PL) studies

PL spectroscopy provides a non-destructive method to explore the electronic and optical characteristics of organic compounds by analyzing the light emitted upon excitation. PL responses provide comprehensive information about the electronic structure, molecular organization, and general purity of the material, all of which have a significant impact on how well the material performs in optoelectronic devices [32]. Materials showing intense, well-defined emission in the visible spectrum are particularly promising for applications including OLEDs, optical sensors, and display technologies [33,34]. By assessing

emission wavelength, intensity, and color fidelity, these materials can be precisely tuned to meet specific device requirements, supporting the design of efficient and color-stable photonic components [35].

In this study, the PL properties of the synthesized DHN compound were investigated to understand its emission behaviour. An excitation wavelength of 340 nm was employed to collect the emission spectrum of DHN at room temperature. This wavelength was chosen based on the UV–Vis absorption profile in ethanol. The spectrum shows a single, intense emission peak at 492 nm (Fig. 5(a)), corresponding to the blue region of the visible spectrum. The sharp and well-defined emission, along with the absence of secondary peaks, indicates that the luminescence originates primarily from the lowest singlet excited state through a direct  $\pi$ – $\pi^*$  transition [36]. The absence of defect- or trap-mediated emission suggests a well-ordered molecular arrangement and high material purity which are critical for optoelectronic applications. To further characterize the emission, the chromaticity coordinates were determined and plotted on the CIE 1931 diagram (Fig. 5(b)). The coordinates ( $x = 0.2290$ ,  $y = 0.2533$ ) fall within the blue region, closely matching the ideal values for pure blue light. This confirms that DHN is a promising candidate for applications such as blue OLEDs, solid-state lighting, and fluorescence-based sensors, as it can generate high-purity blue emission. The potential of DHN for photonic and optoelectronic devices that necessitate stable and color-accurate light emission is emphasized by the combination of sharp emission intensity, precise chromaticity, and emission in the blue spectral range [34].

### 3.2.3. TD-DFT absorption calculations

The electronic absorption behaviour of the DHN compound was investigated using the TD-DFT method. The solvent effects of ethanol, DMSO, and toluene were incorporated into the PCM-IEFPCM model to evaluate the influence of different dielectric environments on the electronic transitions [37]. The theoretical UV–Vis spectrum shown in Fig. 6 was generated by Gaussian convolution of the discrete TD-DFT excitation energies and oscillator strengths using the GaussSum program [38]. In the experimental UV–Vis spectrum, the compound shows a prominent absorption peak at 340 nm (see Fig. 6). In ethanol, the TD-DFT calculations predict a corresponding transition at 352.17 nm (3.52 eV) with a high oscillator strength of 0.9244, which is in good agreement with the measured spectrum. Orbital analysis performed using GaussSum reveals that this excitation originates mainly from a HOMO  $\rightarrow$  LUMO transition ( $\sim 96\%$ ), with a minor contribution from HOMO–1  $\rightarrow$  LUMO ( $\sim 3\%$ ). This dominant excitation corresponds to a delocalized  $\pi \rightarrow \pi^*$  transition with intramolecular charge-transfer character distributed over the conjugated framework of the DHN chromophore. Such a locally excited or short-range intramolecular charge-transfer transition is well

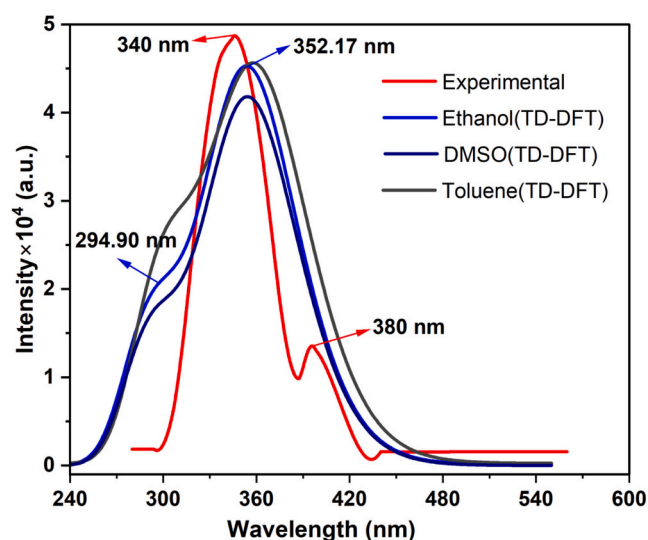
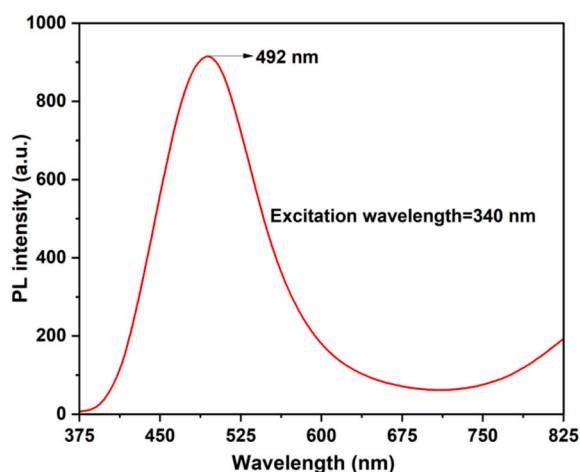


Fig. 6. Experimental and TD-DFT-simulated UV–Vis absorption spectra of the DHN compound.

described by the B3LYP functional, particularly when solvent effects are included through the PCM model [39].

When different PCM solvents are considered, the calculated absorption maxima for the main transition appear at 356.66 nm in DMSO, and 362.35 nm in toluene, indicating small to moderate solvent-dependent shifts. Despite these variations in excitation energy, the dominant HOMO  $\rightarrow$  LUMO character (96 to 98%) and high oscillator strength are preserved in all three solvents, confirming that the transition is primarily  $\pi \rightarrow \pi^*$  in nature with limited long-range charge-transfer character. Since the excitation involves intramolecular charge redistribution within a relatively compact conjugated framework rather than a pronounced long-range donor–acceptor state, the B3LYP functional provides a reasonable and reliable description of the electronic transitions. In addition to the main transition, the TD-DFT calculations predict a weaker electronic excitation around  $\sim 295$  nm in all solvents. In ethanol, this band appears at 294.90 nm ( $f = 0.3717$ ), mainly arising from a HOMO  $\rightarrow$  LUMO+1 transition (89%) with a minor contribution from HOMO–3  $\rightarrow$  LUMO (9%). Comparable excitation energies are obtained in DMSO and toluene, although the oscillator strength in toluene is significantly reduced. After Gaussian convolution, this transition produces a shoulder on the higher-energy (shorter-wavelength) side of the simulated absorption band. In contrast, the experimentally observed



CIE 1931

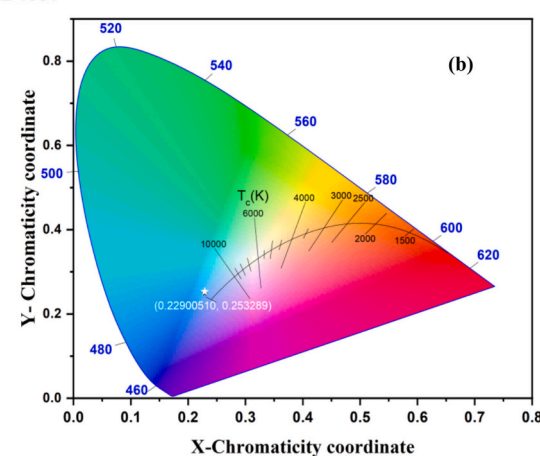


Fig. 5. (a) PL spectrum and (b) CIE chromaticity diagram of DHN compound.

shoulder appears at lower energy ( $\sim 380$  nm). This difference arises from the vertical excitation approximation inherent in TD-DFT calculations performed within the PCM framework, which evaluate transitions at the equilibrium ground-state geometry and treat the solvent as a static polarizable continuum [40]. Such calculations do not explicitly account for vibronic structure or dynamic solvent–solute interactions, which can influence band broadening and intensity redistribution in experimental spectra [41,42]. Overall, the primary absorption features are reasonably reproduced across the three solvent environments, demonstrating the reliability of the computational approach. A detailed comparison between the experimental and calculated UV–Vis data in ethanol, DMSO, and toluene is provided in Table 3.

### 3.3. Thermogravimetric (TG) and differential thermal analysis (DTA) measurements

The thermal behaviour of the DHN Schiff base was investigated through simultaneous TG and DTA under an inert nitrogen environment, covering the range from 30 to 1200 °C (see Fig. 7). The TG curve indicates a stepwise decomposition process. The initial stage, showing a small mass loss of approximately 3% between 30 °C and 222.54 °C, is due to the evaporation of physically absorbed water molecules and traces of residual solvents. The first major decomposition step occurs between 222.54 °C and 386.82 °C, during which a weight loss of approximately 28.81% (from 97.56% to 68.75%) is observed. This stage is mainly associated with the detachment of labile substituents, particularly the methoxy groups, along with the initial weakening of the Schiff-base linkage. The next decomposition step extends from 386.82 °C to 522.68 °C, accompanied by an additional weight loss of about 15.54% (from 68.75% to 53.21%), which can be attributed to further cleavage of the hydrazone (Schiff-base) moiety and progressive degradation of the conjugated molecular framework. The decomposition step, observed between 522.68 °C and 852.74 °C, results in a further 10.36% weight loss (from 53.21% to 42.85%) and is associated with the breakdown of the aromatic ring system [43]. The final decomposition step observed between  $\sim 853$  °C and 1200 °C, reflects the slow breakdown of the remaining carbonaceous material, ultimately leaving a stable carbon-rich residue. The DTA profile exhibits distinct thermal events. The melting of DHN is attributed to a sharp endothermic peak around  $\sim 310$  °C, suggesting that the sample has a well-ordered crystalline structure [44]. An exothermic peak around 417.54 °C is attributed to partial carbonization or structural rearrangements of the degraded material under nitrogen. Table 4 shows a comparison of the thermal stability of the DHN compound with that of several hydrazone-based organic compounds reported in previous studies [44–48]. Overall, DHN exhibits excellent thermal stability up to approximately 223 °C, with decomposition primarily occurring through endothermic processes rather than oxidative reactions. Due to its stability, it can be used in moderately heated environments for possible NLO applications.

**Table 3**  
Experimental and TD-DFT-simulated UV–Vis absorption spectra of the DHN compound.

| Solvents | Experimental wavelength (nm) | Theoretical wavelength (nm) | E (eV) | f      | Major transitions                       |
|----------|------------------------------|-----------------------------|--------|--------|-----------------------------------------|
| Ethanol  | 340                          | 352.17                      | 3.52   | 0.9244 | HOMO→LUMO (96%)<br>HOMO-1 → LUMO (3%)   |
|          | –                            | 294.90                      | 4.204  | 0.3717 | HOMO→LUMO+1 (89%)<br>HOMO-3 → LUMO (9%) |
| DMSO     | –                            | 356.66                      | 3.47   | 0.9508 | HOMO→LUMO (96%)<br>HOMO-1 → LUMO (3%)   |
|          | –                            | 294.75                      | 4.206  | 0.3655 | HOMO→L + 1 (89%)<br>HOMO-3 → LUMO (9%)  |
| Toluene  | –                            | 362.35                      | 3.42   | 0.825  | HOMO→LUMO (98%)<br>HOMO-4 → LUMO (92%)  |
|          | –                            | 295.10                      | 4.201  | 0.0002 | HOMO-6 → LUMO (3%)                      |

### 3.4. Solvatochromic analysis

#### 3.4.1. Solvents effect on DHN's absorption and fluorescence spectra

DHN's solvatochromic studies were investigated by recording its UV–visible absorption and fluorescence spectra in a variety of solvents, such as methanol, ethanol, ethyl acetate, acetonitrile, toluene, and DMSO. A thorough examination of solvent effects on the electronic transitions of the compound under study was made possible by the selection of these solvents, which span a wide range of dielectric constants and hydrogen-bonding capacities [49]. All spectral measurements (both absorption and emission) were carried out at room temperature. The resulting spectra are shown in Fig. 8, and the corresponding photophysical parameters are summarized in Table 5.

In all solvents, from ethanol to DMSO, the DHN absorption spectra (Fig. 8(a)) display a broad band from 240 to 600 nm. In addition to the main absorption maximum, a noticeable shoulder is observed in the high-energy region, particularly in methanol. Such shoulders are attributed to overlapping localized  $\pi$ – $\pi^*$  transitions of the aromatic framework occurring alongside the principal intramolecular charge-transfer (ICT) band [50]. In polar protic solvents, hydrogen-bonding interactions with carbonyl or hydrazone groups can perturb excited-state energies and modify band shapes, leading to partial resolution of electronic transitions and the appearance of shoulders [51]. A bathochromic shift of about 45 nm is seen across these solvents, suggesting that solvent polarity has very little effect on the molecule's ground-state electronic structure. This slight alteration implies that the ground state electron density is not greatly redistributed, which is consistent with the neutral DHN molecule's comparatively low polarity. However, the fluorescence spectra (Fig. 8(b)) show a clear bathochromic shift, with emission maxima in the same solvent series ranging from 438 nm (methanol) to 478 nm (toluene). The emission bands are broad in all solvents, exhibiting asymmetric profiles with a gradual decrease in intensity toward longer wavelengths. The spectra lack resolved vibronic fine structure, indicating emission from a relaxed excited state [52]. This change implies that when the molecule is photoexcited, electrons move from the 2,6-dimethoxybenzylidene donor toward the naphthoyl-hydrazone acceptor, resulting in an internal electron transfer. The observed red shift in less polar solvents such as toluene suggests that solvent–solute interactions influence the excited-state energy. The fluorescence intensity also tends to vary across solvents, which may be attributed to solvent-dependent stabilization of the emissive state. Overall, this solvent-dependent behaviour emphasizes the strong charge-transfer nature of DHN and offers a helpful foundation for solvatochromic estimation of its nonlinear optical properties.

#### 3.4.2. Estimation of NLO properties ( $\alpha_{CT}$ , $\beta_{CT}$ and $\gamma_{CT}$ ) via solvatochromic analysis

The DHN compound's NLO response was investigated using the solvatochromic approach, which is widely employed to estimate the static

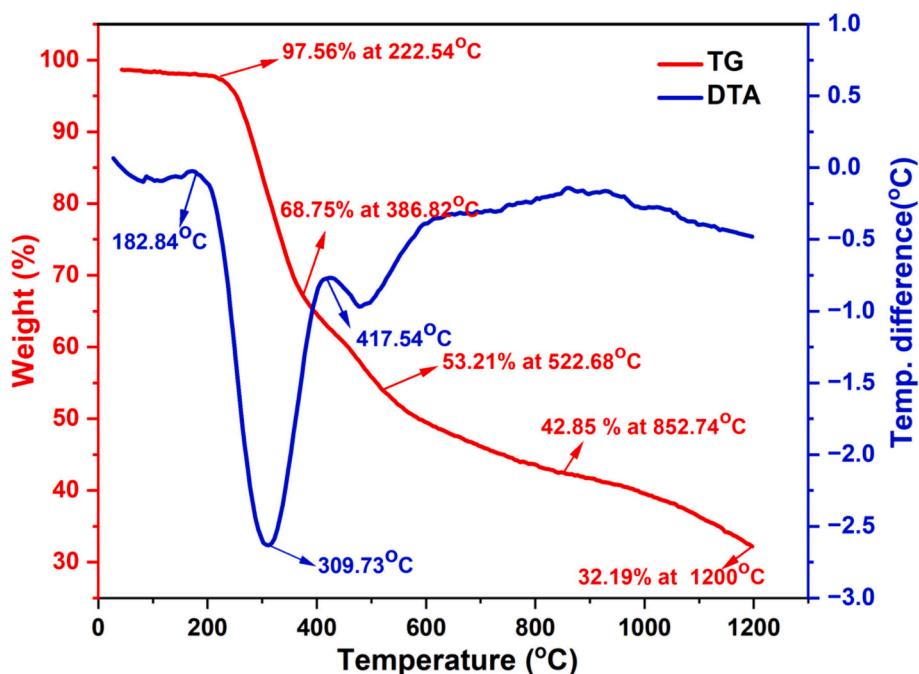


Fig. 7. TG–DTA curve of DHN compound.

Table 4

Comparison of thermal stability of DHN with reported organic compounds.

| Compound | Thermal stability (°C) | References   |
|----------|------------------------|--------------|
| DHN      | 222.54                 | Present work |
| 4CP4MPEA | 203                    | [44]         |
| 4CBTCA   | 146                    | [45]         |
| DAMC     | 215                    | [46]         |
| BTDPA    | 200                    | [47]         |
| 4BATH    | 180                    | [48]         |

polarizability ( $\alpha_{CT}$ ), first-order hyperpolarizability ( $\beta_{CT}$ ), and second-order hyperpolarizability ( $\gamma_{CT}$ ). This approach is based on analyzing solvent-dependent changes in the UV–Vis absorption spectra and

provides insight into solvent-induced modulation of donor–acceptor charge redistribution. Since the charge-transfer direction is aligned along the molecular longitudinal axis, the charge-transfer polarizability is expressed as the  $\alpha_{xx}$  component of the polarizability tensor. The linear polarizability  $\alpha_{CT}$  was calculated using a two-level model [53,54] according to below expression.

$$\alpha_{xx} = \alpha_{ct} = 2 \frac{\mu_{eg}^2}{E_{eg}} = 2 \frac{\mu_{eg}^2 \lambda_{eg}}{hc} \quad (6)$$

where  $\mu_{eg}$  is the transition dipole moment,  $E_{eg}$  is the transition energy,  $\lambda_{eg}$  is the absorption wavelength,  $h$  is Planck's constant, and  $c$  is the speed of light. The transition dipole moment was obtained from the oscillator

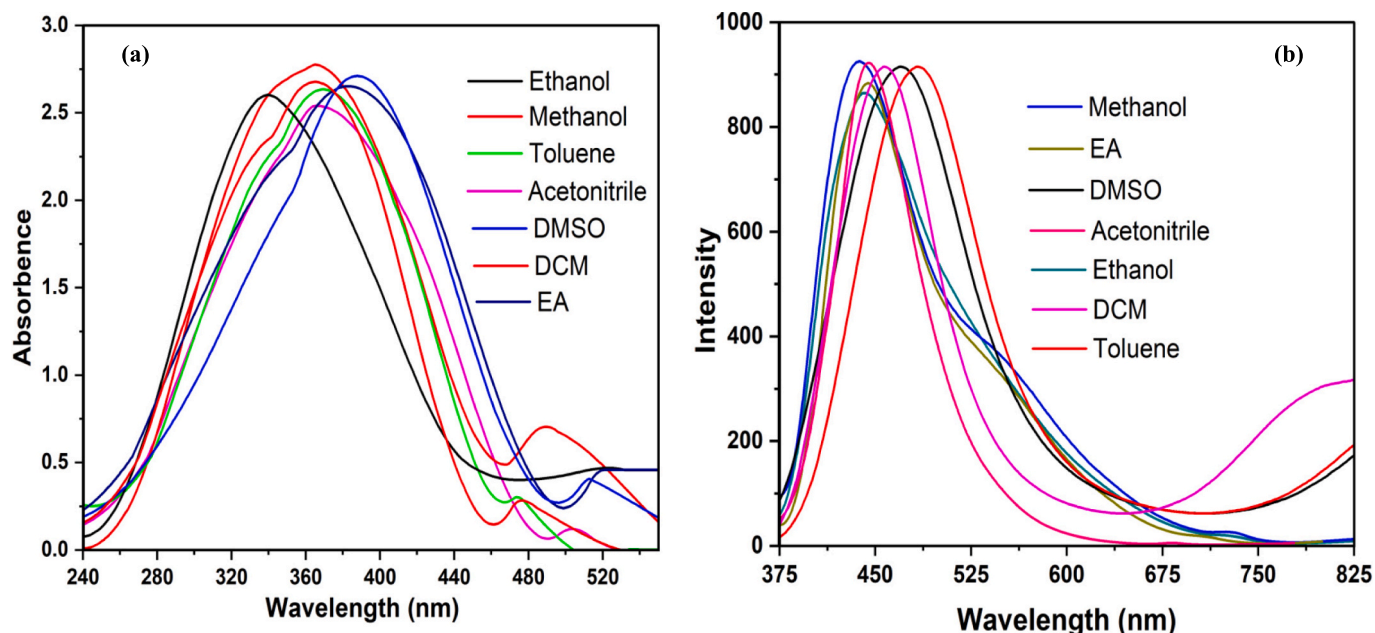


Fig. 8. (a) Absorption and (b) Emission spectra in different solvents.

**Table 5**

Experimental photophysical properties of DHN compound.

| Solvents      | $\lambda_{abs}^a$ (nm) | $\lambda_{abs}^b$ (cm <sup>-1</sup> ) | $\lambda_{emi}^c$ (nm) | $\lambda_{emi}^d$ (cm <sup>-1</sup> ) | FWHM (cm <sup>-1</sup> ) | $\epsilon^e \times 10^3$<br>Lmol <sup>-1</sup> cm <sup>-1</sup> | $f_{abs}^g$ |
|---------------|------------------------|---------------------------------------|------------------------|---------------------------------------|--------------------------|-----------------------------------------------------------------|-------------|
| Ethanol       | 340                    | 29,411                                | 442                    | 22,624                                | 9855                     | 5.20                                                            | 0.238       |
| Methanol      | 365                    | 27,397                                | 438                    | 22,831                                | 9524                     | 5.56                                                            | 0.246       |
| DCM           | 365                    | 27,397                                | 460                    | 21,739                                | 9691                     | 5.36                                                            | 0.241       |
| Acetonitrile  | 368                    | 27,173                                | 448                    | 22,321                                | 10,502                   | 5.04                                                            | 0.246       |
| Toluene       | 370                    | 27,027                                | 478                    | 20,920                                | 9257                     | 5.24                                                            | 0.225       |
| Ethyl acetate | 382                    | 26,178                                | 447                    | 22,371                                | 9205                     | 5.30                                                            | 0.226       |
| DMSO          | 385                    | 25,974                                | 473                    | 21,141                                | 8962                     | 5.40                                                            | 0.224       |

<sup>a</sup>Absorption maxima in nm.<sup>b</sup>Absorption maxima in cm<sup>-1</sup>.<sup>c</sup>Emission maxima in nm.<sup>d</sup>Absorption maxima in cm<sup>-1</sup>.<sup>e</sup>Molar extinction coefficient at absorption maxima.<sup>g</sup>Oscillator strength.

strength using expression;

$$\mu_{eg}^2 = \frac{3e^2h}{8\pi^2mc} X \frac{f}{\nu_{max}} \quad (7)$$

where,  $m$  is the electron mass,  $\nu_{max} = \Delta E$  is the absorption frequency, and  $f$  is the oscillator strength determined from below equation.

$$f = 4.32 \times 10^{-9} \int \epsilon(\nu) d\nu \quad (8)$$

where  $\epsilon$  is the extinction coefficient (CGS units). Using oscillator strength values,  $\mu_{eg}^2$  is calculated and substituted into Eq. (6) to obtain  $\alpha_{CT}$ . The calculated  $\alpha_{CT}$  values are listed in Table 6.

A solvent-dependent first hyperpolarizability was evaluated using the two-level microscopic model originally proposed by Oudar [54,55], which describes charge-transfer-dominated nonlinear optical responses. Within this framework, the first-order hyperpolarizability along the charge-transfer direction is expressed as follows:

$$\beta_{xxx} = \beta_{CT} = \frac{3}{2h^2c^2} \frac{\partial^2 \mu_{eg}^2 \Delta \mu_{CT}}{(\partial_{eg}^2 - \partial_L^2) (\partial_{eg}^2 - 4\partial_L^2)} \quad (9)$$

where  $\nu_L$  denotes the frequency of the incident radiation,  $\nu_{eg}$  is the transition frequency, and  $\Delta \mu_{CT}$  represents the change in dipole moment between the excited and ground states. The dipole moment difference  $\Delta \mu_{CT}$  was estimated based on MacRae's treatment of solvatochromic shifts [56]. The quantity  $\beta_{xxx}$ , commonly referred to as  $\beta_{CT}$ , corresponds to the dominant tensor component associated with intramolecular charge-transfer transitions. Under static conditions, where the incident field frequency approaches zero ( $\nu_L = 0$ ), Eq. (9) simplifies to the static first hyperpolarizability expression shown below:

$$\beta_{xxx} = \beta_{CT} = \frac{3}{2} \frac{\mu_{eg}^2 \Delta \mu_{CT}}{E_{eg}^2} \quad (10)$$

**Table 6**Transition dipole moment ( $\mu_{eg}$ ), polarizability ( $\alpha_{CT}$ ), first and second hyperpolarizability ( $\beta_{CT}$  and  $\gamma_{CT}$ ) of the DHN compound.

| Solvents      | $\mu_{eg}^2 \times 10^{-36}$ e.s.u. | $\alpha_{CT} \times 10^{-24}$ e.s.u. | $\beta_{CT} \times 10^{-28}$ e.s.u. | $\gamma_{CT} \times 10^{-32}$ e.s.u. |
|---------------|-------------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| Ethanol       | 17.27                               | 5.91                                 | 6.04                                | 5.48                                 |
| Methanol      | 19.15                               | 7.04                                 | 7.72                                | 7.53                                 |
| DCM           | 18.79                               | 6.90                                 | 7.57                                | 7.38                                 |
| Acetonitrile  | 19.30                               | 7.15                                 | 7.91                                | 7.77                                 |
| Toluene       | 17.78                               | 6.62                                 | 7.37                                | 7.28                                 |
| Ethyl acetate | 18.46                               | 7.10                                 | 8.15                                | 8.31                                 |
| DMSO          | 18.44                               | 7.16                                 | 8.28                                | 8.51                                 |

The values of  $\beta_{CT}$  were obtained by substituting the calculated transition energy  $E_{eg}$ , transition dipole moment  $\mu_{eg}$ , and dipole moment difference  $\Delta \mu_{CT}$  into Eq. (10) for different solvent environments. The resulting first hyperpolarizability values are summarized in Table 6.

The molecular second hyperpolarizability  $\langle \gamma \rangle_{CT}$ , associated with  $\pi$ -electron polarization in the non-resonant regime, was evaluated using a simplified quasi-two-level model derived from three-level formulation reported in the literature [57,58]. This approach, based on density matrix formalism, provides an efficient description of the second-order nonlinear response. The expression for  $\gamma_{CT}$  is given by

$$\gamma_{CT} = \frac{1}{E_{eg}^3} \mu_{eg}^2 (\Delta \mu - \Delta \mu_{CT}^2) \quad (11)$$

where  $\mu_{eg}$  and  $E_{eg}$  denote the transition dipole moment and transition energy, respectively, as defined in Eq. (6). The calculated NLO parameters for DHN are summarized in Table 6 and reveal a clear dependence on solvent polarity. Among the solvents investigated, DMSO exhibits the highest values, with  $\alpha_{CT}$  ( $7.16 \times 10^{-24}$  esu),  $\beta_{CT}$  ( $8.28 \times 10^{-28}$  esu), and  $\gamma_{CT}$  ( $8.51 \times 10^{-32}$  esu), which is consistent with enhanced stabilization of the charge-transfer excited state in this highly polar medium [59]. In contrast, ethanol shows the lowest values ( $\alpha_{CT} = 5.91 \times 10^{-24}$  esu,  $\beta_{CT} = 6.04 \times 10^{-28}$  esu,  $\gamma_{CT} = 5.48 \times 10^{-32}$  esu), reflecting limited solvent-induced stabilization. The polarity and hydrogen-bonding capabilities of the other solvents—methanol, DCM, acetonitrile, ethyl acetate, and toluene are reflected in their intermediate values. Based on these findings, it is evident that the ambient medium significantly impacts the NLO response of DHN. Intramolecular charge redistribution is facilitated by polar solvents, which stabilize the excited state and increase hyperpolarizability. Conversely, less polar or weakly hydrogen-bonding solvents restrict this effect, resulting in lower NLO parameters. DHN's potential for photonic and optoelectronic applications is underscored by its solvent-dependent tunability, which can be optimized through environmental control [60].

### 3.5. Hirshfeld surface analysis (HSA)

HSA is a well-established crystallographic approach for examining and quantifying intermolecular interactions that govern crystal packing. Unlike conventional approaches, which focus solely on bond lengths and angles, HSA allows three-dimensional visualization of the molecular environment, highlighting noncovalent contacts such as hydrogen bonds, van der Waals forces, and  $\pi$ -stacking between aromatic systems [61]. This approach offers both qualitative insights and quantitative evaluation of the contributions of these interactions, making it an effective tool for understanding the role of weak forces in stabilizing the crystal lattice. In the present study, the molecular surface was generated from the electron density of the crystal, constructed by summing the

spherical electron densities of its constituent atoms. A central parameter in this analysis is the normalized contact distance, which highlights regions of close intermolecular approach and distinguishes between attractive and repulsive contacts within the crystal lattice. It is defined as [62]:

$$d_{\text{norm}} = \frac{di - r_i^{\text{vdw}}}{r_i^{\text{vdw}}} + \frac{de - r_e^{\text{vdw}}}{r_e^{\text{vdw}}} \quad (12)$$

where  $di$  and  $de$  represent the distances from a point on the surface to the nearest nuclei inside and outside the surface, respectively, and  $r_i^{\text{vdw}}$  and  $r_e^{\text{vdw}}$  correspond to the van der Waals radii of the internal and external atoms. Mapping these distances onto the normalized contact surface results in a color-coded representation of intermolecular interactions: red regions correspond to contacts that are shorter than the sum of van der Waals radii, which typically indicates strong interactions such as hydrogen bonds; white areas represent contacts that are near the van der Waals limit; and blue regions indicate longer, weaker contacts [63]. Additional surface characteristics, such as the shape index and curvedness, were examined to learn more about the crystal packing; the former helps identify  $\pi$ - $\pi$  stacking interactions, while the latter differentiates between curved molecular regions and flat stacked planes.

The HS mapped over  $d_{\text{norm}}$  for the DHN (see Fig. 9) displays red patches that indicate close hydrogen-bonding contacts, while white and blue areas correspond to interactions at or beyond van der Waals separations. C-H...O and C-H...C interactions, which are crucial for stabilizing the crystal packing, are confirmed by the red patches situated near donor and acceptor atoms (marked in black circles in Fig. 9). These findings are consistent with the hydrogen-bonding interactions that were revealed in the SCXRD study (see Table 2), underscoring their significance in the supramolecular framework as a whole. The shape index surface (Fig. 10) provides further insight into the  $\pi$ - $\pi$  stacking and C-H... $\pi$  interactions. The  $\pi$ - $\pi$  stacking between cg2 and cg3 is revealed by the bow-tie patterns formed by red concave and blue convex regions (marked in black circle in Fig. 10(a)). Triangular red and blue patches above cg1 and adjacent hydrogen atoms (marked in black circle in Fig. 10(b)) indicate C-H... $\pi$  contacts. These interactions are further supported by the C...H/H...C fingerprint plots, which show characteristic wing-like features, demonstrating that both  $\pi$ - $\pi$  stacking and C-H... $\pi$  interactions contribute to the stability of the crystal lattice. The curvedness surface (see Fig. S4) highlights the differences between flat and curved molecular regions. Extended green areas correspond to planar regions that are involved in  $\pi$ - $\pi$  stacking, while deep blue ridges indicate curved boundaries between neighboring molecules.

Collectively, these visualizations underscore the fact that the three-dimensional crystal packing of DHN is the result of the combined influence of aromatic stacking and hydrogen bonding.

The two-dimensional fingerprint plots (see Fig. 11) were examined to quantify the different types of intermolecular contacts in the DHN. Hydrogen-Hydrogen (H...H) interactions account for the largest proportion, representing 44.5% of all contacts, reflecting the predominance of hydrogen atoms in the structure. Oxygen-hydrogen contacts (O...H/H...O) contribute 17.1%, highlighting the role of C-H...O hydrogen bonds in reinforcing the crystal lattice. C...H/H...C interactions constitute 24.6% of the total, indicating the importance of C-H... $\pi$  interactions in stabilizing the supramolecular framework. Despite the fact that C...C contacts are less common (5.9%), they confirm the presence of  $\pi$ - $\pi$  stacking, which is consistent with the shape index analysis. Minor contributions from C...O/O...C (2.8%), C...N/N...C (1.2%), and N...O/O...N (0.8%) further refine the overall three-dimensional arrangement. In conclusion, these findings indicate that hydrogen bonding is the primary stabilizing force, with  $\pi$ - $\pi$  stacking and additional weaker heteroatomic interactions serving as supplementary forces that collectively regulate the three-dimensional packing of the DHN.

### 3.6. NBO analysis

Natural Bond Orbital (NBO) analysis reveals significant intramolecular charge redistribution and donor-acceptor interactions governing the electronic structure of the Schiff-base chromophore [64]. This approach gives a chemically intuitive explanation of electron delocalization, and the computed second-order perturbation energies ( $E^2$ ) show the lone-pair,  $\pi$ -conjugative, and principal hyperconjugative interactions that contribute to the nonlinear optical (NLO) response of the molecule [65,66]. The dominant interactions identified from the second-order perturbation analysis are summarized in Table 7.

The perturbation data (Table 7) reveal an exceptionally strong network of  $\sigma \rightarrow \sigma^*$  hyperconjugative interactions. The  $\sigma(\text{C29-H43}) \rightarrow \sigma^*(\text{C17-C21})$  interaction provides the largest stabilization ( $E^2 = 1039.16 \text{ kJ mol}^{-1}$ ), followed by  $\sigma(\text{C29-H42}) \rightarrow \sigma^*(\text{C17-C21})$  ( $1006.10 \text{ kJ mol}^{-1}$ ) and  $\sigma(\text{C22-H39}) \rightarrow \sigma^*(\text{C17-C21})$  ( $813.84 \text{ kJ mol}^{-1}$ ). Significant Fock matrix elements, relatively small donor-acceptor energy gaps ( $\Delta E$ ), and high  $E^2$  values all point to effective charge delocalization into the  $\sigma(\text{C17-C21})$  antibonding orbital and strong orbital overlap [65]. These dominant interactions establish the C17-C21 region as a key electron-accepting site, underscoring its critical role in the electronic polarization. Other significant  $\sigma \rightarrow \sigma^*$  interactions, such as  $\sigma(\text{O28-C29}) \rightarrow \sigma(\text{C17-C21})$ ,  $\sigma(\text{C21-C22}) \rightarrow \sigma(\text{C17-C21})$ , and  $\sigma(\text{C29-H44}) \rightarrow \sigma^*$

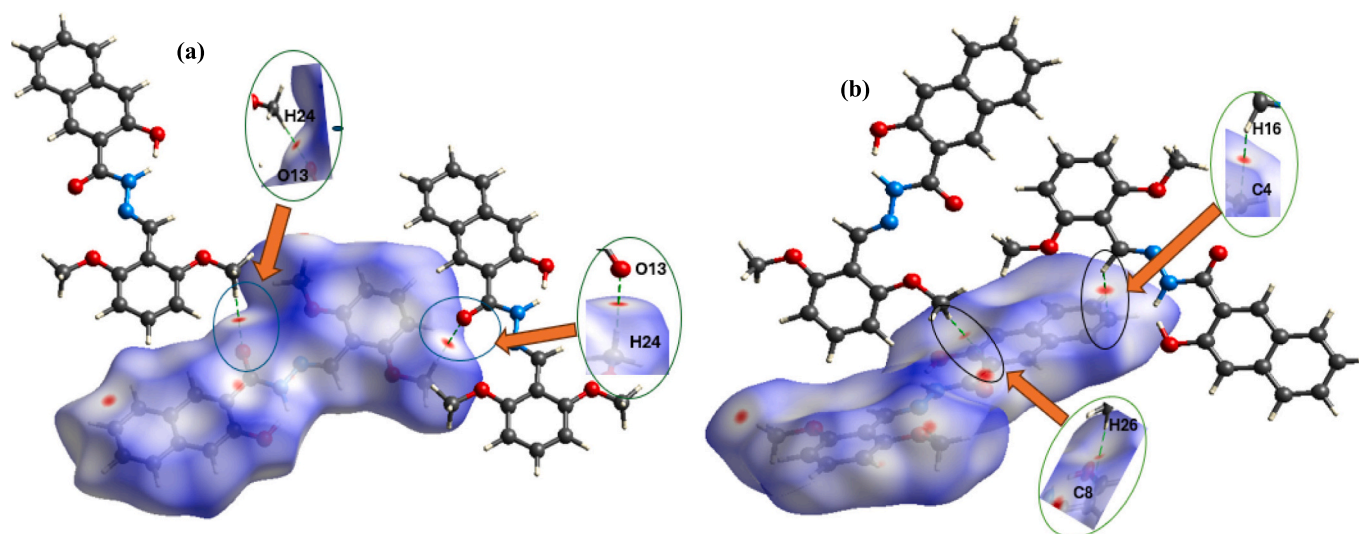


Fig. 9. Hirshfeld surfaces of the DHN mapped with  $d_{\text{norm}}$  (a) Front and (b) Back view.

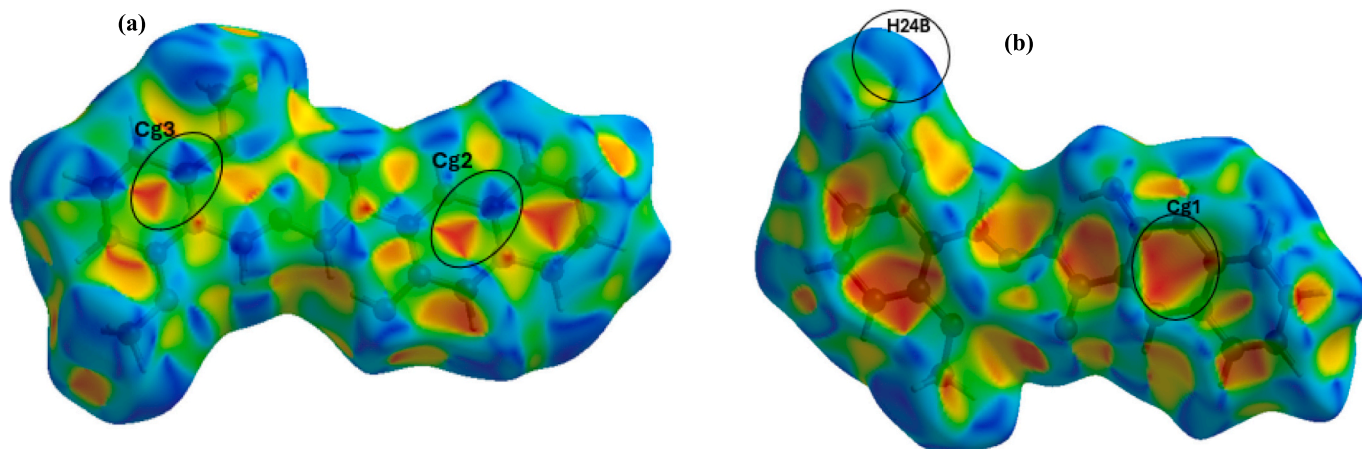


Fig. 10. Hirshfeld surfaces of the DHN mapped with Shape index (a) Front and (b) Back view.

(C17–C21), also contribute appreciably to molecular stabilization. These pathways show that intramolecular charge redistribution involves an extended  $\sigma$ -network rather than being limited to a single bond, which promotes improved molecular polarizability [67].

In addition to the  $\sigma$ -driven effects, the  $\pi$ -system and heteroatom lone pairs play a major role in electron delocalization. The  $\pi(\text{C4}–\text{C5}) \rightarrow \pi(\text{C7}–\text{C8})$  interaction ( $107.34 \text{ kJ mol}^{-1}$ ) confirms conjugation within the aromatic framework, while the  $\text{LP}(\text{O28}) \rightarrow \pi(\text{C21}–\text{C22})$  interaction ( $138.44 \text{ kJ mol}^{-1}$ ) indicates active resonance-assisted delocalization involving the oxygen atom [66]. These channels reinforce long-range electron transfer and facilitate intramolecular charge transfer (ICT). Overall, the strong  $\sigma \rightarrow \sigma^*$  hyperconjugation, supported by  $\pi$ -delocalization and lone-pair donation, creates a highly polarizable electronic environment conducive to efficient charge redistribution. The enhanced third-order nonlinear optical response of the Schiff-base chromophore is clearly elucidated by the substantial stabilization energies in Table 7, which are indicative of this electronic character.

### 3.7. Frontier molecular orbital (FMO) and global chemical descriptors (GCRD)

FMO analysis provides a clear understanding of the intramolecular charge-transfer pathways and electron distribution that control the DHN compound's optical and nonlinear optical response [68,69]. In the DHN compound, FMO analysis shows that the HOMO and LUMO energies are  $-5.665 \text{ eV}$  and  $-1.840 \text{ eV}$ , respectively, corresponding to an energy gap of  $3.825 \text{ eV}$ . The molecule's electronic properties are highlighted by the spatial distribution of these orbitals, which is depicted in Fig. 12. The HOMO is primarily localized on the electron-rich regions, including the methoxy-substituted phenyl ring, the azomethine ( $–\text{C}=\text{N}–$ ) bridge, and the oxygen atom, reflecting the main donor sites. In contrast, the LUMO extends over most of the molecular framework, excluding some carbons in the methoxy-phenyl group and the oxygen in the fused phenyl moiety, identifying the principal acceptor regions. This pronounced separation between electron-rich and electron-deficient regions establishes a clear intramolecular charge-transfer (ICT) pathway upon excitation.

The observed ICT behaviour plays a crucial role in enhancing the nonlinear optical response of DHN. According to simplified electronic models [70], the first-order hyperpolarizability ( $\beta$ ) is determined by both the extent of charge redistribution during excitation and the transition strength, and it varies inversely with the cube of the transition energy ( $\Delta E^3$ ). The moderate HOMO–LUMO gap in DHN facilitates efficient electronic excitation, promoting higher  $\beta$  values and larger third-order susceptibility ( $\chi^3$ ) [71]. Furthermore, the spatial separation of donor and acceptor regions reduces electron–hole recombination and helps sustain polarization under an applied electric field, which is

beneficial for both second- and third-order NLO effects [3].

Global reactivity parameters derived from the HOMO and LUMO energies of the DHN compound were used to further investigate its electronic properties and nonlinear optical potential. The ionization potential ( $I = 5.665 \text{ eV}$ ) represents the energy needed to remove an electron from the HOMO, reflecting the molecule's electron-donating nature, while the electron affinity ( $A = 1.840 \text{ eV}$ ) indicates its tendency to accept electrons into the LUMO. The chemical potential ( $\mu = -3.752 \text{ eV}$ ) provides insight into the overall electronic stability, with the negative value suggesting resistance to spontaneous electron loss. The hardness ( $\eta = 1.912 \text{ eV}$ ) and softness ( $S = 0.261 \text{ eV}^{-1}$ ) describe the electron cloud's adaptability, where higher softness indicates increased polarizability. Electronegativity ( $\chi = 3.752 \text{ eV}$ ) reflects a balanced capacity to attract electrons, maintaining donor–acceptor equilibrium, while the electrophilicity index ( $\omega = 3.681 \text{ eV}$ ) estimates the stabilization gained upon electron acceptance, supporting effective intramolecular charge transfer. Together, these results support the HOMO–LUMO analysis by demonstrating that the DHN molecule has strong ICT character, moderate hardness, and noticeable softness—all of which support nonlinear optical activity. Table 8 provides a summary of the HOMO–LUMO energies and associated reactivity parameters. Ultimately, the combination of electronic distribution, energy gap, and reactivity descriptors makes the DHN compound especially well-suited for applications that require effective optical and photonic performance.

### 3.8. Molecular electrostatic potential

The electrostatic potential (ESP) map of the DHN molecule provides detailed information on its charge distribution and potential reactive sites. The corresponding MEP plot, depicted with a distinct color gradient, is shown in Fig. 13. In this plot, red regions indicate areas of negative electrostatic potential, representing electron-rich sites that are susceptible to electrophilic attack. These regions are mainly associated with the oxygen atoms in the carbonyl group and the methoxy-substituted phenyl ring, reflecting their high electronegativity. Conversely, blue regions correspond to areas of positive electrostatic potential, marking electron-deficient sites prone to nucleophilic attack, mainly associated with the hydrogen atoms of the hydroxyl groups in the fused phenyl framework. Green regions represent areas of relatively neutral potential, largely along the hydrocarbon backbone. Overall, the MEP analysis demonstrates that DHN facilitates intramolecular charge transfer and highlights regions that may participate in intermolecular interactions, consistent with its predicted nonlinear optical behaviour and electronic characteristics [72].

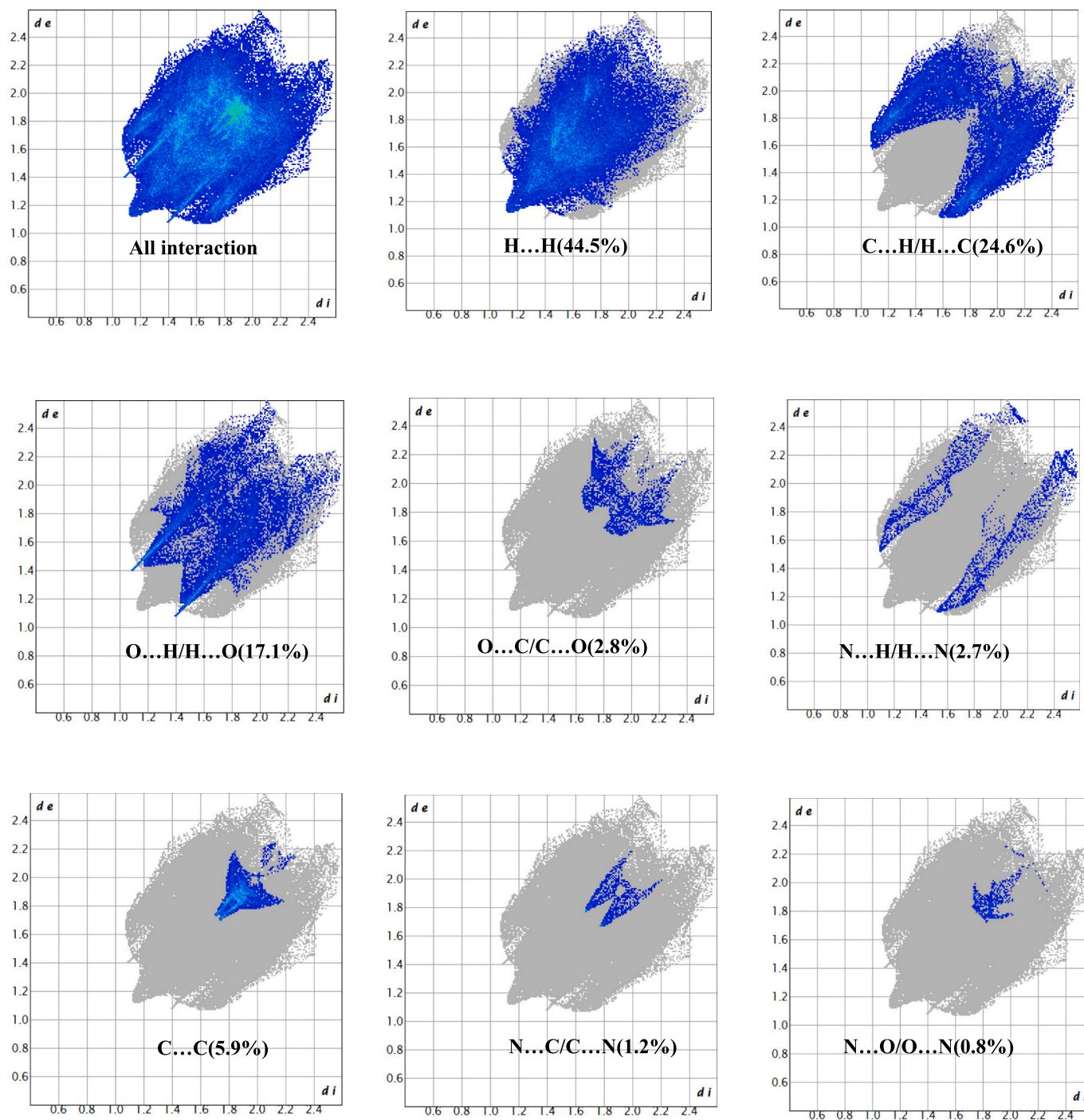


Fig. 11. Fingerprint plots of the DHN showing interactions.

### 3.9. Nonlinear optical studies

#### 3.9.1. Third-order nonlinear optical studies

Research on third-order NLO materials has expanded rapidly as a result of their critical role in the development of contemporary photonic and optoelectronic devices. These materials are particularly important for applications such as optical switching, data transmission, and protection from intense laser radiation [73]. The nonlinear optical responses of Schiff base derivatives are significantly improved by their efficient charge-transfer pathways and  $\pi$ -conjugated molecular frameworks, which are extensively investigated in this context [74]. The Z-scan technique, introduced by Sheik-Bahae and colleagues [75], is

commonly applied to measure NLO parameters. It enables the simultaneous determination of both the refractive index ( $n_2$ ) and nonlinear absorption ( $\beta$ ) in a single experiment, providing a clear understanding of the third-order properties of these organic systems.

In this study, a single-beam Z-scan setup using a continuous-wave source was used to investigate the third-order NLO behaviour of the DHN Schiff-base compound. The objective of the experiment was to evaluate the sample's suitability for photonic applications and to identify the dominant nonlinear processes that govern its response. A diode-pumped solid-state laser with a wavelength of 532 nm and an output power of 100 mW was used to produce a TEM<sub>00</sub> Gaussian beam that was sharply focused with a 100 mm focal length plano-convex lens. This

**Table 7**  
Selected Lewis and non-Lewis interactions from Second order perturbation theory analysis of Fock matrix for DHN molecule.

| Donor NBO (i) | ED (i) (e) | Acceptor NBO (j) | ED (j) (e) | E <sup>(2)</sup> (kJ mol <sup>-1</sup> ) | ΔE <sup>a</sup> (a.u.) | F(i,j) (a.u.) |
|---------------|------------|------------------|------------|------------------------------------------|------------------------|---------------|
| π (C4–C5)     | 1.5282     | π* (C7–C8)       | 0.2772     | 107.34                                   | 0.05                   | 0.066         |
| σ (C17–C21)   | 1.966      | σ* (C7–H37)      | 0.0162     | 173.07                                   | 0.42                   | 0.242         |
|               |            | σ* (C17–C21)     | 0.0286     | 100.39                                   | 0.32                   | 0.159         |
| σ (C20–C22)   | 1.974      | σ* (C7–H37)      | 0.0162     | 154.22                                   | 0.43                   | 0.231         |
| σ (C21–C22)   | 1.977      | σ* (C7–C8)       | 0.277      | 100.3                                    | 0.51                   | 0.217         |
|               |            | σ* (C17–C21)     | 0.0286     | 431.56                                   | 0.34                   | 0.34          |
| σ (C21–O28)   | 1.991      | σ* (C7–H37)      | 0.0162     | 268.92                                   | 0.64                   | 0.37          |
|               |            | σ* (C17–C21)     | 0.0286     | 291.51                                   | 0.53                   | 0.354         |
| σ (C22–H39)   | 1.975      | σ* (C7–C8)       | 0.277      | 128.51                                   | 0.4                    | 0.215         |
|               |            | σ* (C7–H37)      | 0.0162     | 489.4                                    | 0.32                   | 0.354         |
|               |            | σ* (C17–C21)     | 0.0286     | 813.84                                   | 0.22                   | 0.374         |
| σ (O28–C29)   | 1.990      | σ* (C7–H37)      | 0.0162     | 258.39                                   | 0.53                   | 0.331         |
|               |            | σ* (C17–C21)     | 0.0286     | 592.4                                    | 0.43                   | 0.451         |
|               |            | σ* (C24–H25)     | 0.018      | 438.74                                   | 0.18                   | 0.253         |
| σ (C29–H42)   | 1.989      | σ* (C7–H37)      | 0.0162     | 394.35                                   | 0.25                   | 0.279         |
|               |            | σ* (C17–C21)     | 0.0286     | 1006.1                                   | 0.14                   | 0.34          |
|               |            | σ* (C29–H42)     | 0.0095     | 187.22                                   | 1.58                   | 0.485         |
| σ (C29–H43)   | 1.993      | σ* (C7–H37)      | 0.0162     | 380.51                                   | 0.25                   | 0.274         |
|               |            | σ* (C17–C21)     | 0.0286     | 1039.16                                  | 0.14                   | 0.345         |
|               |            | σ* (O23–C24)     | 0.0095     | 147.01                                   | 3.39                   | 0.631         |
|               |            | σ* (C29–H44)     | 0.018      | 132.5                                    | 2.29                   | 0.494         |
| σ (C29–H44)   | 1.993      | σ* (C19–H40)     | 0.0139     | 114.87                                   | 0.35                   | 0.178         |
|               |            | σ* (C29–H42)     | 0.0095     | 207.01                                   | 1.16                   | 0.438         |
|               |            | σ* (C29–H44)     | 0.018      | 125.71                                   | 1.88                   | 0.435         |
| LP (1) O28    | 1.960      | σ* (C7–H37)      | 0.0162     | 247.38                                   | 0.24                   | 0.221         |
|               |            | σ* (C17–C21)     | 0.0286     | 203.15                                   | 0.14                   | 0.151         |
| LP (2) O28    | 1.810      | π* (C21–C22)     | 0.403      | 138.44                                   | 0.13                   | 0.127         |

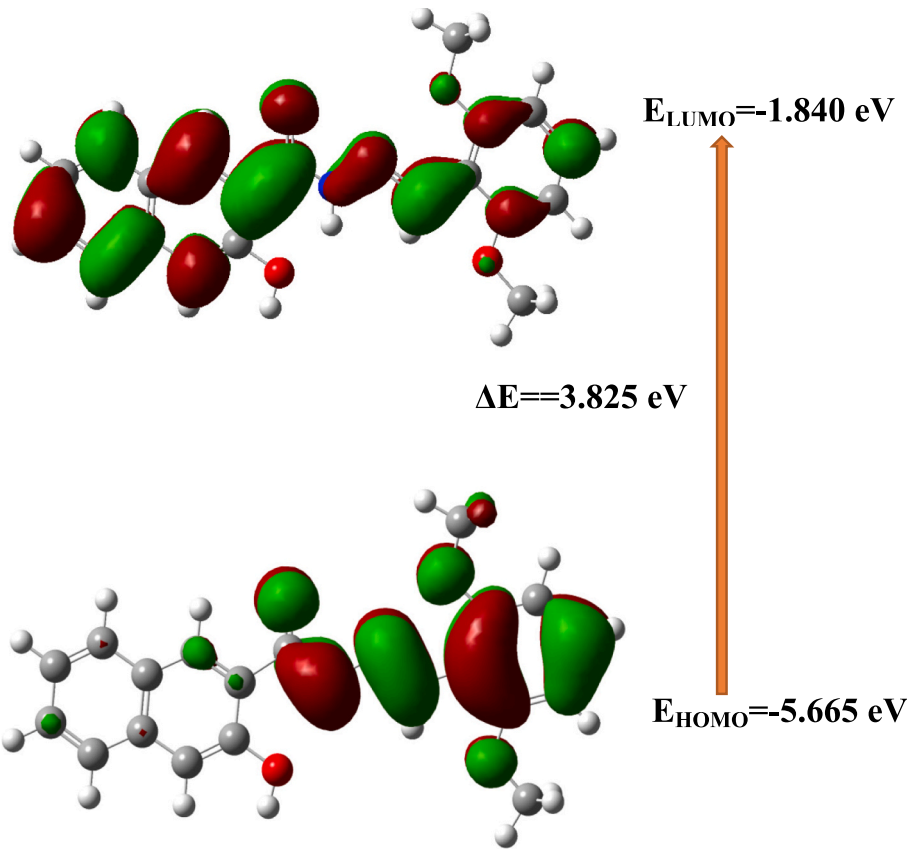


**Fig. 12.** HOMO and LUMO orbitals of the DHN molecule.

configuration produced a beam waist of about 0.00338 cm and a Rayleigh range of approximately 1.69 mm. Since the sample thickness (1 mm cuvette) is significantly smaller than the Rayleigh range ( $Z_0$ ), the experiment satisfies the thin-sample approximation required for reliable Z-scan analysis. The sample was placed on a motorized translation stage, allowing precise movement through the focal region along the Z-axis. Measurements were carried out in two configurations: open-aperture (to study nonlinear absorption by collecting the full transmitted signal) and

**Table 8**

FMO's energies with global reactivity descriptor properties.

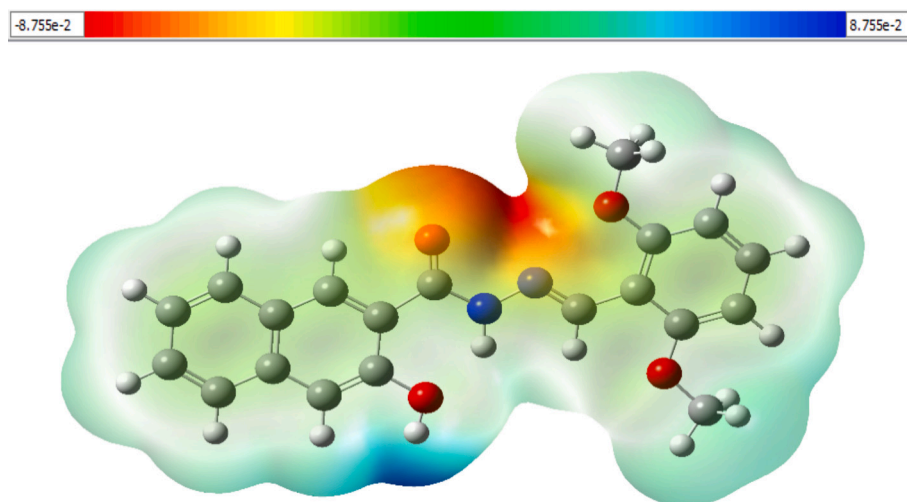
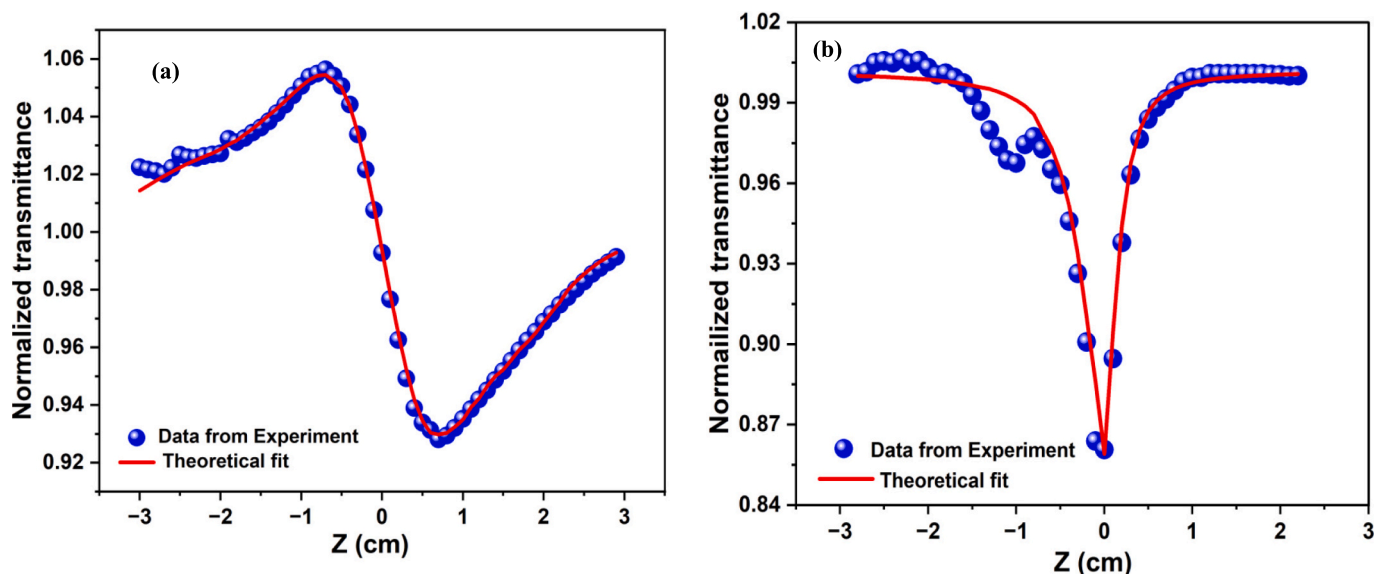
| Properties                    | Symbol and formula                                  | Values |
|-------------------------------|-----------------------------------------------------|--------|
| $E_{\text{HOMO}}$             | $E_{\text{H}}$ (eV)                                 | -5.665 |
| $E_{\text{LUMO}}$             | $E_{\text{L}}$ (eV)                                 | -1.840 |
| $\Delta E_{\text{LUMO-HOMO}}$ | $E_{\text{g}} = E_{\text{L-H}}$ (eV)                | 3.825  |
| Ionization potential (I)      | $I = -E_{\text{HOMO}}$ (eV)                         | 5.665  |
| Electron affinity (A)         | $A = -E_{\text{LUMO}}$ (eV)                         | 1.840  |
| Global Hardness ( $\eta$ )    | $\eta = (E_{\text{LUMO}} - E_{\text{HOMO}})/2$ (eV) | 1.912  |
| Softness (S)                  | $S = 1/2\eta$ (eV) <sup>-1</sup>                    | 0.261  |
| Chemical potential ( $\mu$ )  | $\mu = (E_{\text{LUMO}} + E_{\text{HOMO}})/2$ (eV)  | -3.752 |
| Electronegativity ( $\chi$ )  | $\chi = -\mu$ (eV)                                  | 3.752  |
| Electrophilicity ( $\psi$ )   | $\psi = \mu^2/2\eta$ (eV)                           | 3.681  |

closed-aperture (to evaluate both nonlinear absorption and refraction by partially restricting the transmitted beam). The absorption coefficient ( $\beta$ ) and nonlinear refractive index ( $n_2$ ) were precisely determined by comparing data from these two modes.

In Fig. 14(b), the DHN compound OA Z-scan response showed a distinct symmetric valley centered at the focal position, indicating an intensity-dependent optical absorption phenomenon. This third-order

NLO behaviour of the DHN arises from its extended  $\pi$ -conjugated framework encompassing the naphthohydrazide core and the benzyldene segment, which facilitates efficient delocalization of  $\pi$ -electrons throughout the molecular structure. Moreover, the molecule's donor-acceptor (D-A) interactions are essential for adjusting its nonlinear properties. Specifically, the methoxy substituents on the benzyldene moiety act as potent electron donors, while the carbonyl and hydrazide functional groups serve as strong electron-withdrawing acceptors. This electronic arrangement enables effective ICT upon optical excitation, which leads to a substantial localized thermal response and enhanced nonlinear absorption in the focal region.

As the laser intensity peaks near the focal point, the absorbed energy produces a radial temperature gradient within the compound. Since the refractive index ( $n$ ) depends on temperature ( $\partial n/\partial T$ ), this gradient acts as a thermal lens, giving rise to RSA, where absorption increases with incident intensity which is an important feature for optical limiting [76]. The  $\beta$  was extracted by fitting the OA transmittance curve utilizing the below relation.

**Fig. 13.** MEP surface of DHN molecule.**Fig. 14.** (a) Closed aperture (b) Open aperture Z-scan curves of DHN compound.

$$T_{OA} = \frac{1}{1 + \left( \beta \times L_{eff} \left[ \frac{I_0}{1+x^2} \right] \right)} \quad (13)$$

where  $I_0$ ,  $L_{eff}$  and  $X = Z/Z_0$  are the intensity at the focal point, effective length and, the normalized position respectively. From the best-fit curve, the  $\beta$  was found to be  $0.0265 \times 10^{-4} \text{ cm/W}$ .

The CA Z-scan profile exhibited the characteristic peak–valley configuration (see Fig. 14(a)), confirming a negative nonlinear refractive index [3]. This effect arises from the formation of a thermal lens, generated by the radial temperature gradient within the compound when the laser intensity is highest at the focus. The temperature-dependent refractive index ( $\partial n/\partial T$ ) causes the illuminated region to act as a divergent lens, defocusing the transmitted beam [76]. The strong self-defocusing (negative nonlinear refractive index) observed in DHN can be directly linked to its molecular structure [77]. Effective delocalization of  $\pi$ -electrons is facilitated by the extended  $\pi$ -conjugated system that spans the naphthohydrazide core and benzylidene unit, thereby increasing absorption and local heating. The DHN molecule's donor–acceptor configuration promotes intramolecular charge transfer, with carbonyl–hydrazide units acting as electron acceptors and methoxy groups acting as electron donors. The observed nonlinear optical response is a result of this charge redistribution under optical excitation, which also strengthens the thermal gradient and increases energy deposition [78]. The CA data were analyzed using the normalized transmittance relation for a nonlinear sample:

$$T_{CA} = \frac{4x\Delta\varphi}{(1+x^2)(9+x^2)} \quad (14)$$

where  $\Delta\varphi$  representing the phase change along the central axis at the focus, was obtained from the measured transmittance contrast between the peak and valley value ( $\Delta T_{p-v}$ ) using;

$$|\Delta\phi| = \frac{\Delta T_{p-v}}{0.406(1-S)^{0.25}} \quad (15)$$

The nonlinear refractive index ( $n_2$ ) was then determined using below relation.

$$n_2 = \frac{\Delta\varphi}{K I_0 L_{eff}} \text{ (cm}^2/\text{W)} \quad (16)$$

In this expression,  $K = 2\pi/\lambda$  denotes the propagation constant of the laser. For the DHN compound, the  $n_2$  was measured as  $2.032 \times 10^{-7} \text{ cm}^2/\text{W}$ . Using the experimentally obtained  $n_2$  and  $\beta$  values, the corresponding real,  $\chi_R^{(3)}$  and imaginary  $\chi_I^{(3)}$  components of the third-order optical susceptibility were evaluated through the following relationships [75]:

$$\chi_R^{(3)} = \frac{10^{-4}(\epsilon_0 c^2 n_0^2 n_2)}{\pi} \text{ (cm}^2/\text{W)} \quad (17)$$

$$\chi_I^{(3)} = \frac{10^{-2}(\epsilon_0 c^2 n_0^2 \lambda \beta)}{4\pi^2} \text{ (cm/W)} \quad (18)$$

where  $\epsilon_0$  (vacuum permittivity), and  $c$  (velocity of light in free space) are universal constants.  $\lambda$  is the incident wavelength. The total third-order susceptibility was then obtained from below expression.

$$\chi^{(3)} = \sqrt{\left(\chi_R^{(3)}\right)^2 + \left(\chi_I^{(3)}\right)^2} \text{ (esu)} \quad (19)$$

The third-order susceptibility  $\chi^{(3)}$  along with the corresponding nonlinear optical parameters ( $n_2$  and  $\beta$ ), are summarized in Table 9. The  $\chi^{(3)}$  value for the DHN compound was examined in comparison with previously reported schiff base derivatives containing a hydrazide group [45,79–83], measured under continuous-wave 532 nm laser irradiation (see Table 10), highlighting the notable third-order nonlinear behaviour of DHN. Overall, the DHN compound exhibits pronounced nonlinear

absorption and self-defocusing, demonstrating its potential for photonic applications, including optical limiting, signal modulation, and laser protection.

### 3.9.2. Optical limiting study

Materials that can prevent potential damage to optical components under high-intensity illumination are desperately needed as lasers are incorporated into photonic devices more frequently. Optical limiters provide this protection by attenuating transmitted light once the incident intensity exceeds a specific threshold. Material that exhibits RSA is particularly effective, as their absorption increases with light intensity, rendering them promising candidates for signal modulation and photonic protection.

In this study, the DHN Schiff base compound, (*E*)-N'-(2,6-dimethoxybenzylidene)-3-hydroxy-2-naphthohydrazide, was evaluated for its optical limiting properties using open-aperture Z-scan measurements under continuous-wave (CW) laser excitation at 532 nm. The OA Z-scan of DHN revealed a clear reduction in transmitted intensity at the center of the focused beam, indicative of pronounced intensity-dependent absorption [12]. Continuous irradiation generates localized heating within the compound, further enhancing absorption and reducing the transmitted signal [75]. The conjugated molecular framework, along with electron-donating and electron-accepting regions, facilitates intramolecular charge redistribution, promoting efficient energy deposition and amplifying the nonlinear optical response. This RSA behaviour under CW excitation is highly effective for optical limiting [3]. To quantify the variation of intensity along the beam propagation axis, the position-dependent intensity,  $I(z)$ , was calculated using the following relation:

$$I(z) = 4\sqrt{\ln 2} \left( \frac{E_{in}}{\pi^2 \omega(z)^2} \right) \quad (20)$$

In this expression,  $\omega(z) = \omega_0 [1 + (z/z_0)^2]$  represents the radius of the Gaussian beam at a distance  $z$  from the focal point, where  $\omega_0$  represents the beam waist and  $Z_0$  corresponds to the Rayleigh range. Fig. 15 shows the intensity-dependent transmission curve of the DHN compound derived from OA Z-scan measurements. The OL threshold of DHN compound was determined to be  $3.65 \times 10^3 \text{ W/cm}^2$ . This value is in good agreement with reported thresholds for other Schiff-base derivatives and  $\pi$ -conjugated organic compounds under CW conditions. For example, similar studies reported threshold values of  $2.511 \times 10^3 \text{ W/cm}^2$  for CDA [23],  $3.437 \times 10^3 \text{ W/cm}^2$  for BCA [84],  $3.44 \times 10^3 \text{ W/cm}^2$  for 4MPB [85] and  $1.91 \times 10^3 \text{ W/cm}^2$  for CPDAPP [86], indicating that DHN exhibits a competitive OL performance. The combination of strong RSA and the molecule's extended  $\pi$ -conjugation with D–A functionalities confirm the DHN Schiff base as a promising candidate for optical limiting applications, such as protecting sensitive photodetectors and optical sensors from high-intensity laser irradiation.

### 3.9.3. Computational nonlinear optical (NLO) studies

Computational nonlinear optical (NLO) studies were performed using the GAMESS software [22] to elucidate the electronic origins of

**Table 9**  
Third-order nonlinear optical parameters of DHN.

| Parameters                                                                           | Values                                       |
|--------------------------------------------------------------------------------------|----------------------------------------------|
| Nonlinear refractive index ( $n_2$ )                                                 | $2.032 \times 10^{-7} \text{ cm}^2/\text{W}$ |
| Nonlinear absorption coefficient ( $\beta$ )                                         | $0.0265 \times 10^{-4} \text{ cm/W}$         |
| Real part of third-order nonlinear optical susceptibility (Re ( $\chi^{(3)}$ ))      | $6.695 \times 10^{-6} \text{ esu}$           |
| Imaginary part of third-order nonlinear optical susceptibility (Im ( $\chi^{(3)}$ )) | $3.692 \times 10^{-8} \text{ esu}$           |
| Third-order nonlinear optical susceptibility ( $\chi^{(3)}$ )                        | $6.689 \times 10^{-6} \text{ esu}$           |

**Table 10**  
Comparison of  $\chi^{(3)}$  values of DHN with reported nonlinear optical materials.

| Molecules | Third order susceptibility ( $\chi^{(3)}$ ) | References   |
|-----------|---------------------------------------------|--------------|
| DHN       | $6.689 \times 10^{-6}$ esu                  | Present work |
| 4HBI      | $1.918 \times 10^{-8}$ esu                  | [79]         |
| DMBH      | $4.900 \times 10^{-6}$ esu                  | [80]         |
| 4CBTCA    | $1.357 \times 10^{-6}$ esu                  | [45]         |
| AMP4N     | $2.48 \times 10^{-8}$ esu                   | [81]         |
| VMST      | $9.69 \times 10^{-12}$ esu                  | [82]         |
| AAP       | $6.20 \times 10^{-9}$ esu                   | [83]         |

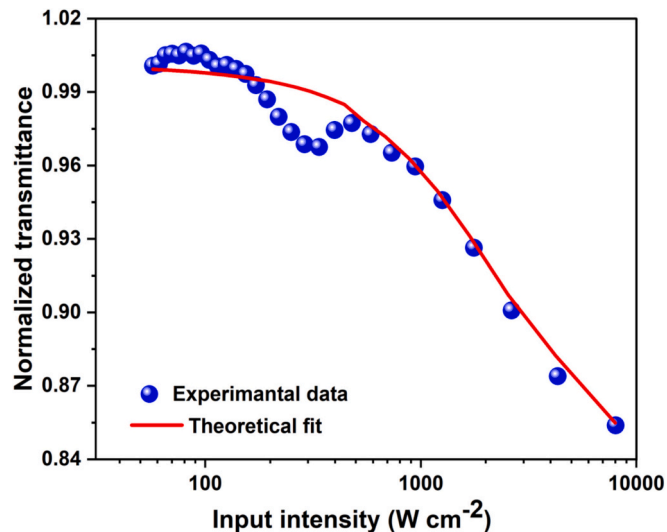


Fig. 15. Optical limiting pattern of DHN compound.

the NLO behaviour of the DHN molecule. The TDHF approach was employed to evaluate the frequency-dependent electronic response, including diffuse and polarization functions to accurately capture charge redistribution within the  $\pi$ -extended donor–acceptor framework. Calculations were conducted at incident field frequencies  $\omega = 0$ , 0.04282, 0.05695, and 0.08564 a.u., corresponding to static conditions and laser wavelengths of 1064 nm (Nd:YAG fundamental), 800 nm (Ti: Sapphire), and 532 nm (second harmonic of 1064 nm), respectively. These frequencies were selected because they correspond to commonly used experimental laser sources in nonlinear optical studies. From these simulations, the polarizability ( $\alpha$ ), first hyperpolarizability ( $\beta$ ), and second hyperpolarizability ( $\gamma$ ) were determined (Tables 11–13). The variation of these parameters with frequency highlights the electronic transitions responsible for enhancing the NLO response and demonstrates the effect of near-resonant excitation on the molecular electronic distribution.

**Table 11**  
Dipole moment, static and dynamic polarizability by TDHF at 6–311++G(d, p) of DHN.

| Dipole moment ( $\mu$ ) |                   | Polarizability ( $\alpha$ )                 |              |                                                |                                               |                                               |
|-------------------------|-------------------|---------------------------------------------|--------------|------------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Components              | Values<br>(Debye) | Components                                  | $\omega = 0$ | $\omega = 0.04282$ a.u.<br>$\lambda = 1064$ nm | $\omega = 0.05695$ a.u.<br>$\lambda = 800$ nm | $\omega = 0.08564$ a.u.<br>$\lambda = 532$ nm |
| $\mu_x$                 | 3.466             | $\alpha_{xx}$                               | 390.79       | 400.14                                         | 407.83                                        | 433.11                                        |
| $\mu_y$                 | −2.134            | $\alpha_{xy}$                               | 11.96        | 12.64                                          | 13.21                                         | 15.15                                         |
| $\mu_z$                 | −0.700            | $\alpha_{yy}$                               | 238.84       | 241.82                                         | 244.26                                        | 252.14                                        |
| $\mu_{\text{total}}$    | 4.130             | $\alpha_{xz}$                               | 15.03        | 15.48                                          | 15.85                                         | 17.07                                         |
|                         |                   | $\alpha_{yz}$                               | −8.30        | −8.53                                          | −8.72                                         | −9.42                                         |
|                         |                   | $\alpha_{zz}$                               | 104.49       | 105.03                                         | 105.47                                        | 106.85                                        |
|                         |                   | $\alpha_{\text{total}}$ a.u.                | 244.71       | 249.03                                         | 252.52                                        | 264.04                                        |
|                         |                   | $\alpha_{\text{total}} \times 10^{-23}$ esu | 3.67         | 3.73                                           | 3.78                                          | 3.96                                          |
|                         |                   | $\Delta\alpha$ a.u.                         | 617.19       | 628.50                                         | 637.80                                        | 668.26                                        |
|                         |                   | $\Delta\alpha \times 10^{-23}$ esu          | 9.25         | 9.42                                           | 9.56                                          | 10.02                                         |

The DHN molecule exhibits a pronounced dipole moment predominantly along the donor–acceptor axis, indicating effective ICT. The total dipole moment is calculated to be 4.13 Debye, with the x-component contributing  $\mu_x = 3.47$  Debye, reflecting the primary direction of electronic polarization within the conjugated framework. The isotropic polarizability ( $\langle\alpha\rangle$ ) was computed as 244.71 a.u. ( $3.67 \times 10^{-23}$  esu) in the static regime and showed a gradual increase with frequency, increasing from  $3.67 \times 10^{-23}$  esu at 1064 nm to  $3.96 \times 10^{-23}$  esu at 532 nm. This frequency dependence arises from the contribution of low-lying electronic excited states, which significantly affect the linear and higher-order nonlinear optical responses [87]. Additionally, the molecule demonstrates a significant anisotropy in polarizability ( $\Delta\alpha = 617$  to 668 a.u.), suggesting that the electron density is more susceptible to distortion along specific molecular directions. It is consistent with the nearly planar, conjugated geometry that was crystallographically determined. Extended  $\pi$ -delocalization promotes directional polarization, thereby enhancing the molecule's nonlinear optical (NLO) properties [88].

The first-order hyperpolarizability ( $\beta_{\text{tot}}$ ) of the DHN molecule shows a pronounced dependence on the excitation frequency, highlighting its strong nonlinear optical (NLO) activity. The reported dynamic  $\beta$  values correspond to the second-harmonic generation (SHG) response,  $\beta(-2\omega; \omega, \omega)$ , within the TDHF formalism. In the static regime,  $\beta_{\text{tot}}$  is calculated to be 308.85 a.u. ( $2.66 \times 10^{-30}$  esu). Under dynamic conditions,  $\beta_{\text{tot}}$  increased dramatically, from  $3.02 \times 10^{-30}$  esu at 1064 nm to  $682.94 \times 10^{-30}$  esu at 532 nm. This substantial enhancement at shorter wavelengths originates from near-resonance effects, as the second-harmonic frequency ( $2\omega$ ) approaches low-lying electronic transitions [89]. At  $\omega = 0.08564$  a.u.,  $2\omega$  corresponds to  $\sim 260$  nm, which lies close to the

**Table 12**  
The static and dynamic first-order hyperpolarizability by TDHF/6–311++G(d, p) level.

| Components                               | $\omega = 0$ | $\omega = 0.04282$ a.u.<br>$\lambda = 1064$ nm | $\omega = 0.05695$ a.u.<br>$\lambda = 800$ nm | $\omega = 0.08564$ a.u.<br>$\lambda = 532$ nm |
|------------------------------------------|--------------|------------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| $\beta_{xxx}$                            | −151.61      | −198.75                                        | −257.79                                       | −36,167.50                                    |
| $\beta_{xyy}$                            | 29.15        | 38.97                                          | 53.95                                         | 13,338.91                                     |
| $\beta_{xzz}$                            | −26.95       | −28.33                                         | −30.33                                        | 257.01                                        |
| $\beta_{yyy}$                            | −37.40       | −58.72                                         | −93.39                                        | −43,103.40                                    |
| $\beta_{yzz}$                            | −26.73       | −29.83                                         | −33.42                                        | −1167.94                                      |
| $\beta_{yxx}$                            | −204.15      | −206.35                                        | −168.82                                       | 115,740.1                                     |
| $\beta_{zzz}$                            | 5.43         | 6.50                                           | 7.68                                          | 397.489                                       |
| $\beta_{zxx}$                            | 15.15        | −12.82                                         | −58.89                                        | −40,541.30                                    |
| $\beta_{zyy}$                            | 12.34        | 22.93                                          | 39.70                                         | 15,026.34                                     |
| $\beta_x$                                | −149.41      | −188.12                                        | −234.17                                       | −22,571.56                                    |
| $\beta_y$                                | −268.29      | −294.91                                        | −69.77                                        | 71,468.80                                     |
| $\beta_z$                                | 32.94        | 16.60                                          | −11.50                                        | −25,117.51                                    |
| $\beta_{\text{tot}}$ a.u.                | 308.85       | 350.20                                         | 2446.17                                       | 79,045.27                                     |
| $\beta_{\text{tot}} \times 10^{-30}$ esu | 2.66         | 3.02                                           | 21.134                                        | 682.94                                        |

**Table 13**

The static second hyperpolarizability  $\gamma(0;0,0,0)$  and frequency-dependent second hyperpolarizability  $\gamma(-3\omega;\omega, \omega, \omega)$  at 6-311G++(d, p) method (TDHF).

| Components                   | $\omega = 0$ | $\omega = 0.08564$ a.u.<br>( $\lambda = 532$ nm) | $\omega = 0.05695$ a.u.<br>( $\lambda = 800$ nm) | $\omega = 0.08564$ a.u.<br>$\lambda = 532$ nm |
|------------------------------|--------------|--------------------------------------------------|--------------------------------------------------|-----------------------------------------------|
| $\gamma_{xxxx}$              | 230,705.70   | 480,960.70                                       | 1,279,927                                        | 6.9E+07                                       |
| $\gamma_{yyyy}$              | 14,453.87    | 25,434.82                                        | -8275.57                                         | -2E+07                                        |
| $\gamma_{zzzz}$              | 774.41       | 934.59                                           | 1147.95                                          | 22,141                                        |
| $\gamma_{xxyy}$              | 13,927.84    | 25,013.73                                        | 79,069.43                                        | 8,670,274                                     |
| $\gamma_{xxzz}$              | 2635.51      | 4216.94                                          | 8918.61                                          | 986,813                                       |
| $\gamma_{yyzz}$              | 1337.19      | 2082.16                                          | 1138.90                                          | 1,091,904                                     |
| $\gamma$ a.u.                | 56,347.00    | 113,991.16                                       | 290,210.72                                       | 15,287,038.77                                 |
| $\gamma \times 10^{-36}$ esu | 28.39        | 57.45                                            | 146.26                                           | 7704.66                                       |

electronic excitation energies of the molecule. Consequently, the large  $\beta_{tot}$  value at this frequency arises from near-resonance enhancement rather than representing an off-resonant nonlinear optical response [90]. HF-based approaches are known to underestimate first hyperpolarizabilities due to the absence of electron correlation [91]. However, the present analysis focuses on the relative trends and frequency-dependent behaviour of  $\beta$ , which are reasonably captured within the TDHF framework. TDHF provides a consistent, functional-independent description of excitation energies, which is particularly important for the present donor-acceptor system where the response is governed by a charge-transfer transition. Tensorial analysis shows that the dominant component of  $\beta$  is oriented along the donor-acceptor (D-A) axis, consistent with the  $\pi$ -conjugated framework that facilitates efficient intramolecular charge transfer between electron-donating and electron-accepting groups [92].

The second-order hyperpolarizability ( $\gamma$ ) is strongly influenced by the extended  $\pi$ -electron delocalization, the molecular architecture, and the electronic effects of substituents. In DHN, the conjugated framework connecting the dimethoxybenzylidene and naphthohydrazide units enables efficient intramolecular charge redistribution, which significantly enhances the overall NLO response, as evidenced by both static and dynamic hyperpolarizability values [93]. The computed  $\gamma(0;0,0,0)$  value is  $28.39 \times 10^{-36}$  esu, while the dynamic  $\gamma(-3\omega; \omega, \omega, \omega)$  values at 0.04282, 0.05695, and 0.08564 a.u. were calculated as  $57.45 \times 10^{-36}$  esu,  $146.26 \times 10^{-36}$  esu, and  $7704.66 \times 10^{-36}$  esu respectively. Altogether, these findings suggest that DHN combines large first and second-order hyperpolarizabilities, high polarizability anisotropy, and strong dipolar alignment. The frequency-dependent enhancement of  $\beta$  and  $\gamma$  demonstrates the important role of intramolecular charge transfer in enhancing the nonlinear optical response. These characteristics position DHN as a viable option for cutting-edge optoelectronic and photonic applications.

### 3.10. Structure-property relationship

The third-order NLO response observed for the DHN molecule can be directly correlated to its extended  $\pi$ -conjugated system and donor-acceptor molecular architecture, as well as its electronic structure. In DHN, the 2,6-dimethoxybenzylidene moiety serves as an electron-donating group, while the hydrazide linkage ( $-\text{CO}-\text{NH}-\text{NH}-$ ) and hydroxyl group ( $-\text{OH}$ ) act as electron-accepting centers, resulting in a D- $\pi$ -A- $\pi$ -A type configuration. Frontier molecular orbital (FMO) analysis demonstrates that this configuration promotes intramolecular charge transfer (ICT) along the conjugated backbone upon optical excitation, with HOMO electron density primarily localized on the donor sites and LUMO density shifted toward the acceptor groups. The extended  $\pi$ -electron system with strong delocalization provided by the naphthalene ring reduces the energy gap and increases the molecular hyperpolarizability ( $\beta$ ). The conjugated framework's planarity, which

has been verified through SCXRD analysis, guarantees productive  $\pi$ - $\pi$  stacking interactions within the crystal lattice. This, in turn, facilitates charge delocalization and nonlinear polarization in the presence of external optical fields. Consequently, the DHN compound exhibits NLO activity throughout the molecule, as evidenced by both experimental and computational analyses. Therefore, Z-scan studies have demonstrated that the DHN compound demonstrates a significant degree of self-defocusing and RSA behaviour when subjected to continuous-wave laser excitation. Ultimately, these findings show that the molecular design that includes  $\pi$ -conjugation, donor-acceptor substitution, and crystal packing is essential for figuring out the third-order NLO characteristics of DHN, which are helpful in optoelectronics applications.

## 4. Conclusion

In summary, hydrazide-based Schiff-base chromophore (DHN) was successfully synthesized via a reflux method and comprehensively characterized for its structural, optical, thermal, and nonlinear optical properties. Optical measurements showed high transparency ( $\sim 99\%$ ) across the visible region with the onset of absorption occurring at 425 nm and Tauc plot analysis revealed a direct electronic band gap of 3.15 eV. PL measurements revealed intense blue emission, corroborated by CIE chromaticity coordinates, demonstrating its suitability for blue light-emitting applications. Thermogravimetric (TG) analysis revealed that the material exhibits good thermal stability up to 222.54 °C. Solvatochromic analysis unveiled pronounced solvent-dependent ICT effects, with DMSO producing the highest  $\alpha_{CT}$ ,  $\beta_{CT}$ , and  $\gamma_{CT}$  values of  $7.16 \times 10^{-24}$ ,  $8.28 \times 10^{-28}$ , and  $8.51 \times 10^{-32}$  esu, respectively. Computational investigations using TD-DFT calculations predicted an absorption maximum at 352 nm, in close agreement with the experimental observations (340 nm), while the analysis of FMO revealed an energy separation of 3.825 eV between the HOMO and LUMO, along with a global hardness value of 2.074 eV, indicating that the compound possesses appreciable electronic stability and moderate chemical reactivity. Third-order NLO studies demonstrated that the DHN compound exhibits pronounced RSA and self-defocusing behaviour with a high third-order susceptibility ( $6.689 \times 10^{-6}$  esu) and OL threshold ( $3.65 \times 10^3$  W  $\text{cm}^{-2}$ ), establishing DHN as a highly promising candidate for advanced NLO and photonic applications. Collectively, these findings position DHN as a versatile, solvent-tunable chromophore with strong third-order nonlinear optical performance, offering promising opportunities for advanced photonic, optoelectronic, and optical-limiting device applications.

### CRedit authorship contribution statement

**Keerthikumara Venkatesha:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Mahendra Madegowda:** Writing – review & editing, Visualization, Supervision, Resources, Investigation, Formal analysis, Data curation, Conceptualization.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2026.129544>.

## Data availability

Data will be made available on request.

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