Potential Third-Order Nonlinear Optical Response Facilitated by Intramolecular Charge Transfer in a Simple Schiff Base Molecule: Experimental and Theoretical Exploration

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ABSTRACT: A Schiff base, namely, 4-[2-hydroxy-3-methoxybenzylidene] amino] benzoic acid (L1), has been synthesized by the condensation reaction. It has been characterized by Fourier transform infrared spectroscopy, UV−vis spectroscopy, single-crystal X-ray diffraction, and DFT/B3LYP calculations. Single-crystal X-ray crystallographic analysis revealed that L1 exists in the zwitterionic (N−H−...O) form. The supramolecular interactions were investigated by Hirshfeld surface analysis. In addition, third-order nonlinear optical (NLO) properties of L1 were also investigated. The nonlinear refractive index (n2), nonlinear absorption coefficient (β), and the third-order NLO susceptibility (χ(3)) have been estimated at different concentrations and at different laser powers using close and openaperture Z-scan data. The values of the parameters were found to be varying almost linearly with concentration and power. The present study revealed the utility of the material for various optoelectronic devices such as optical switches, optical data storage devices, and optical sensors. The optical limiting study reveals that this material can also be exploited as an instrument protector from unwanted laser illumination. Furthermore, the NLO behavior of L1 has also been studied by B3LYP/6-311++G(d,p) results.

1. INTRODUCTION

Over the last few years, the organic materials for third-order nonlinear optical (NLO) response have occupied a pivotal place due to their potential uses in the fabrication of photonic devices such as self-focusing, high-speed information processing, power limiters, optical switches, and optical data storage. Several organic, inorganic, and semiorganic materials having NLO properties have been successfully designed and developed. The NLO crystals having a low dielectric constant and high optical band gap are in great demand for spectroscopy, imaging, storage devices, optical communication systems, and so forth. Over the wide range of organic crystals, particularly, molecules based on the Schiff base hold special interest toward the development of photonic and optoelectronic devices. This is due to the presence of π-conjugated bonds and the azomethine bridge of the −C═N− bond that boost the nonlinearity response.

In general, o-hydroxy Schiff bases exist in the enol−imine (OH) and the keto−amine (NH) tautomeric forms with two possible types of intramolecular H-bonding interactions: O−H−...N in enol−imine and N−H−...O in keto−amine tautomers. However, an additional form of intramolecular H-bonding is also observed as N+-H−...O−, which is called the zwitterionic form. Based on literature survey, it is known to us that various organic single crystals such as chalcone derivative, potassium dichromate, and Schiff base molecules are reported for third-order NLO response.
above mentioned characteristics of materials excited us to design a simple and new Schiff base molecule (Scheme 1), which could exhibit enhanced third-order NLO response. It is also noteworthy that there is no report available on the present molecule for a NLO study. We also explored the experimental measured values of the nonlinear refractive index (n₂), nonlinear absorption coefficient (β), and third-order optical susceptibility, χ(3), using the Z-scan technique with a CW diode laser. Moreover, experimental results obtained were also theoretically corroborated. The density functional theory (DFT) plays an important role in describing the NLO potential of the molecules. The high value of the first- and second-order hyperpolarizabilities reveals high NLO potential because of intramolecular charge transfer (ICT) mediated through the π-conjugated framework. Therefore, the NLO parameters (static and dynamic) have been computed in the solution phase to study the NLO behavior of L1.

2. RESULTS AND DISCUSSION

2.1. UV−Vis Spectroscopic Study of the Schiff Base Molecule. Electronic absorption spectrum of L1 shows a broad band at 310 nm, which indicates the involvement of π→π* transitions (Figure 1).21 It may have appeared due to the presence of aromatic rings and the (−C=N−) bond in L1. There is another broad and unresolved absorption band at 470 nm that corresponds to n→π* transitions. The concentration-dependent spectra have also been recorded, which show the stability of L1. A slight red shift of absorption bands could be attributed to the proton transfer occurring in L1 (Figure S1).22

2.2. Crystal Structure Description. L1 crystallizes in the orthorhombic system (P2₁2₁2₁), and its asymmetric unit contains a Schiff base unit in the zwitterionic form and a methanol in the lattice. Interestingly, the hydroxyl group of methoxybenzaldehyde is deprotonated to the imine group, forming an intramolecular (imine) N−H⋯O (methoxybenzaldehyde) H-bonding network with graph-set notation S(6). Moreover, herringbone fashion of packing is seen along the b-axis, and the most obvious H-bonding chain pattern involved in crystal packing is formed by methanol, connecting each Schiff base. The chain extends along the c-axis and is designated by the graph set C₂²(16). On the other hand, lattice methanol also interacts with the deprotonated hydroxyl group of L1, forming a ring pattern of R₁²(5) with the O−H⋯O bond. Furthermore, each Schiff base unit is connected to the adjacent unit via C−H⋯O and C−H⋯π interactions, and the ring patterns involved are shown in Figure 1c. Ring patterns and chains involving intricate arrays of noncovalent interactions result in 3D supramolecular architecture (Figure 2a−c).

Furthermore, we employed the graph-theory approach23 to understand the role of all intermolecular contacts in molecular packing. Therefore, in L1, both the Schiff base and methanol molecules can be considered as a building unit of the crystal. However, simplification shows each Schiff base molecule touches 12 other Schiff base molecules and 6 methanol molecules, while each methanol molecule touches 8 other
Schiﬀ base molecules and only 2 methanol molecules, resulting in the 3D framework structure (Figure 3).

2.3. Hirshfeld Surface Analysis. Hirshfeld surface analysis gives both qualitative and quantitative molecular interactions. The Hirshfeld surface of L1 is mapped over $d_{\text{norm}}$ (normalize contact distance) in the range of −0.751 to 1.207 as shown in Figure S2. The deep-red spots indicate classical hydrogen bonding and other short contacts of the neighboring molecule. Hirshfeld surface analysis mapped over curvedness in the color range of −4.0 to 0.40. The curvedness plot of L1 shows the flat green surface on the front and back side of the molecule, which evidences the presence of $\pi$-interactions. At the edges, blue color shows the positive curvedness on the surface of L1 (Figure S3).

Furthermore, Hirshfeld surface analysis of L1 is mapped over the shape index in the color range −1.0 to 1.0. The shape index quantifies the shape of the molecule in terms of principal curvatures $\kappa_1$ and $\kappa_2$. The shape index clearly shows the triangular red and blue regions, which are characteristics of $\pi\cdots\pi$ and C−H⋯$\pi$ interactions (Figure S4).

The two-dimensional fingerprint plots are given in Figure 4a−g; it is evident from the Hirshfeld surface analysis that hydrogen−hydrogen contacts predominate, contributing 42.3% of overall interactions (Figure 4b). Interestingly, O−H/H−O interactions contributing 31.1% attribute to O−H⋯O and C−H⋯O contact that appeared as two sharp symmetrical spikes in Figure 4c of the fingerprint plot. It is followed by C−H/H−C interactions with 15.2% corresponding to C−H⋯$\pi$ contacts showing two broad symmetrical wings (Figure 4d). Moreover, C−C interactions with 7.1% correspond to the $\pi\cdots\pi$ interactions that appeared in the middle of the fingerprint plot (Figure 4e). Other minor interactions contributing 4.1% of the total Hirshfeld surface interactions correspond to C−N/N−C (2.2%), C−O/O−C (1.7%), and so forth (Figure 4f−g).

2.4. Third-Order Nonlinear Optical Measurements. The nonlinear refraction and absorption of L1 have been estimated by recording the closed aperture (CA) and open aperture (OA) Z-scan data, keeping laser power fixed at 42 mW for different concentrations (2.5−10 mM) as well as for

Figure 3. Packing diagram of L1. Brown and light-blue spheres correspond to the Schiff base and methanol molecular centroids, respectively.

Figure 4. Two-dimensional fingerprint plots for L1. $d_{\text{norm}}$ surfaces for each plot, indicating the specific patches corresponding to the percentage of specific contacts, which are shown on the right side- (a) all interactions, (b) H⋯H, (c) O−H/H−O, (d) C−H/H−C, (e) C⋯C, (f) C−N/N−C, and (g) C−O/O−C.
various laser power (30−50 mW) at a fixed concentration of 7.5 mM. The intensity-dependent nonlinear refraction and absorption are related to the following equations:29,30

\[ \alpha(I) = \alpha + \beta_{\text{eff}} I \]  
\[ n(I) = n_0 + n_2 I \]

where \( \alpha \) is the linear absorption coefficient, \( n_0 \) is the linear refractive index, and \( \beta_{\text{eff}} \) and \( n_2 \) are the nonlinear absorption coefficient and refractive index respectively. \( I \) is the intensity of the input laser beam.

The nonlinear refractive index \( (n_2) \) is related to the following relation

\[ |\Delta \Phi| = k n_2 L_{\text{eff}} I_0 \]

where \( |\Delta \Phi| \) is the on-axis phase shift and it is expressed as

\[ \Delta T_{P,V} = 0.406 (1 - S)^{0.25} |\Delta \Phi| \]

The quantity \( \Delta T_{P,V} \) is measurable and is defined as the difference in the peak valley-normalized transmittance, and \( k = 2\pi/\lambda \) is the wave number with laser wavelength \( (\lambda) \); \( L_{\text{eff}} = 1 - \exp(-\alpha L) / \alpha \) defines the effective thickness of the sample, \( \alpha \) is linear absorption coefficient, \( L \) is the actual thickness of the sample, and \( S \) is the linear aperture transmittance. \( I_0 \) is the on-axis irradiance at the focus with \( I_0 = 2P/\pi \omega_0^2 \).

We can obtain the nonlinear refractive index \( (n_2) \) by fitting the normalized transmittance curve with the following equation:31

\[ T(\text{close}) = 1 + \frac{2(-\rho x^2 + 2x - 3\rho)}{(x^2 + 9)(x^2 + 1)} \Delta \Phi_0 \]

where \( \rho = \Delta \Psi/\Delta \Phi_0 \), \( \Delta \Phi_0 \) and \( \Delta \Psi \) are the phase shift due to nonlinear refraction and nonlinear absorption, respectively, and \( \Delta \Psi = \beta_{\text{eff}} L_{\text{eff}} / 2 \) and \( x = Z/Z_R \) are related to the diffraction length of the beam \( (Z_R) \) and position of the sample \( (Z) \). The third-order NLO susceptibility of the materials is described as

\[ \chi^{(3)} = \chi_R^{(3)} + i \chi_I^{(3)} \]

Real \( (\chi_R^{(3)}) \) and imaginary parts \( (\chi_I^{(3)}) \) of third-order susceptibility \( (\chi^{(3)}) \) are related to the nonlinear refraction \( (n_2) \) and nonlinear absorption \( (\beta) \), respectively, which are expressed as

\[ \chi_R^{(3)} = 10^{-4} \varepsilon_0 n_0^2 n_2^2 (\text{cm}^2 / \text{W}) \]
\[ \chi_I^{(3)} = 10^{-4} \varepsilon_0 n_0^2 n_2^2 \beta (\text{cm} / \text{W}) \]

where \( \varepsilon_0 \) is the permittivity of free space, \( c \) is the speed of light in vacuum, and \( n_0 \) is linear refractive index of the sample. The absolute value of third-order susceptibility is calculated as

\[ |\chi^{(3)}| = \sqrt{(\chi_R^{(3)})^2 + (\chi_I^{(3)})^2} \]

Figures 5a,b and 6a,b show, respectively, the closed aperture (CA) and open aperture (OA) normalized transmittance with the sample position for different concentrations and different powers at 520 nm. The dots represent experimental Z-scan data, whereas the solid lines represent the least square fitting (theoretical fitting). The CA normalized transmittance of L1 shows a peak-valley configuration and is induced due to the self-defocusing nature of the sample, which is an indication of the negative nonlinear refractive index \( (n_2 < 0) \).33 This self-defocusing characteristic may be the effect of thermal nonlinearity of the sample which occurs due to the heat released, resulting from the absorption of laser radiation, and consequently, the temperature-dependent refractive index is produced in the sample and it behaves like a thermal lens.
However, the OA normalized transmittance reveals the symmetric peak near the focus, suggesting the saturable absorption (SA) nature of the sample, which is the signature of negative nonlinear absorption, ($\beta < 0$), in the crystal. It is also observed in Figure 6a,b that there is a slight dip on either side of the peak, indicating the involvement of reverse saturable absorption (RSA), but saturable absorption (SA) dominates, and earlier, it was also reported by several researchers. These SA and RSA behaviors can be explained by the five energy level model of the molecules, where SA and RSA may be attributed to the two photon absorption (TPA) and the excited-state absorption (ESA), respectively. Hence, the nonlinear absorption of L1 confirms the multi-photon absorption with ESA and TPA. The calculated NLO parameters ($n_2, \beta$, and $\chi^{(3)}$) are given in Tables 1 and 2 for different concentrations and different powers, respectively. The values of these parameters for L1 are found to be comparable with those of the earlier reported Schiff base molecules, as listed in Table 3. The comparative analysis evidences the good NLO performance of L1 over other reported molecules.

The variation in $n_2$ and $\beta$ with concentration and power has been shown in Figure 7a,b. These figures reveal that the absolute values of $n_2$ and $\beta$ increase linearly with concentration and laser power. This implies that as the concentration increases, the number of molecules increases to participate in laser interaction. Hence, the number of molecules gets thermally agitated, and consequently, the thermal nonlinearity increases. Also, as the laser power increases, the thermal nonlinearity of the sample gets enhanced with laser power.

The optical limiting behavior of the present crystal represented in Figure 8a shows the variation of transmitted power as a function of input power at various concentrations. This demonstrates that for lower input power up to limiting threshold power, the transmitted power linearly increases, and at higher input power, it becomes saturated. After a further increase in input power, the transmitted power decreases, which is the characteristic nature of the good optical limiter. The optical limiting behavior in the crystal may be produced through several mechanisms such as RSA, multiphoton absorption, ESA, free carrier absorption, nonlinear scattering, photorefraction, and so forth. The measured optical limiting parameters of L1 are given in Table 4. The limiting threshold power and the saturated transmitted power decrease with concentration, as shown in Figure 8b. This implies that at higher concentration, the limiting threshold becomes low due to high nonlinear absorption of the sample results for high optical nonlinearity.

2.5. DFT Calculation Results. 2.5.1. Optimized Geometry and IR Spectrum. The optimized geometry was obtained with a self-consistent field energy of $-586,932,8369$ kcal/mol at B3LYP/6-311++G(d,p) level of theory. Some important theoretical geometrical parameters (bond length, bond angle, and dihedral angle) are compared with the X-ray diffraction (XRD) data (Table S1), and the optimized structure is shown in Figure S5. The optimized structural parameters have reproduced the XRD data very well. The dihedral angles reveal that for both rings, their linkage C−NH−C and COOH are in the same plane. Both XRD and optimized geometries have been also compared globally by atom-by-atom superposition, and the root-mean-square deviation is found to be 0.1946 Å (Figure 9). The discrepancies derived may be due to different phases and limitation of model calculations.

The simulated and experimental IR spectra were well corroborated. Some important IR bands have been assigned with great accuracy by visualization of atom displacements, as shown in Figure S7. The wavenumber of bands appearing in the FTIR are found in good agreement with the corresponding theoretically scaled wavenumbers. The frequencies of corresponding vibrations are also in accordance with those reported in the literature.

2.5.2. Electronic Spectra and Highest Occupied Molecular Orbital–Lowest Unoccupied Molecular Orbital Analysis. The UV–Vis absorption of L1 is analyzed at the TD-B3LYP/6-311++G level of theory. The experimental spectrum shows one band at 310 nm with high absorbance, while another broad peak at 470 nm with very low absorbance. These bands could be attributed to the electronic transitions from $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively. The electronic spectra simulated in gaseous and solvent phases are found in good agreement with the corresponding theoretically scaled wavenumbers. The frequencies of corresponding vibrations are also in accordance with those reported in the literature.

Table 1. Concentration Dependent Third-Order NLO Parameters of L1 at a Laser Power of 42 mW

| Concentration [mM] | $n_2 \times 10^{-4}$ [cm/W] | $\beta \times 10^{-4}$ [cm/W] | $\chi^{(3)} \times 10^{-6}$ [esu] |
|-------------------|----------------------------|-----------------|-----------------|
| 2.5               | $-6.68$                    | $-3.60$         | $3.13$          |
| 5.0               | $-18.90$                   | $-9.59$         | $8.85$          |
| 7.5               | $-27.51$                   | $-12.90$        | $12.89$         |
| 10.0              | $-47.02$                   | $-23.70$        | $22.03$         |

Table 2. Power Dependent Third-Order NLO Parameters of L1 at a Fixed Concentration of 7.5 mM

| Laser Power [mW] | $n_2 \times 10^{-4}$ [cm/W] | $\beta \times 10^{-4}$ [cm/W] | $\chi^{(3)} \times 10^{-6}$ [esu] |
|------------------|----------------------------|-----------------|-----------------|
| 30               | $-9.56$                    | $-3.77$         | $4.48$          |
| 35               | $-18.08$                   | $-6.97$         | $8.47$          |
| 40               | $-22.96$                   | $-9.45$         | $10.75$         |
| 45               | $-26.66$                   | $-10.70$        | $12.49$         |
| 50               | $-31.30$                   | $-11.60$        | $14.66$         |

Table 3. Comparison of NLO Parameters of L1 with Other Reported Molecules

| Schiff base molecules | $n_2$ [cm/W] | $\beta$ [cm/W] | $\chi^{(3)}$ [esu] | References |
|----------------------|--------------|----------------|------------------|------------|
| L1                   | $-4.70 \times 10^{-7}$ | $-2.37 \times 10^{-3}$ | $2.20 \times 10^{-5}$ | this work  |
| heterocyclic azomethine compound | $-1.91 \times 10^{-4}$ | $12.2 \times 10^{-4}$ | $12.2 \times 10^{-4}$ | 20 |
| hydrazinecarboxamide (BDMHC) | $1.00 \times 10^{-9}$ | $3.84 \times 10^{-5}$ | $1.24 \times 10^{-6}$ | 37 |
| stilbazolium derivative (4MSTB) | $3.96 \times 10^{-6}$ | $6.62 \times 10^{-2}$ | $9.45 \times 10^{-4}$ | 38 |
plots of HOMO − 1, HOMO, LUMO, and LUMO + 1 along with energy eigen values and highest occupied molecular orbital (HOMO)—lowest unoccupied molecular orbital (LUMO) energy gap related to L1 are illustrated in Figure 10. The HOMO—LUMO energy gap is found to be 2.88 eV. The molecule with a less HOMO—LUMO energy gap can be considered as a soft molecule with low stability and high chemical reactivity. The HOMO—LUMO energies explain that the charge transfer occurs within the molecule. The energy eigenvalues of these orbitals are generally used to define various reactivity descriptors such as ionization, electron affinity, hardness, softness, chemical potential, and so on. The capability of molecules to undergo charge transfer from
Table 5. B3LYP/6-311++G(d,p) and PCM-B3LYP/6-311++G(d,p) Results for Average Linear Polarizability and First and Second Hyperpolarizabilities (Static and Dynamic)

| parameters                      | B3LYP/6-311++G(d,p) | PCM-B3LYP/6-311++G(d,p) |
|---------------------------------|---------------------|-------------------------|
| Polarizability, \(\alpha\) (x10^-22 esu) | 0.374               | 0.499                   |
| anisotropy                       | 0.447               | 0.566                   |
| \(\alpha\) (\(\omega_1; \omega_2\), \(\lambda = 520.0\) nm) | 0.714               | 0.827                   |
| anisotropy                       | 1.372               | 1.605                   |
| First Dipole Hyperpolarizability, \(\beta\) (x10^-30 esu) | 33.839              | 71.946                  |
| \(\beta\) (\(-\omega_1; \omega_2, 0\), \(\lambda = 520.0\) nm) | 2731.535            | 4663.182                |
| \(\beta\) (\(-2\omega_1; \omega_2, \omega_2\), \(\lambda = 520.0\) nm) | 1090.953            | 1139.238                |
| Second Dipole Hyperpolarizability, \(\gamma\) (x10^-36 esu) | 167.904             | 483.535                 |
| \(\gamma\) (\(-\omega_1; \omega_1, 0, 0\), \(\lambda = 520.0\) nm) | 49605.334           | 116815.960              |
| \(\gamma\) (\(-2\omega_1; \omega_1, \omega_1, 0\), \(\lambda = 520.0\) nm) | -22256.933          | -38784.898              |
| \(\gamma\) (\(-\omega_1; \omega_1, 0, -\omega_f\), \(\lambda = 520.0\) nm) | 99042.764           | 233148.386              |
| \(\gamma\) (\(-3\omega_1; \omega_1, \omega_1, \omega_1\), \(\lambda = 520.0\) nm) | 296792.486          | 698478.089              |

“Kerr effect. "dc-SHG. "Nonlinear optical process of the IDRI. "THG."
The obtained high values of nonlinear refraction (n²), nonlinear absorption (β), and the third-order NLO susceptibility, χ(3), of L1 have been measured using a very simple and highly sensitive Z-scan technique based on spatial beam distortion, which was proposed by Sheikh-Bahae et al.33,48,49 Moreover, this technique is widely used because it provides sign and accurate magnitude of third-order susceptibility.50 Here, a tightly focused Gaussian beam of continuous wave diode laser (Thorlabs) with 120 mW laser power at 820 nm has been employed for the interaction with L1 dissolved in the acetone and poured in the cuvette of 1 mm thickness. The sample cuvette has been fixed on a computer-controlled translation stage, moving at 1 mm/s, so that it can be accurately moved through the focal region of the laser beam. The sample experiences different laser intensities at each Z-position, and the position-dependent transmission is measured using a photomultiplier tube (PMM01-1, Thorlabs). However, the detected signals are acquired, stored, and processed by a D/A converter and computer. The self-focusing (positive n²) or defocusing (negative n²) nature of the beam has been recorded by PMT as the cuvette is translated along the axis of the beam. To record the scans for closed and open aperture, an aperture is kept in the far field in front of the PMT. For the accuracy of the results, the data was recorded three times and averaged for the sample and the solvent in both OA and CA methods. The averaged data of the sample was also divided by solvent data to exclude the optical nonlinearity of the solvent.

4.5. Computational Details. The theoretical calculations have been performed for the ground state of L1 using the hybrid functional (B3LYP) with the 6-311+G(d,p) basis set, as implemented in Gaussian 09 software.51 The coordinates of the input geometry for the theoretical calculations were taken from the crystallographic information file.37 The geometry of L1 was fully optimized without using any symmetry constraints under tight convergence criterion, and subsequently, harmonic IR frequencies were obtained with positive values in vacuum and solution phases. The simulated IR spectrum was plotted with pure Lorentzian band shapes with a full width at half-maximum of 5 cm⁻¹. Vibrational assignments of some important modes were made with great care by visualization of animation of modes using the Gauss View 5 program.52 The frontier molecular orbitals, that is, HOMO and LUMO, their energy Eigen values, and HOMO–LUMO gap were obtained at the same level of theory. The NBO analysis was carried out to study hyperconjugative interactions that play a significant role in stabilizing the molecule. The electronic spectra were studied in both vacuum and solution (ethanol) phases using TD-DFT/B3LYP calculations using the same basis set. The polarizable continuum model (PCM) was incorporated for the calculations in solution phase. The nonlinear optical behavior of L1 was also studied using theoretical NLO parameters (static and dynamic) such as polarizability and hyperpolarizability values (first and second order) in vacuum and solution phases.
absorption spectra of L1, representation of the molecular structure of L1, close interaction in the title molecule with its neighbouring species, optimized geometry of L1, simulated and experimental IR spectra along with band assignments for L1, theoretical and experimental UV–vis absorption spectra of L1, and FTIR spectrum of L1 (PDF)

Single crystal data of L1 (https://doi.org/10.1107/S2056989018016262) with CCDC1879300 (CIF)

This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail:deposit@ccdc.cam.ac.uk

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**Notes**

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