Synthesis, Crystal Structure, Hirshfeld Surface Analysis, and Computational Study of a Novel Organic Salt Obtained from Benzylamine and an Acidic Component

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ABSTRACT: A novel Schiff base compound named as phenylmethanamine (E)-4-((benzylimino)methyl)benzoate C_{19}H_{20}N. C_{13}H_{13}NO_{2} (A) is synthesized by the chemical reaction of benzylamine and 4-carboxybenzaldehyde in ethanol, and the structure of the titled compound is verified using the single-crystal X-ray diffraction technique. Structural investigation inferred that the crystal packing is mainly stabilized by N···O and comparatively weak C···O interactions. Hirshfeld surface analysis is employed to explore the noncovalent interactions that are responsible for crystal packing quantitatively. Furthermore, we have used state-of-the-art quantum chemical calculations to get comprehensive insights into the structure—optoelectronic property relationship for the entitled compound. The molecular geometry of compound A is optimized at the M06/6-311G* level of theory. The linear polarizability, third-order nonlinear optical (NLO) polarizability, total and partial density of states, and UV—visible spectrum are calculated through quantum chemical calculations. We believe that compound A is not only a new addition to crystallographic data but also possesses good optical and NLO properties for its potential use in lasers and frequency-converting applications.

1. INTRODUCTION

Schiff bases are getting increasing interest nowadays because of their versatile applications in various fields. These are usually prepared by the condensation of aldehydes and/or ketones with primary amines in a simple way with high yield. The Schiff bases derived from aromatic aldehydes are more stable due to the presence of conjugation as compared to those which were prepared from aliphatic aldehydes. These aliphatic aldehydes may be polymerized, leading to the generation of undesirable products. Use of aldehydes is usually preferred over ketones due to the faster rate of condensation reaction. Schiff bases have azomethine (−HC≡N) linkage, where the nitrogen atom is sp²-hybridized and has a lone pair, which is attributed to the potential biological applications in the fields of pharmacology, anticancer, antibacterial, antifungal, antiviral, antioxidant, and anti-parasitic activities.

The azomethine nitrogen of the Schiff base may interact with the active sites of the cell components via hydrogen bonding, which is the central point to recognize them as versatile pharmacophores. Besides their biological role, they are also equally important in organic synthesis, dyes and pigments, catalysis, thermochromism, and electroanalytical chemistry. The various systems in which Schiff bases are employed are optical computers, molecular memory storage, optical sound-recording technology, and photodetectors.

Schiff bases with a hydroxyl group at the ortho position led to the evolution of coordination chemistry and bioinorganic chemistry. Schiff bases are excellent chelating agents and can stabilize metal atoms in various oxidation states. These chelated metal complexes are then further utilized as catalysts for the synthesis of many organic compounds in industries. The metal complexes of Schiff bases derived from 4-carboxybenzaldehyde have potential antimicrobial, antibacterial (Gram positive and Gram negative), cytotoxic, antioxidant, and urease inhibition activities. Priyadarshini et al. have explored quinoline-based Schiff bases for the calculation of their optical and nonlinear optical (NLO) properties. From an experimental point of view, the studies of Kamaal et al. and Ani et al. are very interesting where they performed...
experimental investigations to study the NLO properties of Schiff bases consisting of 4-[(2-hydroxy-3-methoxybenzilidene) amino] benzoic acid and methanamine/phenylethanamine derivatives, respectively. In lieu of the immense potential application of Schiff bases and in continuation of our previous research, we are reporting the synthesis, crystal structure, Hirshfeld surface (HS) analysis, and density-functional theory (DFT) studies of a novel Schiff base.

2. RESULTS AND DISCUSSION

2.1. Crystal Structure of A. The title compound C16H12N6O2 (Figure 1) comprises the (E)-4-[(benzylimino)methyl]benzoate anion (C1–C8/C9A–C15A/N1/O1/O2) and phenylmethanaminium cation (C16–C22/N2). Some selected bond lengths and bond angles are specified in Table 1. The C8–N1 bond length is found to be 1.250 (5) Å, indicating that it is a typical double bond.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for Compound A

| selected bond lengths | selected bond angles |
|-----------------------|----------------------|
| C1–O1                 | 1.230 (4) C4–C5–C8  |
| C1–O2                 | 1.274 (4) C5–C8–N1  |
| C4–C5                 | 1.385 (5) C8–N1–C9A |
| C5–C8                 | 1.459 (5) N2–C16–C17|
| C8–N1                 | 1.250 (5) C2–C1–O1  |
| N1–C9A                | 1.453 (18) C2–C1–O2 |
| C16–N2                | 1.464 (5) C6–C5–C8  |
| C16–C17               | 1.504 (5) O1–C1–O2  |

Each cation is directly connected with three neighboring anions through N–H···O and comparatively weak C–H···O interactions, where NH is from protonated nitrogen and CH is from the benzene ring of the benzoato moiety and each anion is connected with three cations through the same type of H-bonding. The anions are also directly interlinked through C–H···O bonding to form a chain named as C5 along the b-crystallographic axis, whereas no H-bonding connects cations directly with each other. R3(9) and R2(7) loops are formed by N–H···O and C–H···O types of H-bonding between cations and anions, as shown in Figure 2 and given in Table 2. The cations and anions form a 2D network along the ac crystallographic plane through H-bonding. The cations are also interlinked through weak C–H···π interactions, in which CH is from the carbon directly attached to the protonated N atom, whereas anions are connected with each other through the C–O···π interaction with an O···π distance of 3.437 (3) Å. C–H···π and C–O···π interactions result in the formation of a one-dimensional chain of cations and anions, respectively, along the b crystallographic axis, as shown in Figure 3 and given in Table 2. A Cambridge structural database search is performed for phenylmethanaminium benzoate. It gives lots of crystal structures containing the phenylmethanaminium cation and carboxylate anion. Two closely related crystal structures
the crystal packing of KALJUF. and weak H-bonding, but the C—H···π interactions in terms of strong and weak H-bonding, but the C—O···π interaction is absent in the crystal packing of KALJUF.

2.2. HS Analysis. The concept of HS is evolved from an attempt to specify the space occupied by a molecule in a crystal in order to divide the electron density of the crystal into molecular fragments of electron densities. A HS investigation is an effective way to quantify the nature of the intermolecular interactions. The HS computations were done by the usage of CrystalExplorer17.5. Figure 4a represents the HS plotted over a property named as \( d_{\text{norm}} \) in the range from −0.6254 (red) to 1.2455 (blue) a.u.27 Color coding is used in order to show intermolecular contacts. Red, white, and blue spots show intermolecular contacts with distances less than, equal to, and larger than van der Waal radii, respectively. The dark-red regions around the protonated amino group of the cation and one of the O atom of carbonyl groups of the anion indicate the presence of the N—H···O interaction in crystal packing, whereas the comparatively light-red spot on HS indicates the C—H···π interaction. Not only hydrogen bonding interactions can be explored by HS analysis but also comparatively weak interactions involving phenyl rings can be explored. The triangular-shaped regions on the HS plotted over the shape index (Figure 4b) around phenyl rings indicate that π···π stacking interactions are present in the crystal packing, but it is found that the π···π stacking interaction is very weak as the centroid-to-centroid separation ranges from 4.755 (3) to 5.963 (1) Å. The donor and acceptor groups can be classified by plotting the HS over electrostatic potential. Red and blue regions on this HS represent the H-bond acceptor and donor, respectively. Two views of this HS are shown in Figure S1. The blue spot on the HS near the protonated amino group represents that it acts as a H-bond acceptor, whereas the red spot on the HS close to one of the O atom of the carbonyl group indicates that it acts as a H-bond donor.

Furthermore, two-dimensional (2D) fingerprint (FP) plots are used to provide quantitative information related to the nature and the type of intermolecular contacts experienced by the molecules in the crystal packing.22–24 2D FP plots are computed for each interatomic contact and for overall interactions. In the computation of individual interatomic contacts, the reciprocal contact of each interatomic contact is also included. Figure 5a shows the 2D FP plot for overall interactions. On this plot, spikes represent the interatomic contacts that have a significant contribution to crystal packing. \( d_i \) stands for distance from the HS to the nearest nucleus inside the HS, whereas \( d_o \) stands for the distance from the HS to the nearest nucleus outside the HS. The interatomic contacts that

Table 2. Hydrogen Bonding Geometrical Parameters and C—H···π and C—O···π Interactions (Å, °) for A

| D—H···A | D—H | H···A | D—A | <(D—H···A) (deg) |
|--------|------|-------|-----|-----------------|
| N2—H2A···O1 | 0.89 | 1.95 | 2.838 (4) | 173 |
| C18—H18···O1 | 0.93 | 2.50 | 3.305 (5) | 144 |
| N2—H2B···O2 | 0.89 | 1.87 | 2.736 (4) | 165 |
| N2—H2C···O2 | 0.89 | 1.92 | 2.776 (4) | 161 |
| C7—H7···O2 | 0.93 | 2.51 | 3.289 (5) | 142 |

Symmetry codes: (i) x, y − 1, z; (ii) x + 1, y + 1, z; (iii) x + 1, y, z − 1/2; (iv) x, −y + 2, z − 1/2; (v) x, y − 1, z; and (vi) x, y + 1, z. Here, Cg(1) is the centroid of the phenyl ring of the cation (C17—C22) and Cg(2) is the phenyl ring of the anion (C2—C7).

Figure 3. Graphical representation of C—H···π and C—O···π interactions for Schiff base compound A. Selected H atoms are shown for clarity. The distances are measured in Å.

Figure 4. HS plotted over (a) \( d_{\text{norm}} \) and (b) shape index for compound A.
have stronger contribution to crystal packing as compared to other interatomic contacts are H···H, C···H, and O···H with percentage contributions of 53.8% (Figure 5b), 25.8% (Figure 5c), and 11.2% (Figure 5d), respectively. The other interatomic contacts that have comparatively less contribution to crystal packing are C···C, N···H, O···C, and N···C with percentage contributions of 3.8, 3.4, 1.8, and 0.3%, respectively.

Figure 5. 2D FP plot for (a) overall interactions and (b–h) individual interactions in crystal packing of A.

Figure 6. (a) Percentage contributions of the interaction of all the atoms present inside the HS to an atom outside the HS. (b) Percentage contributions of the interaction of an atom present inside the HS to all the atoms present in the surrounding of the HS.
The interaction of all the atoms present inside the HS to an atom present in the vicinity of the HS is explored, as shown in Figure 6a. This investigation inferred that all the HS-contained atoms interact strongly with the H atoms located in the vicinity of the HS, and the percentage contribution of the ALL−H interaction is 76.9%. Other such interactions are ALL−C, ALL−O, and ALL−N with percentage contributions of 15.2, 6.2, and 1.7%, respectively. These interactions are important to discuss as they help better understand the crystal packing.33–38 Similarly, the interaction of an atom present inside the HS with all the atoms located in the vicinity of the HS is computed to further explore crystal packing, as shown in Figure 6b. This investigation inferred that the H atom present inside the HS has the strongest interaction with the atoms of neighboring molecules present as compared to other atoms. The percentage contribution of this particular interaction is found to be 71%. Other such interactions are C−ALL, O−ALL, and N−ALL with percentage contributions of 20.2, 6.8, and 2%, respectively.

Void analysis is performed, as it helps to investigate the mechanical strength of the single crystals. These voids are computed by summing up the spherical electron densities at the suitable nuclear positions, as displayed in Figure S2.39 If a unit cell contains a small percentage of voids, then, it will be inferred that the molecules will be strongly packed with each other. This analysis inferred that the volume of voids in the crystal packing is 113.24 Å³ and the percentage of voids is found to be 12.2%, indicating that the cation and anion are strongly packed with each other and no large cavity is found in the crystal packing. The surface area of the void, globularity, and asphericity are found to be 380.03 Å², 0.298, and 0.195, respectively.

3. DETAILS OF THE APPLIED COMPUTATIONAL METHODOLOGY

All the quantum chemical computations are done through the use of GAMESS.40 The optimization of compound A was achieved by applying the B3LYP functional of the density functional theory method31 and 6-31G* basis sets. This B3LYP/6-31G* level of theory is considered as a gateway method to get reliable geometries for computational purposes. For the purpose of optimization, no symmetry constraints were used in the present calculations. The optimized geometry was further subjected to its Hessian calculations, and the absence of negative frequency confirms the optimized structure as a global minimum. The M06 functional42 is used for the calculation of linear polarizability and second- and third-order NLO polarizabilities. This is because B3LYP has been extensively tested as an overestimating functional, while M06 shows several reasonable results for higher order polarizabilities. The UV-visible spectrum was calculated using a time-dependent-DFT method (TD-M06). The linear and NLO polarizabilities were calculated through a well-known finite field methodology where a finite value of 0.001 a.u. is adopted. Further details about this method can be obtained from our earlier studies.43,44 The equations used to calculate the electronic part of the dipole moment, linear polarizability, and higher order NLO polarizabilities are given below

\[ \mu = (\mu_x^2 + \mu_y^2 + \mu_z^2) \]

Similarly

\[ a_0 = \frac{1}{3}(a_{xx} + a_{yy} + a_{zz}) \]

\[ \Delta \alpha = \frac{1}{\sqrt{2}} \sqrt{[(a_{xx} - a_{yy})^2 + (a_{yy} - a_{zz})^2 + (a_{zz} - a_{xx})^2 + 6a_{xy}^2]} \]

where \( a_0 \) is average polarizability and \( \Delta \alpha \) is anisotropy of polarizability.

\[ \langle \gamma \rangle = \frac{1}{15} \sum_{ij=x,y,z} (\gamma_{ijj} + \gamma_{ijj} + \gamma_{ijj}) \]

Under the assumption of “Kleinman symmetry”, all components can be decreased to six only.

\[ \langle \gamma \rangle = \frac{1}{5}(\gamma_{xxx} + \gamma_{yyx} + \gamma_{zzz} + 2(\gamma_{xxy} + \gamma_{xyx} + \gamma_{yxz})) \]

All abovementioned individual tensors of \( \gamma \) are obtained from the output file of GAMESS in terms of Cartesian coordinates.

3.1. Molecular Geometry of Compound A

The optimized molecular geometry is shown in Figure 7. Numerical values of its bond lengths and bond angles are given in Table 3, while the optimized coordinates are given in Table S1. It is important to mention that a comparison between main backbone atoms is given in Table 3. Overall, there is a reasonable agreement among the bond lengths of experimental geometry and its calculated coordinates. A comparison of some important bond lengths shows that there are no catastrophic deviations. For instance, C3−N31 and O1−C4 bonds show deviations which are 0.023 Å and 0.112 Å, respectively, which are reasonable at the B3LYP/6-31G* level of theory.
The significant differences among the bond lengths of N$_3$H$_2$ and H$_3$O$_2$ were seen in the gas-phase optimization of compound A because zwitterions almost do not exist in the gas phase. Given the inherent instability of charges in the gas phase, the proton shifts more toward carboxylate because carboxylate is a stronger base than amines. Among the triangles, C$_{15}$N$_1$−C$_{17}$ shows a maximum 4.1° difference between calculated and experimental values.

3.2. Electronic Dipole Moment and Linear and NLO Polarizabilities of Compound A. There are several parameters to explore the polarization of a molecule, which include the dipole moment, linear polarizability, and higher order NLO polarizabilities. The linear polarizability provides us with a better understanding of the structure of a chemical material and its interaction with light. The linear polarizability indicates the linear response of materials to light, while nonlinear polarizabilities are important to observe NLO responses by intense laser light at various levels. The NLO response properties are very useful in current technological aspects consisting of laser frequency modulations and telecommunications. In current work, we have explored the dipole moment, linear polarizability, and second hyperpolarizability (third-order NLO polarizability) at the molecular level (Table 4). The calculated electronic dipole moment was found to be 2.182 a.u., which is equal to 3.708 debye. The dipole moment is an indication of charge difference between the two moieties of a chemical compound. As the molecule is not perfectly in a 2D space, the dipole moment is observed along all three axes depending upon the nature of ground-state charge distributions. The linear polarizability ($\alpha$) is calculated as isotropic and anisotropic tensors, which are found to be 272 and 756 a.u., respectively. The larger amplitude of anisotropic linear polarizability indicates the direction effects of our molecules in the applied electric field. Furthermore, we also calculated the third-order NLO response ($\gamma$) of compound A, which is very crucial for guessing the NLO response of materials under intense laser light. A reasonably good $\gamma$ amplitude for system A is calculated to be $91.599 \times 10^3$ a.u. at the M06/6-31G* level of theory. Among the individual components, the $\gamma_{xxx}$ (153.794 $\times 10^3$ a.u.) and $\gamma_{yyz}$ (71.934 $\times 10^3$ a.u.) are found to be larger as compared to others because these two axes are along the molecular plane and also along the intramolecular charge transfer direction, as shown in Figure 7 and also in the frontier molecular orbital (FMO) diagram of compound A in the following UV–visible section. For semi-quantitative comparative purposes, the $\gamma$ amplitude of "para-nitroaniline (p-NA)" is also determined in the current investigation, which is often considered as a prototype NLO molecule. The $\gamma$ amplitude of the p-NA molecule is found to be 24.346 $\times 10^3$ a.u. The ratio between the $\gamma$ amplitudes of the p-NA and studied compound is found to be 3.75, which indicates that the third-order nonlinear polarizability of a given compound is ~4 times larger than that of the standard p-NA molecule.

3.3. TDOS and PDOS of Compound A. The total density of states (TDOS) represents the number of particular states at a specific energy level that electrons are allowed to occupy, while the partial density of state (PDOS) indicates a relative contribution to the TDOS by an atom or a fragment of a molecule. Herein, the M06/6-31G* method is also applied to calculate the DOS. The partial densities were projected over individual fragments of the 4-((benzylimino)methyl)benzoxate group and phenylmethanaminium group to see their individual contributions to the TDOS. The x-axis represents the energy level, while the y-axis shows the number of states per eV, as shown in Figure 8. An insightful view of Figure 8 shows that

Table 3. Geometrical Parameters (Å, °) of Calculated (Cal.) and Experimental (Exp.) Geometries for Compound A with the B3LYP Functional and 6-31G* Basis Set

| bond lengths | Exp. (Å) | Cal. (Å) | bond lengths | Exp. (Å) | Cal. (Å) |
|--------------|---------|---------|--------------|---------|---------|
| C$_{14}$−C$_{14}$ | 1.367 | 1.395 | C$_{15}$−N$_1$ | 1.249 | 1.269 |
| C$_{41}$−C$_{39}$ | 1.382 | 1.391 | N$_3$−C$_{17}$ | 1.451 | 1.451 |
| C$_{39}$−C$_{38}$ | 1.379 | 1.400 | C$_{17}$−C$_{20}$ | 1.495 | 1.519 |
| C$_{38}$−C$_{35}$ | 1.503 | 1.512 | C$_{20}$−C$_{23}$ | 1.386 | 1.398 |
| C$_{35}$−N$_31$ | 1.464 | 1.487 | C$_{29}$−C$_{31}$ | 1.380 | 1.391 |
| N$_{31}$−H$_{32}$ | 0.889 | 0.773 | C$_{15}$−C$_{15}$ | 1.378 | 1.394 |
| H$_{32}$−O$_1$ | 1.952 | 1.001 | bond angles | Exp. (deg) | Cal. (deg) |
| O$_1$−C$_4$ | 1.229 | 1.341 | C$_{43}$−C$_{41}$−C$_{49}$ | 119.88 | 120.34 |
| C$_4$−C$_5$ | 1.502 | 1.506 | C$_{59}$−C$_{58}$−C$_{55}$ | 123.38 | 120.76 |
| C$_5$−C$_6$ | 1.381 | 1.379 | C$_{38}$−C$_{35}$−N$_{31}$ | 114.63 | 111.48 |
| C$_6$−C$_8$ | 1.379 | 1.389 | C$_{17}$−C$_{17}$−C$_{15}$ | 120.04 | 117.00 |
| C$_8$−C$_{10}$ | 1.385 | 1.400 | C$_{38}$−C$_{38}$−C$_{29}$ | 120.63 | 120.66 |
| C$_{10}$−C$_{15}$ | 1.459 | 1.473 | C$_{15}$−N$_1$−C$_{17}$ | 114.26 | 118.36 |

Table 4. Calculated Values of the Dipole Moment [debye, (D)], Linear Polarizability ($\alpha$, a.u.), and Third-Order NLO Polarizability ($\times 10^3$ a.u.) at the M06/6-31G* Level of Theory

| $\mu$ and $\alpha$ components | amplitudes (a.u.) | $\gamma$ components | amplitudes ($\times 10^3$ a.u.) |
|-------------------------------|-------------------|---------------------|-----------------------------|
| $\mu_x$ | 0.14 | $\gamma_{xxx}$ | 153.794 |
| $\mu_y$ | −0.102 | $\gamma_{yyz}$ | 71.341 |
| $\mu_z$ | −0.192 | $\gamma_{zzz}$ | 7.084 |
| $\alpha_{xx}$ | 307 | $\gamma_{xx}$ | 18.486 |
| $\alpha_{xy}$ | −865 | $\gamma_{xy}$ | 22.519 |
| $\alpha_{yz}$ | 279 | $\gamma_{yz}$ | 91.599 |
| $\alpha_{zx}$ | −34 | ($\gamma$ (p-NA)) | 24.346 |
| $\alpha_{zy}$ | 15 | $\eta$ | 3.75 |
| $\alpha_{zz}$ | 233 |
| $\alpha_{xx}$ | 272 |
| $\alpha_{zz}$ | 756 |

$\gamma$ of p-NA is also calculated at the M06/6-31G* level of theory. $\eta$ is the ratio between ($\gamma$) amplitudes of p-NA and compound A.

Figure 8. Graphical representation of the TDOS and PDOS determined using the M06/6-31G* method.
the 4-((benzylimino)methyl)benzoate group presents more contributions both in valence and conduction bands owing to its larger size and more atoms as compared with the phenylmethaninium moiety. Interestingly, there is no contribution of states from phenylmethaninium in the highest occupied molecular orbital (HOMO) and orbitals in its vicinity, which is also reflected in HOMO and HOMO − 2 orbital diagrams, as given in the following UV−visible section, while, on the other hand, in the lowest unoccupied molecular orbital (LUMO), there are states from both of the fragments. It would be rational to say that the valence band of compound A can be tuned by making changes on the 4-((benzylimino)-methyl)benzoate moiety, while to affect the conduction band, both moieties are important here.

3.4. UV−Visible Spectrum of Compound A. The UV−visible spectrum is mainly used to see how much light is absorbed by a chemical material. Herein, we have also calculated computationally the UV−visible spectrum of compound A using the TD-M06/6-31G* method. Interestingly, the FMOs involved in major transitions were also visualized to see the charge transfer character for compound A. There was no absorption found in the visible region. Two major transitions with higher oscillator strengths of 0.128 and 0.448 at 286 and 259 nm, respectively, were found in the UV region. A further 3D frontier orbital analysis was performed to look for the FMOs involved in these two major transitions. It was found that the transition at the higher wavelength of 286 nm is mainly composed of the HOMO and LUMO, while the transition at 259 nm is contributed mainly from HOMO − 2 and LUMO, as shown in Figure 9. Both the electronic transitions indicate the intermolecular charge redistribution characteristics from the 4-((benzylimino)methyl)benzoate group to the phenylmethaninium moiety, which is perhaps owing to the N−H···O and comparatively weak C−H···O bonding characteristics between both the moieties. It is well known that an efficient intramolecular and/or intermolecular charge redistribution usually causes the origin of non-zero NLO response properties.

4. CONCLUSIONS AND PERSPECTIVES

A novel Schiff base compound A is synthesized, and its structure is verified using the single-crystal X-ray diffraction technique. H-bonding of the types N−H···O and C−H···O results in the formation of layers parallel to the ac crystallographic plane. Further stabilization in the crystal packing is due to the presence of comparatively weak C−H···π interactions. HS analysis is performed for further exploration of noncovalent interactions and shows the H−H interatomic contact, whose contribution to the crystal packing is the strongest with a percentage contribution of 55.5%. The void analysis showed that only 12.2% of the space in the unit cell is occupied by voids, which indicates that the cations and anions are strongly packed through noncovalent interactions and there is no large cavity in the crystal packing. Additionally, quantum computational analysis revealed that the amplitude of third-order NLO polarizability (⟨γ⟩) is 91.599 × 10^3 a.u. in the M06/6-31G* method, which is about four times larger than that of the p-NA molecule, often considered as a prototype NLO molecule. The calculation of the UV−visible spectrum showed that the intramolecular electronic transition at a higher wavelength of 286 nm is mainly composed of the HOMO and LUMO, while the transition at 259 nm is contributed mainly from the HOMO − 2 and LUMO. Both of the transition indicated the charge transfer characteristics from the 4-((benzylimino)methyl)benzoate group to the phenylmethaninium moiety, which is further confirmed by the calculation of total and partial densities of states as projected over individual fragments of the 4-((benzylimino)methyl)benzoate group and phenylmethaninium group of compound A. Thus, we have not only successfully synthesized a new compound but also performed its crystallographic analysis and calculated many optoelectronic and NLO properties to explore it for laser applications.

5. EXPERIMENTAL SECTION

5.1. Synthesis. For the efficient synthesis, a mixture of benzylamine (0.218 mL, 2 mmol) and 4-carboxybenzaldehyde (0.150 g, 1 mmol) was refluxed in a flask having a round bottom with 50 mL of ethanol solvent for nearly 3 h. At room temperature, the mixture is allowed to cool, and then, the single crystals of the titled compound are acquired (0.283 g, yield 82%), as shown in Scheme 1.
Table 5. Single-Crystal-Related Experimental Details of Schiff Base A

| crystal data                                      |
|--------------------------------------------------|
| CCDC number                                      | 2011322 |
| chemical formula                                 | C₇H₁₀N⁺, C₁₅H₁₂NO₂⁻ |
| M_r                                              | 346.41  |
| crystal system, space group                       | monoclinic, Pcc |
| temperature                                       | 296     |
| a, b, c (Å)                                       | 17.177 (3), 4.7551 (8), 11.918 (2) |
| α, β, γ (deg)                                     | 90, 107.222 (7), 90 |
| V (Å³)                                           | 929.8 (3) |
| Z                                                 | 2       |
| calculated density (mg/cm³)                       | 1.237   |
| F(000)                                           | 368     |
| type of radiation                                 | Mo Kα   |
| wavelength (Å)                                    | 0.71073 |
| μ (mm⁻¹)                                         | 0.08    |
| size of the crystal                               | 0.44 × 0.24 × 0.18 |

| data collection                                   |
|--------------------------------------------------|
| diffractometer                                    | Bruker APEX-II CCD diffractometer |
| absorption correction                             | multiscan |
| number of measured, independent, and observed [1 > 2σ(I)] reflections | 7816, 3475, 2266 |
| R_int                                             | 0.038 |
| theta range for data collection (deg)             | 2.483 to 27,000 |
| index ranges                                      | −21 ≤ h ≤ 21, −3 ≤ k ≤ 6, −15 ≤ l ≤ 15 |
| (sin θ/λ)_{max} (Å⁻¹)                             | 0.639 |

| data refinement                                   |
|--------------------------------------------------|
| R[F₂ > 2σ(F²)], wR(F²), S                        | 0.051, 0.106, 1.00 |
| number of reflections                             | 3475 |
| number of parameters                              | 294 |
| number of restraints                              | 62 |
| H atom treatment                                  | H atom parameters constrained |
| Δρ_{max}, Δρ_{min} (eÅ⁻³)                         | 0.13, −0.16 |

5.2. Crystal Structure Measurement. The data related to the single-crystal structure were gathered on the Bruker Kappa APEXII CCD X-ray diffractometer equipped with a graphite monochromator. The needle-shaped white crystal of the entitled compound was fixed for the sake of data collection on the Bruker APEX-II. The data were integrated by utilization of Bruker SAINT software, and raw data were solved by a direct method on SHELX97. Data refinement was done by the utilization of SHELXL-2018/3 and WinGX-2021.3 software. Refinement of all H atoms was performed using isotropic displacement parameters and included in calculated locations. They are treated as riding on their parent C atom with C–H = 0.93–0.97 Å with U_{eq}(H) = 1.5U_{eq}(protonated N atom) and 1.2U_{eq}(C) for all other H atoms, whereas refinement of all atoms other than H atoms was performed using anisotropic displacement parameters. For graphical representation of results of single-crystal investigation, ORTEP-3, PLATON, and Mercury 4.0 software were utilized. Experimental parameters are specified in Table 5. The Flack parameter cannot be computed reliably because of the absence of X-ray anomalous scattering, as no heavy atom is present in the crystal structure.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03078.

Hirshfeld surface plotted over electrostatic potential of compound A, graphical view of voids in crystal packing of compound A, calculated IR spectrum of compound A, optimized coordinates of compound A at the B3LYP/6-31G* level of theory, and details of the finite field method (PDF)

Crystallographic data for compound A (TXT)

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REFERENCES

(1) Munawar, K. S.; Haroon, S. M.; Haroon, S. M.; Hussain, S. A.; Raza, H. Schiff bases: multipurpose pharmacophores with extensive biological applications. J. Basic Appl. Sci. 2018, 14, 217–229.
(2) Acar, N.; Selcuk, C.; Coskun, E. DFT and TDDFT investigation of the Schiff base formed by tetracne and saccharin. J. Mol. Model. 2017, 23, 17.
(3) Malakyan, M.; Babayan, N.; Grigoryan, R.; Sarkisyan, N.; Tonoyan, V.; Tadevosyan, D.; Matosyan, V.; Aroutiounian, R.; Arakelyan, A. Synthesis, characterization and toxicity studies of pyridinecarboxaldehydes and L-tryptophan derived Schiff bases and...
corresponding copper (II) complexes. F1000Research 2016, 5, 1921–
1932. (4) Hu; J.; Gao, Y.-Q.; Xu, D.; Chen, L.; Wen, W.; Hou, Y.; Chen, L.; Xie, W. Highly enantioselective addition of aliphatic aldehydes to 2-hydroxyalchone enabled by cooperative organocatalysts. Chem. Commun. 2020, 56, 10018–10021. (5) Rauf, A.; Shah, A.; Munawar, K. S.; Ali, S.; Nawaz Tahir, M.; Javed, M.; Khan, A. M. Synthesis, physicochemical elucidation, biological screening and molecular docking studies of a Schiff base and its metal(II) complexes. Arab. J. Chem. 2020, 13, 1130–1141. (6) Shabbir, M.; Akther, Z.; Ashraf, A. R.; Bolte, M.; Wahid, S.; Mirza, B. Pharmacological evaluation of ONNO donor quindrate Schiff bases. Eur. J. Chem. 2017, 8, 46–51. (7) Kargar, H.; Behjatmanesh-Ardakani, R.; Fallah-Mehrjardi, M.; Torabi, V.; Munawar, K. S.; Ashfaq, M.; Tahir, M. N. Ultrasound-based synthesis, SC-XRD, NMR, DFT, HSA of new Schiff bases derived from 2-aminoxydine: Experimental and theoretical studies. J. Mol. Struct. 2021, 1233, 101055. (8) Vashi, K.; Naik, H. B. Synthesis of novel Schiff base and azetidinone derivatives and their antibacterial activity. Eur. J. Chem. 2004, 1, 272–275. (9) Nejati, K.; Rezvani, Z.; Massoumi, B. Syntheses and investigations of thermal properties of copper complexes with azo-containing Schiff-base dyes. Dyes Pigm. 2007, 75, 653–657. (10) Kargar, H.; Forootan, P.; Fallah-Mehrjardi, M.; Behjatmanesh-Ardakani, R.; Amiri Rudbari, H.; Shahzad Munawar, K.; Ashfaq, M.; Nawaz Tahir, M. Novel oxovanadium and dioxomolybdenum complexes of tridentate ONO DONOR Schiff base ligand: Synthesis, characterization, crystal structures, Hirshfeld surface analysis, DFT computational studies and catalytic activity for the selective oxidation of benzylic alcohols. Inorg. Chem. Acta 2021, 523, 120414. (11) Ebrahimipour, S. Y.; Khazazadeh, H.; Castro, J.; Sheikhsheh, I.; Crochet, A.; Fromm, K. M. cis-Dioxido-molybdenum(VI) complexes of tridentate ONO hydrazine Schiff base: Synthesis, characterization, X-ray crystal structure, DFT calculation and catalytic activity. Inorg. Chem. Acta 2015, 427, 52–61. (12) Taha, N. I.; Tabapashi, N. O.; El-Subeyhi, M. N. Green Synthesis of New Tetra Schiff Bases and Bis-Azo Bis-Schiff Bases Derived from 2-aminoxydine: Experimental and theoretical studies. J. Mol. Struct. 2018, 1155, 39–50. (13) Wen, X.; Jin, X.; Lu, C.; Jin, S.; Zheng, X.; Liu, B.; Wang, D.; Guo, M.; Xu, W. Crystal structures of seven molecular salts derived from benzylamine and organic acidic components. J. Mol. Struct. 2018, 1139, 87–103. (14) Taha, N. I.; Ashfaq, M.; de la Torre, A. F.; Caballero, J.; Hernández-Rodríguez, E. W.; Ali, A. Rationalizing the stabilization and interactions of 2,4-diamino-5-(4-chloro-phenyl)-6-ethylpyrimidin-1-ium 2-hydroxy-3,5-dinitrobenzoate salt. J. Mol. Struct. 2020, 1193, 185–194. (15) Ali, A.; Zakerman-Schector, J.; Weber Paixão, M.; Jotani, M.; Tiekink, E. R. T. 7-Methyl-5-[(4-methylbenzene)sulfonyl]-2-hydroxy-3,5-dinitrobenzoate salt. Acta Crystallogr., Sect. E: Crystallogr. Commun. 2012. (16) Ali, A.; Khalid, M.; Rehman, M. F. U.; Haq, S.; Ali, A.; Tahir, M. N.; Ashfaq, M.; Asghar, M.; Rasool, F.; Braga, A. C. Efficient Synthesis, SC-XRD, and Theoretical Studies of O-Benzene sulfonlated Pyrimidines: Role of Noncovalent Interaction Influence in Their Supramolecular Network. ACS Omega 2020, 5, 15115–15128. (17) Ashfaq, M.; Bogdanov, G.; Ali, A.; Tahir, M. N.; Abdullah, S. Pyrimethamine-Based Novel Co-Crystal Salt: Synthesis, Single-Crystal Investigation, Hirshfeld surface analysis and DFT inspection of the 2,4-diamino-5-(4-chlorophenyl)-6-ethylpyrimidin-1-ium 2-hydroxy-3,5-dinitrobenzoate salt. J. Mol. Struct. 2019, 1193, 185–194. (18) Ali, A.; Zakerman-Schector, J.; Weber Paixão, M.; Jotani, M.; Tiekink, E. R. T. 7-Methyl-5-[(4-methylbenzene)sulfonyl]-2-H5H-1,3-dioxolo[4,5-f]-indo: crystal structure and Hirshfeld analysis. Acta Crystallogr., Sect. E: Crystallogr. Commun. 2018, 74, 184–188. (19) Ali, A.; Khalid, M.; Rehman, M. F. U.; Haq, S.; Ali, A.; Tahir, M. N.; Ashfaq, M.; Asghar, M.; Rasool, F.; Braga, A. C. Efficient Synthesis, SC-XRD, and Theoretical Studies of O-Benzene sulfonlated Pyrimidines: Role of Noncovalent Interaction Influence in Their Supramolecular Network. ACS Omega 2020, 5, 15115–15128. (20) Ali, A.; Zakerman-Schector, J.; Weber Paixão, M.; Jotani, M.; Tiekink, E. R. T. 7-Methyl-5-[(4-methylbenzene)sulfonyl]-2-H5H-1,3-dioxolo[4,5-f]-indo: crystal structure and Hirshfeld analysis. Acta Crystallogr., Sect. E: Crystallogr. Commun. 2018, 74, 184–188. (21) Ali, A.; Khalid, M.; Rehman, M. F. U.; Haq, S.; Ali, A.; Tahir, M. N.; Ashfaq, M.; Asghar, M.; Rasool, F.; Braga, A. C. Efficient Synthesis, SC-XRD, and Theoretical Studies of O-Benzene sulfonlated Pyrimidines: Role of Noncovalent Interaction Influence in Their Supramolecular Network. ACS Omega 2020, 5, 15115–15128. (22) Ali, A.; Khalid, M.; Tahir, M. N.; Imran, M.; Ashfaq, M.; Hussain, R.; Assiri, M. A.; Khan, I. Synthesis of Diaminopyrimidine
Sulfonate Derivatives and Exploration of Their Structural and Quantum Chemical Insights via SC-XRD and the DFT Approach. ACS Omega 2021, 6, 7047–7057.

(35) Madni, M.; Ahmed, M. N.; Hafeez, M.; Ashfaq, M.; Tahir, M. N.; Gil, D. M.; Galmés, B.; Hameed, S.; Frontera, A. Recurrent \( \pi \)–\( \pi \) stacking motifs in three new 4,5-dihydropyrazolyl-thiazole-coumarin hybrids: X-ray characterization, Hirshfeld surface analysis and DFT calculations. New J. Chem. 2020, 44, 14592–14603.

(36) Khalid, M.; Ali, A.; Tariq, J.; Tahir, M. N.; Aliabad, H. A. R.; Hussain, I.; Ashfaq, M.; Khan, M. U. Stabilization of Supramolecular Assembly of N-Substituted Benzylidene Acetohydrazide Analogs by Non-Covalent Interactions: A Concise Experimental and Theoretical Approach. ChemistrySelect 2020, 5, 10618–10631.

(37) Khalid, M.; Ali, A.; Haq, S.; Tahir, M. N.; Iqbal, J.; Braga, A. A. C.; Ashfaq, M.; Akhtar, S. U. H. O-4-Acetylamino-benzenesulfonylated pyrimidine derivatives: synthesis, SC-XRD, DFT analysis and electronic behaviour investigation. J. Mol. Struct. 2021, 1224, 129308.

(38) Ali, A.; Kuznetsov, A.; Khan, M. U.; Tahir, M. N.; Ashfaq, M.; Raza, A. R.; Muhammad, S. 2-Amino-6-methylpyridine based co-crystal salt formation using succinic acid: Single-crystal analysis and computational exploration. J. Mol. Struct. 2021, 1230, 129893.

(39) Turner, M. J.; McKinnon, J. J.; Jayatilaka, D.; Spackman, M. A. Visualisation and characterisation of voids in crystalline materials. CrystEngComm 2011, 13, 1804–1813.

(40) Shao, Y.; Molnar, L. F.; Jung, Y.; Kussmann, J.; Ochenfeld, C.; Brown, S. T.; Gilbert, A. T. B.; Slipchenko, L. V.; Levchenko, S. V.; O’Neill, D. P. Advances in methods and algorithms in a modern quantum chemistry program package. Phys. Chem. Chem. Phys. 2006, 8, 3172–3191.

(41) Becke, A. D. A new mixing of Hartree-Fock and local density-functional theories. J. Chem. Phys. 1993, 98, 1372–1377.

(42) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, non-covalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. Theor. Chem. Acc. 2008, 120, 215–241.

(43) Muhammad, S. Second-order nonlinear optical properties of diecophenazine and TTF derivatives: A butterfly effect of dimalononitrile substitutions. J. Mol. Graphics Modell. 2015, 59, 14–20.

(44) Muhammad, S. Quantum chemical design of triple hybrid organic, inorganic and organometallic materials: An efficient two-dimensional second-order nonlinear optical material. Mater. Chem. Phys. 2018, 220, 286–292.

(45) Kurtz, H. A.; Stewart, J. J. P.; Dieter, K. M. Calculation of the nonlinear optical properties of molecules. J. Comput. Chem. 1990, 11, 82–87.

(46) Sheldrick, G. M. A short history of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112–122.

(47) Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Crystallogr., C 2015, 71, 3–8.

(48) Farrugia, L. J. WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. 2012, 45, 849–854.

(49) Burnett, M.; Johnson, C. Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure; Illustrations, Oak Ridge National Laboratory Report ORNL-6895, Oak Ridge, TN, 1996.

(50) Spek, A. L. Structure validation in chemical crystallography. Acta Crystallogr., Sect. D: Biol. Crystallogr. 2009, 65, 148–155.

(51) Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P.; T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M.; Wood, P. A. Mercury 4.0: From visualization to analysis, design and prediction. J. Appl. Crystallogr. 2020, 53, 226–235.