Crystal Structure and Theoretical Investigation of Thiobarbituric Acid Derivatives as Nonlinear Optical (NLO) Materials

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Abstract: Here we report on the crystal structure of three enamine/imine TBA derivatives (1–3). Since the derivatives can take the form of enamine or imine tautomers, theoretical calculations were made to confirm that the former predominates due to higher stability (thermodynamic calculations). The enamines’ form was further corroborated by high activation energy ($\Delta G^\#$; which is $>60$ kcal/mol in all the cases), thus requiring a large amount of energy to pass the barrier (kinetics calculations). Furthermore, 1–3 were found to show high static hyperpolarizability ($\beta_{tot}$), thereby making them potential candidates as nonlinear materials for electro-optical devices and crystal engineering.

Keywords: crystals; Enamine/imine tautomer; DFT; NLO; hyperpolarizability

1. Introduction

Proper designing, or the development of new materials, requires accurate knowledge of molecular structure, which is accomplished by X-ray diffraction techniques [1–4]. Due to the interrelation of structure and application, accurate configuration plays a critical role [5]. Barbituric acid (BA) and thiobarbituric acid (TBA) derivatives have been known since the last century as pharmaceuticals [6]. These derivatives serve as antianxiety agents in the central nervous system by binding to the $\gamma$-aminobutyric acid (GABA) receptor. However, their potential as electro-optical materials has also been explored in crystal engineering [7–9]. Nonlinear optical (NLO) materials have found application...
in optical storage communications and optical computing systems [8,10]. The budding field of NLO research and application requires extensive exploration of new materials for a large variety of processes [11]. Organically based NLO materials offer several advantages over inorganic systems, including high electronic susceptibility, high molecular polarizability and fast response time [12]. Although noncentrosymmetric crystals have found application as NLO materials, there are also a few reports where centrosymmetric crystals have been shown to possess NLO properties [12–15]. In recent years, BA/TBA-based derivatives have also been studied as NLO materials as they hold both hydrogen bond donors and acceptors, a feature that makes them suitable as crystal engineering materials with specific programmed properties [7,12,16–20].

Our group has synthesized BA/TBA-based derivatives for application in chemical biology [21–23]. Here we report on the crystal structures of three enamine/imine TBA derivatives (Figure 1) and provide confirmation of the tautomers by theoretical calculations. We also evaluate the hyperpolarizability of these compounds and thus their potential use as NLO materials.

![ Structures of the three enamine/imine TBA derivatives 1–3.](image)

**Figure 1.** Structures of the three enamine/imine TBA derivatives 1–3.

### 2. Materials and Methods

#### 2.1. General

Compounds 1–3 were synthesized as reported by our group earlier [23]. Melting points and $^1$H NMR were in good agreement with the reported data. The X-ray crystallographic analysis was collected by using a Bruker SMART APEX II D8 Venture diffractometer (Karlsruhe, Germany) Gaussian09 (Wallingford, CT, USA) was used for theoretical calculations.

#### 2.2. Structure Determination

The title compounds were obtained as crystalline materials obtained by recrystallization from ethanol with slow evaporation at room temperature. Data were collected on a Bruker APEX-II D8 Venture area diffractometer, equipped with graphite monochromatic Mo K$_\alpha$ radiation, $\lambda$ = 0.71073 Å at 100 (2) K. Cell refinement and data reduction were carried out using the Bruker SAINT program [24]. SHELXS was used to solve structure [25]. The final refinement was carried out using full matrix least squares techniques with anisotropic thermal data for nonhydrogen atoms. All the C-bound H atoms were located with idealized geometry and refined with C–H = 0.95–1.00 Å having Uiso(H) = 1.2Ueq (CH$_3$) and 1.5Ueq (CH$_2$, CH, Aromatic-H). The N-bound H atoms were found in difference Fourier maps and their positions were freely refined with Uiso (H) = 1.2Ueq (N). CCDC 1967289, 1967290 and 1967294 contain the supplementary crystallographic data for these compounds and can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### 2.3. Theoretical Calculations

Based on the above crystal structures, a crystal unit was selected as the initial structure in each case. DFT-B3LYP/6–31G++(d,p) methods in Gaussian 09 [26] were used to optimize the structure of the title compounds. Vibration analysis showed that the optimized structure represented a minimum on the potential energy surface (no negative eigenvalues). TS calculations were performed using
the B3LYP functional and 6-311++G(d,p) basis set, and were confirmed by IRC calculations [27]. Static hyperpolarizability calculations were performed using the “polar” keyword in gaseous state and using the SCRF model. Methanol, chloroform and acetonitrile were used as solvents.

3. Results

All the derivatives (Figure 1) were synthesized earlier by our group and were well characterized by NMR and MS techniques [23].

3.1. Single Crystal X-ray Analysis

The single-crystal X-ray diffraction data of 1–3 were carried out by mounting suitable crystals for data collection. Data were collected on a Bruker D8 Venture equipped with a CCD Photon II detector and graphite monochromator with Cu Kα radiation (λ = 1.54178 Å) at T = 100 K. Data were integrated and reduced using the SAINT program [24]. Direct method and Fourier transformation techniques were used to solve the structures which were further refined by full matrix least squares techniques on F² using the SHELXL–2018 program (Table 1). Final refinement of the solved structures was carried out by means of the PLATON [28] and SHELXL programs [25]. The 3D structures were represented by an ORTEP diagram, while intermolecular interactions in the crystal packing were demonstrated by the Mercury program (Figure 2).

![Figure 2. The ORTEP view of compounds 1–3 drawn at 30% probability level.](image)

The structure of 1 was found to be similar to that of 3 with the difference being that, in the former, a pyridine ring (N1/C1-C5) was linked to 1,3-diethyl-2-thiobarbituric acid moiety (C7-C14/S1/N3-N4/O1-O2) via imine group (N2/C6) at C5 atom instead of N-methylmethanimine linkage. The dihedral angle between the pyridine ring (N1/C1-C5) and 1,3-diethyl-2-thiobarbituric acid moiety (C8-C15/S1/N3-N4/O1-O2) was 6.83(8)°, with a maximum deviation of 0.060(1) Å for N3 atom at r.m.s. plane.
Table 1. Summary of data collection and structure refinements of crystals 1–3.

| #  | 1                | 2                | 3                |
|----|------------------|------------------|------------------|
|    | Empirical formula | C₁₅H₁₈N₄O₂S     | C₁₅H₂₄N₄O₃S     | C₁₄H₁₆N₄O₂S     |
|    | Formula weight    | 318.39           | 340.44           | 304.37           |
|    | Temperature       | 100(2) K         | 100(2) K         | 173(2) K         |
|    | Wavelength        | 1.54178 Å        | 1.54178 Å        | 1.54178 Å        |
|    | Crystal system    | Triclinic        | Monoclinic       | Monoclinic       |
|    | Space group       | P − 1            | P 21/c           | P 21/n           |
|    | Unit cell dimensions |               |                  |                  |
|    | a = 4.8848(2) Å  | a = 9.7627(3) Å  | a = 11.3925(3) Å |
|    | α = 93.6450(10)° | α = 90°          | α = 90°          |
|    | b = 11.8126(4) Å | b = 19.5503(5) Å | b = 8.9642(3) Å  |
|    | β = 100.1890(10)°| β = 94.6850(10)°| β = 108.7440(10)°|
|    | c = 13.2589(4) Å | c = 8.9301(3) Å | c = 14.6437(3) Å|
|    | γ = 93.9350(10)° | γ = 90°          | γ = 90°          |
|    | Volume            | 748.99(5) Å³    | 1698.74(9) Å³    | 1416.17(7) Å³    |
|    | Z                 | 2                | 4                | 4                |
|    | Density (calculated) | 1.412 Mg/m³    | 1.327 Mg/m³      | 1.428 Mg/m³      |
|    | Absorption coefficient | 2.037 mm⁻¹   | 1.839 mm⁻¹       | 2.129 mm⁻¹       |
|    | F(000)            | 336              | 728              | 640              |
|    | Crystal size (mm³) | 0.170 × 0.040 × 0.020 | 0.170 × 0.120 × 0.070 | 0.160 × 0.140 × 0.090 |
|    | Theta range for data collection | 3.397 to 68.333° | 4.523 to 68.224° | 5.877 to 68.226° |
|    | Index ranges      | −5 ≤ h ≤ 5      | −11 ≤ h ≤ 11     | −13 ≤ h ≤ 13     |
|    |                   | −14 ≤ k ≤ 14    | −23 ≤ k ≤ 23     | −10 ≤ k ≤ 10     |
|    |                   | −15 ≤ l ≤ 15    | −10 ≤ l ≤ 10     | −17 ≤ l ≤ 17     |
|    | Reflections collected | 19056        | 22428            | 40991            |
|    | Independent reflections | 2729 [R(int) = 0.0636] | 3114 [R(int) = 0.0316] | 2593 [R(int) = 0.0381] |
|    | Completeness to theta = 67.679° | 100.0%        | 99.9%            | 99.6%            |
|    | Refinement method | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
|    | Data/restraints/parameters | 2729/0/203      | 3114/0/212       | 2593/0/196       |
|    | Goodness-of-fit on F² | 1.067           | 1.054            | 1.089            |
|    | Final R indices [I > 2σ(I)] | R₁ = 0.0598, wR₂ = 0.1802 | R₁ = 0.0323, wR₂ = 0.0846 | R₁ = 0.0353, wR₂ = 0.0881 |
|    | R indices (all data) | R₁ = 0.0652, wR₂ = 0.1868 | R₁ = 0.0347, wR₂ = 0.0866 | R₁ = 0.0359, wR₂ = 0.0885 |
|    | Largest diff. peak and hole | 0.622 and 0.737 and 0.396 and | −0.672 e.Å⁻³ and −0.240 e.Å⁻³ and −0.241 e.Å⁻³ |

The structure of 2 comprised a morpholine ring (C₁–C₄/O₁/N₁) in chair conformation linked to 1,3-diethyl-2-thiobarbituric acid moiety (C₈/C₁₅/S₁/N₃/N₄/O₂-O₃) via an N-ethylmethanimine chain (C₅-C₆/N₂) at the N₁ atom. The dihedral angle between the morpholine ring (C₁–C₄/O₁/N₁) and 1,3-diethyl-2-thiobarbituric acid moiety (C₈–C₁₅/S₁/N₃/N₄/O₂–O₃) was 89.96(7)°, with a maximum deviation of 0.245(1) Å for the O₁ atom at r.m.s. plane.
The structure of 3 was formed by a pyridine ring (N1/C1-C5) linked to 1,3-diethyl-2-thiobarbituric acid moiety (C8-C15/S1/N3-N4/O1-O2) via an N-methyleneamine chain (C6-C7/N2) at the C5 atom. The dihedral angle between the pyridine ring (N1/C1-C5) and 1,3-diethyl-2-thiobarbituric acid moiety (C8-C15/S1/N3-N4/O1-O2) was 3.48(10)°, with a maximum deviation of 0.025(2) Å for the N4 atom at r.m.s. plane.

3.2. Crystal Packing

In the crystal lattice of 1, molecules interact with each other in parallel chains via H7A···O2 with a donor-acceptor distance of 3.174(3) Å to form the R\textsuperscript{2}(10) ring motif. The π···π, C-O···π and C-H···π interactions further strengthen the crystal structure with a Cg1-Cg1 (N1/C1-C5) distance of 4.8848(14) Å, Cg1-Cg2 (N1/C1-C5 and N3/N4/C8-C11) distance of 5.0633(13) Å, Cg2-Cg2 (N3/N4/C8-C11) distance of 4.8847(12) Å, O1···Cg2 (N3/N4/C8-C11) distance of 3.6957(17) Å and H12B···Cg2 (N3/N4/C8-C11) distance of 2.99 Å, respectively (Table 2, Figure 3).

| D    | H   | A   | D-H  | H···A | D···A  | D-H···A |
|------|-----|-----|------|-------|--------|---------|
| C1   | H25 | O2  | 0.99 | 2.58  | 3.4464(18) | 146     |
| C5   | H6  | O1  | 0.95 | 2.60  | 3.4395(17) | 148     |
| C9   | H9  | O2  | 0.98 | 2.57  | 3.3370(18) | 135     |
| C15  | H20 | O3  | 0.99 | 2.40  | 3.3831(19) | 171     |

Symmetric codes: -X, 1/2 + Y, 1/2 – Z.

Table 2. The list of selected hydrogen bonds’ geometry Å in compound 1.

In the crystal lattice of 2, molecules are found to be connected in zigzag chains via H6···O1, H9···O2, H20···O3, H25···O2 with a donor-acceptor distance of 3.4395(17) Å, 3.3370(18) Å, 3.4395(17) Å and 3.4464(18) Å, respectively, to form a R\textsuperscript{2}(8) ring motif. The π···π and C-H···π interactions further strengthen the crystal structure with a Cg2-Cg2 (N3-N4/C6-C7/C10/C13) distance of 3.4573(7) Å and H19···Cg2 (N3-N4/C6-C7/C10/C13) distance of 2.91 Å, respectively (Table 3, Figure 4).

In the crystal lattice of 3, molecules are linked via H4···O1, H12A···O1, and H14C···O2 with a donor-acceptor distance of 3.3420(19) Å, 3.531(2) Å and 3.442(2) Å, respectively. The π···π, C-O···π and C-S···π interactions further strengthen the crystal structure with a Cg1-Cg1 (N1/C1-C5) distance of 5.6787(10) Å, Cg1-Cg2 (N1/C1-C5 and N3/N4/C7-C10) distance of 3.6959(9) Å, Cg2-Cg2 (N3/N4/C7-C10) distance of 3.9269(9) Å, O1···Cg1 (N1/C1-C5) distance of 3.9718(14) Å and S1···Cg1 (N1/C1-C5) distance of 3.7580(8) Å (Table 4, Figure 5).
Table 3. The list of selected hydrogen bond Å in compound 2.

|     |     |     | D-H | H···A | D···A | D-H···A |
|-----|-----|-----|-----|-------|-------|---------|
| C7  | H7A | O2  | 0.95| 2.28  | 3.174(3)| 156     |

Symmetric codes: -x, -y, -z.

Figure 4. Crystal packing diagram of compound 2.

Table 4. The list of selected hydrogen bond Å in compound 3.

|     |     |     | D-H | H···A | D···A | D-H···A |
|-----|-----|-----|-----|-------|-------|---------|
| C4  | H4  | O1  | 0.95| 2.40  | 3.3420(19)| 172     |
| C12 | H12A| O1  | 0.98| 2.58  | 3.531(2)  | 163     |
| C14 | H14C| O2  | 0.98| 2.58  | 3.442(2)  | 147     |

Symmetric codes: -x + 1/2, y + 1/2, -z + 1/2.

Figure 5. Crystal packing diagram of compound 3.
3.3. Hirshfeld Surface Analysis

Figure 6 shows the Hirshfeld surface mapped over $d_{\text{norm}}$ based on van der Waals radii of all three crystals. Dark blue indicates positive $d_{\text{norm}}$ values (contacts longer than the van der Waals radii), dark red indicates negative $d_{\text{norm}}$ values (contacts shorter than the sum of van der Waals radii) and white indicates zero values $d_{\text{norm}}$ (contact distances close to van der Waals). Figure 7 shows the percentage contribution of each bond in the molecule. The central sharp spike of the fingerprint plot corresponds to the H–H-type intermolecular interactions for 1–3, which was found to be 51.7%, 62.7% and 52.9% respectively. The O–H/H–O interactions in 1–3 (11.5%, 17.1% and 11.8% respectively) are shown by the large spikes on both sides. The percentage of contribution of C–H-type interactions in the total Hirshfeld surface in 1–3 in the total Hirshfeld surface is 15.6%, 5.9% and 6.6% respectively. Figure 7 shows the interhydrogen bonding pattern in the three crystals. The bond distances were found to be in good agreement with those of crystal data. Figure 8 shows the electronic cloud around the molecule along with interactions with the adjacent molecule. The red circles in each structure indicate areas of high hydrogen bonding, whereas the white circles indicate the weak van der Waals force of attraction.

![Fingerprint plot for compounds 1–3 showing percentages for all interactions and O–H, N–H and C–H contacts in the total Hirshfeld surface area.](image)

**Figure 6.** Fingerprint plot for compounds 1–3 showing percentages for all interactions and O–H, N–H and C–H contacts in the total Hirshfeld surface area.

![Percentage contribution of each interaction between atoms in 1–3.](image)

**Figure 7.** Percentage contribution of each interaction between atoms in 1–3.
3.4. Theoretical Calculations

Density functional theory (DFT) calculations were performed in the gaseous phase with the Gaussian 09 program, using the B3LYP correlation function and 6-311G++(d,p) basis set [26]. Geometry optimization was performed in the gaseous phase. No solvent corrections were made with these calculations as gaseous phase calculations frequently correspond well with crystal structures. Starting geometries were taken from X-ray refined data. The optimized geometry results in the free molecule state were compared to those in the crystalline state (Figure 9). No negative vibrational modes were obtained. The DFT calculated structure and geometric parameters (bond lengths and bond angles) were compared to those of X-ray data and were found to be consistent with the experimental data.
Frontier molecular orbitals (FMO) in all three cases were analyzed. The electron density in the HOMO for all cases was high over the thiobarbituric ring. However, electron density in LUMO was localized mainly on the pyridine ring in the case of 1 and 3. In 2, the density was localized throughout the thiobarbituric ring (Figure 10).

The HOMO–LUMO gap (which helps to predict the reactivity of the compound) was calculated for the three molecules (Table 5). The HOMO–LUMO gap in 3 (3.49 eV) was smaller than 1 (3.82 eV) and 2 (3.83 eV), thereby indicating its high reactivity [29].

|       | 1          | 2          | 3          |
|-------|------------|------------|------------|
| E<sub>total</sub> in Hartree | −1350.42096974 | −1429.26867147 | −1311.10670189 |
| E<sub>HOMO</sub> in Hartree   | −0.21654     | −0.21799     | −0.22352     |
| E<sub>LUMO</sub> in Hartree   | −0.07593     | −0.07714     | −0.09533     |
| ∆E * in Hartree (eV)          | 0.14061 (3.82)| 0.14085 (3.83)| 0.12819 (3.49)|

* ∆E = LUMO−HOMO; 1 Hartree = 27.2 eV

3.5. Transition State Calculations

A transition state (TS) is a first-order saddle point on the potential energy surface (PES) of the molecular system and it is characterized by one imaginary frequency (implying a negative force constant). One imaginary frequency implies that the energy has a maximum energy in one direction in nuclear configurational space, while in all other orthogonal directions the energy is a minimum [30].

The title compound(s) can exist in tautomeric form as shown in Figure 11. The crystal structures confirm that the molecules exist as I form.

To confirm the form, DFT calculations were made using the B3LYP functional and 6-311++G(d,p) basis set. All the thermodynamic parameters (∆H°, ∆S°, and ∆G°) were calculated at default temperature (298.15 K) and pressure (1 atm). The TS in all cases was confirmed by intrinsic reaction coordinate (IRC) calculations. Activation energy was calculated in all cases, as shown in Table 6 and schematically in Figure 12. The thermodynamic calculations reveal that form I was more predominant as compared to II in all cases, as indicated by large positive values of ∆H° and ∆G°. This finding was further confirmed by calculation of the TS in all cases. Figure 11 shows the higher stability of I (low energy) as compared to II (high energy). This observation also confirms that when a product is present...
in I form, it will not convert to II at room temperature as it would require high energy to pass the large activation energy barrier (ΔG°≠).

![Enamine (I) and Imine (II)](image)

Table 6. Calculated reaction profile using the 6-311G++(d,p) basis set.

| Properties | Compound | ΔH° (kcal/mol) | ΔG°≠ (kcal/mol/K) | ΔS° (cal/mol) |
|------------|----------|---------------|------------------|--------------|
| Thermodynamics | 1 | 24.2 | 23.4 | 3.0 |
| | 2 | 27.2 | 26.5 | 2.5 |
| | 3 | 26.8 | 25.5 | 4.5 |
| Kinetics | 1 | 60.8 | 60.5 | 1.1 |
| | 2 | 61.8 | 61.1 | 2.3 |
| | 3 | 64.3 | 63.7 | 2.1 |

#In case of Kinetics, ΔG°≠ refers to activation energy (ΔG°≠)

![Transition state for intramolecular conversion for all compounds 1–3](image)
3.6. NLO Calculations

The design of new NLO materials is dependent mainly on the synthesis of chromophores with large first or higher-order hyperpolarizabilities. The calculations of the dipole moment, linear and static first-order hyperpolarizability were performed using the 6-311G+(d,p) basis set and the following equations: employing Kleinmann symmetry, the third-rank tensor for hyperpolarizability has been described by 3D matrix and hence reduced to 10 components. The dipole moment, linear polarizability and first-order hyperpolarizability of the three derivatives were calculated by taking the Cartesian coordinate system at the centre of mass of the compound by a finite field of approach, and the results are shown in Table 7.

\[
\begin{align*}
\mu_0 &= \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \\
\alpha_0 &= \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \\
\beta_0 &= \sqrt{(\beta_{xxx} + \beta_{xyy} + \beta_{zzz})^2 + (\beta_{yyx} + \beta_{yzz} + \beta_{xzz})^2 + (\beta_{zxx} + \beta_{xzy} + \beta_{yzz})^2 + (\beta_{zyy} + \beta_{yyz} + \beta_{zzx})^2} \\
\end{align*}
\]

Table 7. Dipole moment, linear polarizability and static hyperpolarizability components in gaseous state.

| Parameter | Gaseous | Chloroform | Methanol | Acetonitrile |
|-----------|---------|------------|----------|-------------|
| $\mu_x$   | -7.40   | 5.22       | 5.78     | 11.82       |
| $\mu_y$   | -1.35   | -2.70      | 1.92     | -2.10       |
| $\mu_z$   | 0.41    | 0.48       | 0.34     | 0.24        |
| total ($\mu$) | 7.53    | 5.90       | 6.10     | 10.04       |
| $\alpha_{xx}$ | -123.63 | -163.28    | -112.49  | -119.27     |
| $\alpha_{yy}$ | -138.94 | -150.12    | -132.80  | -137.75     |
| $\alpha_{zz}$ | -136.63 | -142.71    | -133.62  | -137.91     |
| $\alpha_{xy}$ | 3.23    | -10.22     | 5.78     | 4.12        |
| $\alpha_{xz}$ | -9.15   | -1.02      | 1.15     | -8.78       |
| $\alpha_{yz}$ | 2.38    | 1.94       | 0.13     | 2.72        |
| $\alpha_{tot}(\text{esu}) \times 10^{-23}$ | 1.97    | 2.25       | 1.87     | 1.95        |
| $\beta_{xxx}$ | -237.61 | 21.77      | 282.13   | -339.44     |
| $\beta_{xyy}$ | 31.96   | 17.08      | 23.85    | 34.02       |
| $\beta_{zzz}$ | -5.15   | -1.91      | -0.88    | -6.16       |
| $\beta_{xyy}$ | -26.81  | 44.25      | -2.89    | -43.30      |
| $\beta_{zzz}$ | -38.97  | -100.23    | -5.76    | -58.43      |
| $\beta_{tot}(\text{esu}) \times 10^{-31}$ | 5.39    | 0.11       | 1.00     | 53.85       |

The calculation was initially performed in gaseous state. Furthermore, to analyze the effect of solvents, three solvents; namely, methanol, chloroform and acetonitrile, were chosen. Methanol and acetonitrile are polar protic and polar aprotic solvents respectively, whereas chloroform is nonpolar [11,31]. Dielectric constant plays a crucial role in determining NLO properties [11,32]. Although acetonitrile and methanol showed different behaviors, their dielectric constant was comparable (37.5 for acetonitrile and 33 for methanol). However, the dielectric constant of chloroform was only 4.8. According to the literature, the higher the dielectric constant, the better the NLO properties. Static hyperpolarizability ($\beta_{tot}$) in all cases was comparable for methanol and acetonitrile, which in turn were higher than that of chloroform (Table 8). The $\beta_{tot}$ in all cases was higher than that of urea (0.3728 $\times 10^{-30}$ esu), which, as an NLO material [33], is considered a reference for comparison. Theoretical calculations also support the relevance of solvents in NLO properties, as these properties increased from gaseous to solvent (Table 8). Of the three derivatives, compounds 1 and 3 showed potential as NLO materials, due to their high $\mu_{tot}$ and $\beta_{tot}$ and small band gap, as reflected by the frontier orbitals.
Table 8. Comparison of dipole moment ($\mu_{\text{tot}}$) and static hyperpolarizability ($\beta_{\text{tot}}$) in three solvents.

|           | $\mu$ ($\times 10^{-30}$ esu) | $\beta$ ($\times 10^{-30}$ esu) |
|-----------|-------------------------------|----------------------------------|
|           | 1    | 2         | 3     | 1 | 2 | 3     |
| Gaseous   | 7.53 | 5.90      | 6.10  | 2.96 | 1.38 | 2.40 |
| Acetonitrile (ACN) | 11.02 | 8.57 | 8.93 | 4.10 | 2.07 | 3.36 |
| Chloroform (CHCl$_3$) | 10.04 | 7.73 | 10.01 | 3.76 | 1.84 | 3.09 |
| Methanol (MeOH)         | 11.62 | 8.57 | 8.92 | 4.09 | 2.07 | 3.36 |

* $\beta = 6-311G++(d,p)$.

4. Conclusions

In summary, we report here the crystal structures of three enamine/imine TBA derivatives (1–3). These derivatives are known to exist in several tautomeric forms. In the enamine and imine equilibrium, the former predominates due to high stability (as confirmed by thermodynamics calculations using DFT). The equilibrium is highly favourable towards enamine. This was further confirmed by TS calculations, as the activation energy is very high, thus requiring a large amount of energy to pass the barrier ($\Delta G^* \geq 60$ kcal/mol in all the cases). Due to their hydrogen bond donors and acceptor properties, NLO calculations were performed. Enamine/imine TBA derivatives (1–3) all showed high static hyperpolarizability ($\beta_{\text{tot}}$). The solvent effect on $\beta_{\text{tot}}$ was also studied. It was found that the high dielectric constant of solvents contributes to the NLO properties of the derivatives, thereby making them potential candidates as nonlinear materials for electro-optical application in crystal engineering.

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