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Spectral, optical, thermal, Hirshfeld, antimicrobial studies and computational calculations of a new organic crystal, 1*H*-benzo[*d*]imidazol-3-ium-3,5-dinitrobenzoate

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ABSTRACT

Single crystals of 1*H*-benzo[*d*]imidazol-3-ium-3,5-dinitrobenzoate (BDNB) were grown by reacting 3,5-dinitrobenzoic acid and benzimidazole by slow evaporation method. UV–Vis–NIR spectral studies of the BDNB show that the crystal is excellently transparent in entire visible region. Chemically and magnetically equivalent protons in BDNB were identified by ^{1}H NMR technique. The carbon frame work of the molecule was established by ^{13}C NMR spectroscopy. Proton transfer mechanism was confirmed by the presence of $N^{+}H$ group in BDNB by FT-IR spectroscopic technique. TG/DTA analyses confirmed that the crystal is stable up to172 °C. Single crystal XRD analysis was carried out to ascertain the molecular structure and the crystal belongs to monoclinic system with space group $P2_1/c$. Computational studies that include optimization of molecular geometry, natural bond analysis, Mulliken population analysis and HOMO-LUMO analysis were performed using B3LYP method at 6–31 g level. The low HOMO-LUMO energy gap of BDNB confirms high reactivity of BDNB. Hirshfeld analysis expose that O···H/H···O interactions are the prominent interactions. Theoretical calculations indicate that first order hyperpolarizability is 16 times greater than urea. The results show that the BDNB may be used for opto-electronic applications. The antimicrobial and antioxidant analyses shows concentration of the compound increases inhibition activity also increases.

1. Introduction

Organic materials are attractive due to their inherent electronic and optical properties associated with their molecular structure that can be easily modified depending upon their needs. Of late, the growth of organic single crystals has gained much importance for the fabrication of technologically important devices [1–4]. Organic molecular network is due to the presence of numerous hydrogen atoms and certain electronegative atoms which bring about ionic, covalent and non covalent interactions. Hydrogen bonding is one such noncovalent interaction which is responsible for good crystal packing and self-assembly of molecular units that can be exploited in designing of new crystals with specific physical and chemical properties [5–8]. It also plays a vital role in chemical, catalytic and biochemical processes as well as in supramolecular chemistry [9–11]. The design and construction of multi-component supramolecular arrays utilizing hydrogen bonding is one of the rapidly developing areas in supramolecular synthesis [12]. Organic molecules with salt like structures have attracted attention of crystal researchers in recent years [13,14] because of the presence of ionic centers which can be exploited to alter and optimize physical properties such as crystalline form, solubility and stability of crystals [15]. Nitrogen containing heterocyclic compounds exhibit diverse biological and pharmacological activities [16,17]. Specifically, benzimidazole nucleus is a constituent of several natural products [18,19] which is a crucial pharmacophore in drug discovery. Pharmaceutical properties including antimicrobial [20] anti-bacterial, anti-fungal, anti-viral, anti-inflammatory [21] anticonvulsant, anti-depressant, anti-hypertensive, analgesic, and hypoglycemic properties [22] are unique characteristics known for benzimidazole derivatives. Benzimidazole is not only useful in the pharmaceutical industry but also in several other fields such as agricultural, electronic, and polymer chemistry [23]. An organic Lewis acid 3,5-dinitrobenzoic acid possessing both electron donor group (carboxyl) and electro acceptor groups (nitro) is an excellent molecule to be coupled with Lewis bases like benzimidazole and

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their derivatives to demonstrate ionic environment which can build excellent hydrogen bond network. The presence of electron-pulling moieties like nitro group not only develops the essential diversity in chemical and biological functionality but also attributed to the defiance of these compounds towards possible biodegradation [24]. Numerous reports are also available to establish hydrogen bonded assembly increases the hyperpolarizability in the crystals [25–28]. However, investigations on organic systems synthesized from benzimidazole, a Lewis base and 3,5-dinitrobenzoic acid, a Lewis acid are scarce in literature.

In this paper, we report for the first time structural and spectral characterizations and computational calculations of a new organic molecular crystal, 1H-benzo[*d*]imidazol-3-ium 3,5-dinitrobenzoate (BDNB) synthesized by proton transfer mechanism and their possible optical and biological applications. .

2. Experimental work

2.1. Synthesis

1H-benzo[*d*]imidazol-3-ium-3,5-dinitrobenzoate (BDNB) was synthesized by mixing 1:1 M proportions of benzimidazole and 3,5-dinitro benzoic acid in methanol. The resultant yellow precipitate was re-dissolved in acetone: methanol (1:1) solvent mixture and the solution was allowed to evaporate at room temperature without any mechanical disturbance. In about 12 days, well defined, transparent and yellow coloured crystals were harvested. The crystals were purified by repeated recrystallization using the same solvent mixture. The reaction scheme is given in below (see Scheme 1).

2.2. Physico-chemical characterization of BDNB

Elemental analyses (CHN) were performed on a flash EA 1112 fully automatic trace element analyzer. Experimental and calculated values for BDNB are: Experimental: C = 50.86%; H = 3.12%; N = 16.85%; Found: C = 50.92%; H = 3.05%; N = 16.96%. The FT-IR spectrum of BDNB was recorded in the region 4000-400 cm^{-1} using a JASCO FT/IR 5300 infrared spectrometer. The FT-IR wave numbers (cm^{-1}) of selected bands are: υ = 3415 (N–H), 3100 (N$^+$H), 2788 (Ar-H), 1698 (COO$^-$)asy, 1433 (COO$^-$)sy, 1536 (NO_2)asy, 1343 (NO_2) sy, 1299 (C–C), 1286 (C–N) and 844 (C–N(NO_2)). The FT-IR spectrum is given in Fig. S1. ^{1}H and ^{13}C NMR spectroscopic data were recorded on a Bruker Avance 400 MHz FT-NMR instrument with tetramethylsilane (TMS) as an internal standard using DMSO-d_6 solvent. DEPT-135 technique was used to assign –CH protons in the compound unambiguously.^{1}H NMR chemical shifts δ (in ppm) of various protons are: 12.1 (s, NH), 8.8 (s, for both H1 & H3), 8.9 (s, H2), 8.4 (s, H4) 7.6 (d, J = 8 Hz, H8 & H5) and 7.2 (t, J = 4 Hz, H7 & H6). The chemical shifts (δ ppm) in ^{13}C NMR are: 164 (COO$^-$), 137 (C1), 129 (C2 and C6), 148 (C3 and C5), 115 (C4), 142 (C8), 136 (C9 and C14), 125 (C12 and C11), and 124 (C13 and C10). DEPT-135 spectral data (δ ppm): 142 (C8–H), 129 (C6–H), 123 (C13–H & C10–H), 122 (C11–H &C12–H) and 115 (C4–H). The ^{1}H and ^{13}C NMR spectra are given in Fig. 1 and the DEPT NMR spectrum of BDNB is given in Fig. S2.

3. Results and discussion

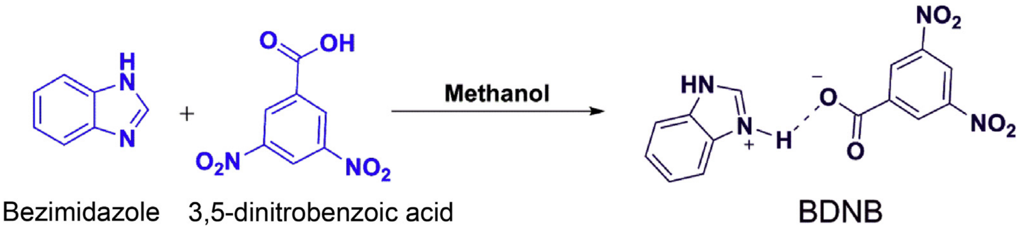
3.1. Single crystal XRD analysis

Single crystal data were collected using Bruker SMART-APEX CCD diffractometer equipped with a graphite monochromator and fine focused sealed tube at 25 °C using Mo Kα radiations (0.71073 Å). The data were reduced using CrysAlis$^{\text{Pro}}$ software and the absorption correction was done using multi Ψ-scans. Structure was solved using SHELXS-97 and refined by full-matrix least squares against F^2 using SHELXL-97 software [29]. Non-hydrogen atoms were refined with anisotropic thermal parameters. BDNB belongs to monoclinic crystal system. The lattice parameters are a = 9.389(5) Å, b = 11.807(6) Å, c = 13.326(7) Å, α = 90.00°, β = 94.824(10)°, γ = 90.00° and the unit cell volume is 1472.1(13) Å^3. The crystallographic refinement data of BDNB is given in Table 1.

The asymmetric unit contains one 1H-benzo[*d*]imidazol-3-ium-cation and one 3,5-dinitrobenzoate anion. The ORTEP plot of BDNB is shown in Fig. 2a. The mono positive charge of 1H-benzo[*d*]imidazol-3-ium- moiety is compensated by mono negative charge of the benzoate anion. In the crystal, the benzimidazolium cation and benzoate anion are linked through N–H···O hydrogen bonds and weak C–H···O interactions, forming a three dimensional supramolecular structure. The 3,5-dinitrobenzoate anion interacts with neighboring 3,5-dinitro benzoate anions through O2···O4 (2.919 Å) and O2···N2 (2.878 Å) interactions. Benzimidazole cation makes short contacts with 3,5- dinitrobenzoate anion through N3···O1 (3.069 Å) and N3···O5 (2.677 Å). The loss of carboxyl proton at the O5 creates specific electron delocalization around C7.

The strong hydrogen bonding interactions, N3–H9···O5 (2.677 Å) and N4–H10···O5 (2.723 Å) create supramolecular synthon and the hydrogen bond details are given in Table 2. The H6 atom of benzimidazole forms bifurcated hydrogen bonding (C11–H6···O4 (3.268 Å) and C11–H6···O1 (3.376 Å)) with O atom of nitro group in 3,5 dinitrobenzoate moiety. Another interesting supramolecular hetrosynthon was observed between cation and anions, through weak C8–H4···O6 (3.065 Å) and C13–H8···O3 (3.416 Å) interactions. Hydrogen bonding interactions and packing diagram of BDNB crystal is shown in Fig. 3. The hydrogen bonds, N3–H9···O5 and C10–H5···O6 generate a ring motif $R_2^2(8)$. The crystal packing of BDNB is further stabilized by the π-π interactions between aromatic rings. In the imidazole cation, the C–N bond lengths are 1.322 Å (N3–C8) and 1.317 Å (N4–C8) which are shorter than the normal C=N bond length (1.270 Å) and longer than the normal C–N bond length (1.450 Å) which prove the electron delocalization in imidazole ring.

Due to electron richness in both benzene ring and carboxylate groups, there exists a repulsion leading to reduction in bond angle C6–C1–C2 (119.4°) compared to planar triangular bond angle



Scheme 1. Synthesis of BDNB.