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# Spectroscopic, Hyperpolarizability and Optical Properties of Nbenzyl-2-methyl-4-nitro aniline (BNA) Single Crystal

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#### Abstract

N-benzyl-2-methyl-4-nitro aniline (BNA) has been investigated with the help of B3LYP density functional theory with 6-31 G (d, p) basis set. Fourier transform infrared Spectrum identifies the various functional groups. The theoretical frequencies showed very good agreement with experimental values. Optical characterization was done by UV-Vis techniques. HOMO and LUMO energies were calculated which reveal the transfer of charge within the molecule. SHG and DFT calculations predicted first order hyperpolarizability of BNA as 0.225355 x 10<sup>-30</sup>esu, which suggests that the title compound is an attractive material for nonlinear optical applications.

**Keywords:** BNA, B3LYP6-31 G (d, p), HOMO and LUMO, SHG, DFT, hyperpolarizability

#### 1. Introduction

Nonlinear optics, referring to spatially and temporally simultaneous mixing process of multiphotons in materials, has attracted a lot of interest in several applications, such as optical frequency or phase modulation, or spectroscopic techniques for probing photo-chemical reactions [1–4]. So far, a lot of inorganic and organic nonlinear optical materials have been developed with large nonlinear optical susceptibility [3]. Among them, 2-methyl-4nitroaniline (MNA) has been known as a prominent organic nonlinear optical material. Recently, we developed the N-benzyl MNA (BNA) with a sufficiently large second harmonic activity and applicability of practical use [5]. BNA is a derivative of MNA, where an amino group is substituted into a benzyl group. Condensation of primary amines with aldehydes or ketones yields Schiff bases containing imine (CaN) function group [6]. Some of these compounds donor-acceptor are benzene derivatives, which can conform conjugated pelectron systems easily, and they are known to exhibit extremely large second order optical nonlinearities, such as 4-nitro-40-methyl benzylidene aniline (NMBA) [7], 4-nitro-40-methoxy benzylidene aniline (NMOBA) [8], N-2-[30-(methoxysalicylideneimino) benzvl]-300methoxysalicylideneimine [9]. Organic crystals in terms of non-linear optical property possess advantages when compared to their inorganic counterparts, and they have larger structural diversity [10], so the preparation of this kind of materials has gained increasing importance. With the advance of quantum chemistry method and high performance computers, the structures of some organic compounds can be theoretically predicted in high accuracy. Density functional theory (DFT) method has recently been successfully applied to investigate the structures and predict properties of some compounds [11,12]. The present work deals with the growth and detailed spectral investigation of BNA.



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#### 2. Synthesis of BNA

The primary amine (aniline) and substituted amine (2-methyl-4-nitro aniline) were used to prepare N-benzyl-2-methyl-4-nitro aniline. The sample was synthesized from aqueous methanol. Using methanol, the BNA ingredients were highly purified by several recrystallization processes to exclude impurities. The photograph of the crystal is shown in Figure 1

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Figure 1. Photograph of as grown BNA crystal

#### 3. FT-IR Analysis

FT-IR spectrum of the grown crystal was recorded in the range 500 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>, using KBr pellet technique on BRUKKER IFS FT-IR Spectrometer. For comparison, the experimental FT-IR and theoretically simulated spectra were presented in Figure 2 and 3.

The analysis of the vibrational spectra is based on the observed and computed wave numbers. The theoretical and experimental wave numbers are in fair agreement and the assignments of wave numbers for different functional groups are discussed below. The heteroaromatic structure shows the presence of C-H stretching vibration in the region 3100–3000 cm<sup>-1</sup> [13,14]. This is the characteristic region for the ready identification of C-H stretching vibration. In this region, the bands are not affected appreciably by the nature of the substitutions. The expected C-H stretching vibrations appeared at 3212 cm<sup>-1</sup> in FT-IR spectrum. computed Theoretically C–H vibrations bv B3LYP/6-31G(d,p) method at 3230 cm<sup>-1</sup> show good agreement with recorded spectrum.



Figure 2. Experimentally obtained FT-IR spectrum of BNA



Figure 3. Theoretically simulated FT-IR spectrum of BNA

There are six equivalent C-C bands in benzene and one band in outside of the ring and consequently there will be seven C-C stretching vibrations. In general, the bands around 1650-1300 cm-1[15,16] in benzene derivatives are assigned to skeletal stretching C-C bands. The title compound posses C-C stretching occurs at 1508 cm-1in experimental and its well matched with theoretical value. And the 1534, 1538, 1549 cm<sup>-1</sup> shows the C-C stretching modes of vibrations.

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The title molecule under investigation possess five NH<sub>2</sub> group and six internal modes of vibrations for NH2group as, the symmetric (sy st) and asymmetric stretchings (asy st), the symmetric planar deformation or scissoring ( $\beta_s$ ), the antisymmetric planar deformation or rocking ( $\beta_{as}$ ), the symmetric non-planar deformation or wagging  $(\omega)$  and the anti-symmetric non-planar deformation or torsion ( $\tau$ ). The NH<sub>2</sub> group has five N–H stretching vibrations, one being asymmetric (asy st) stretching modes. The NH<sub>2</sub> asymmetric stretching vibrations give rise to a strong band in the region 3390±60cm<sup>-1</sup> and the Assignment shows The NH<sub>2</sub> asymmetric occurs in IR spectrum at 3470 and theoretically at 3450 cm<sup>-1</sup> this shows that both value are matched with the literature value.

#### 4. Optical absorption spectrum

The UV-Vis spectral analysis of the crystal is recorded between 200 and 1200 nm using a Varian Cary 5E UV-VIS-NIR spectrometer. The absorption spectrum obtained is shown in Figure 4 When absorbance is monitored from longer to shorter wavelength, the absorbance is less and almost insignificant between 500 and 1200 nm, which may be important for the materials possessing NLO properties. At the wavelength just above 500 nm, there is a sudden increase in absorbance in the crystal due to the electronic excitation, since the crystal has a delocalized electronic cloud it shows less absorbance between 500 and 1200 nm. Hence, it may be well suited for second harmonic generation devices. The band gap was also studied and the value of the band for BNA is 4.03 eV. Its shows in the Figure 5.



Figure 4. Optical absorption spectrum of BNA crystal



Figure 5. Optical band gap of BNA crystal

## 5. HOMO-LUMO Analysis

Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the main orbital take part in chemical stability. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO energy calculated by B3LYP/6-31G (d, p) method as shown below: HOMO energy (B3LYP) = -0.21711a.u LUMO energy (B3LYP) = -0.07806a.u HOMO-LUMO energy gap (B3LYP) = -0.13905a.u

The HOMO is located over the phenyl ring and the carboxylic acid group attached to the phenyl ring.



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The HOMO→LUMO transition implies an electron density transfer to the carboxylic acid group from phenyl ring. Moreover, these the orbital significantly overlap in their position for BNA (Figure 6). The HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule.



Figure 6. HOMO – LUMO plot of BNA molecule

## 6. Hyperpolarizability studies

Interests in organic optoelectronic materials and devices have motivated experimental and theoretical studies of molecular structures with enhanced hyperpolarizabilities. [17] Molecules with electronic asymmetry, or "push-pull" donorbridge-acceptor electronic framework, have been demonstrated to have large first hyperpolarizabilities ( $\beta$ ) [18]. The first static hyperpolarizability ( $\beta_0$ ) the electric dipole moment µ of the BNA are calculated by finite field method using B3LYP/6-31G (d,p) level The basis sets. calculated first hyperpolarizability of BNA is0.225355 x 10<sup>30</sup>esu. The calculated first hyperpolarizability components are and Dipole moments were given in Table 1 and 2.

Table1. Hyperpolarizability of BNA in esu				
	β <sub>xxx</sub> -28.1633958			
	β <sub>xxy</sub>	12.3885477		
	β <sub>xyy</sub>	5.5313826		
	βууу	27.4244763		
	β <sub>xxz</sub>	133.0376559		
	$\beta_{xyz}$	-16.9692876		
	$\beta_{yyz}$	47.6005725		
	$\beta_{xzz}$	16.3511383		
	β <sub>yzz</sub>	-162.4658587		
	β <sub>zzz</sub>	-2873.2795683		
	$\beta_{tot}$	0.225355 x 10-30		

Table 2. Dipole Moments of BNA in debye

μx	-7.8978	
<b>μ</b> γ	1.1999	
μz	1.0547	
$\mu$ tot	8.0578	

## 7. Conclusion

Good optical quality bulk single crystal of BNA has been grown successfully by slow evaporation growth technique. (DFT) computations of BNA molecule calculated by DFT (B3LYP) level with 6-31G (d,p) basis set gives the optimized structure. The optical properties of the grown crystal were evaluated from the absorption spectrum. Theoretical and experimental IR spectroscopic analyses were carried out and the presence of functional groups in BNA molecule was qualitatively analyzed. HOMO-LUMO analysis reveals the molecular energy gap. SHG and DFT calculations predicted first order hyperpolarizability of BNA as 0.225355 x 10-30esu, which suggests that the title compound is an attractive material for non-linear optical applications.



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