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Synthesis, molecular structure, spectral analysis and nonlinear optical studies on 4-(4-bromophenyl)-1-tert-butyl-3-methyl-1H-pyrazol-5-amine: A combined experimental and DFT approach

Ömer Tamer [a], Barış Seçkin Arslan [b], Davut Avcı [a, *], Mehmet Nebioğlu [b], Yusuf Atalay [a], Bünyemin Çoşut [c]

[a] Sakarya University, Department of Physics, Arts and Sciences Faculty, 54187 Sakarya, Turkey
[b] Sakarya University, Department of Chemistry, Arts and Sciences Faculty, 54187 Sakarya, Turkey
[c] Gebze Technical University, Department of Chemistry, 41400 Gebze, Kocaeli, Turkey

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ABSTRACT

4-(4-bromophenyl)-1-tert-butyl-3-methyl-1H-pyrazol-5-amine (BPTBMPA) crystal was synthesized for the first time and its structural characterization was performed by X-ray diffraction method. The spectroscopic characterization was also performed by the applying of FT-IR, UV–Vis, ^{1}H and ^{13}C NMR spectroscopies. In order to support experimental results, density functional theory calculations have been performed. All of the obtained theoretical results are in a perfect agreement with the experimental ones. The negative HOMO and LUMO energies demonstrated that the molecular structure of BPTBMPA is stable. The small energy gap between the HOMO and LUMO is an indicator of intramolecular charge transfer which is responsible for nonlinear optical properties. Natural bond orbital analysis also indicates the presence of molecular charge transfer within BPTBMPA. Obtained chemical hardness parameter demonstrates that BPTBMPA has considerable electron donor groups. Finally, it has been showed that BPTBMPA exhibits considerable nonlinear optical properties.

1. Introduction

Pyrazoles and its derivatives, a class of well-known nitrogen heterocycles, have attracted considerable interest in the pharmaceutical and agrochemical industries because of their diverse biological activities, such as, anti-inflammatory [1], antiviral [2], antimicrobial [3], anticonvulsant [4], antitumor [5], fungicidal activities [6] and antihistaminic [7]. As pyrazole derivatives rarely exist in nature, probably, due to the difficulty in the construction of N–N bond by living organisms, their availability particularly depends on the synthetic methods [8]. One of the most important derivatives of pyrazoles is 5-aminopyrazoles and their chemistry has been reviewed several times recently [9–12]. The most versatile method available for the synthesis of 5-aminopyrazoles involves the condensation of β-ketonitriles with hydrazines.

Besides of the well-known biological activities, pyrazoles derivatives substituted with electron donor and acceptor groups exhibit considerable nonlinear optical properties [13–15].

Up to now, a number of new organic crystals have been discovered with the aid of experimental and computational molecular engineering approaches and shown to have potential applications in nonlinear optics. But, in order to satisfy day to day increasing technological requirements, the search for new NLO materials has been still receiving great interest. It is well known that NLO properties of organic molecules depend on the intermolecular charge transfer [16–18]. At the same time, the molecular hydrogen bonding has been found to play an important role in adjusting NLO properties. Additionally, the substitution of conjugated π system with appropriate donor acceptor groups increase the asymmetric charge distribution in the ground state and excited state, and this leads to improve NLO properties [19,20]. So, 4-(4-bromophenyl)-1-tert-butyl-3-methyl-1H-pyrazol-5-amine (BPTBMPA) molecule, which is an substituted pyrazole, has been considered as an interesting molecule due to the presence of pyrazole ring, electron donor NH_2 and CH_3 groups and Cl atom. Therefore, BPTBMPA may be exhibit considerable NLO properties.

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* Corresponding author.
E-mail address: davci@sakarya.edu.tr (D. Avcı).

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In this paper, we have synthesized BPTBMPA crystal for the first time and its crystal structure has been characterized by X-ray diffraction method. The spectroscopic properties of BPTBMPA have been evaluated by the applying of FT-IR, NMR and UV–Vis spectroscopies as well as density functional theory (DFT) calculations. Additionally, natural bond orbital analysis and the investigations of NLO properties for BPTBMPA have been performed by DFT method.

2. Experimental details

2.1. Synthesis of 4-(4-bromophenyl)-1-tert-butyl-3-methyl-1H-pyrazol-5-amine

To a solution of 2-(4-bromophenyl)-3-oxobutanenitrile **1** (2 mmol, 0.476 g) and tert-butylhydrazine hydrochloride (1.2 eq., 0.299 g) in toluene (10 mL) was added acetic acid (% 10 mol, 0.0115 mL) and the mixture was heated to reflux temperature for 5 h. The synthesis scheme for BPTBMPA was presented in Fig. 1. After completion of the reaction as monitored by TLC, the solvent was removed under reduced pressure. To this crude concentrate, water was added and extracted into ethyl acetate. The organic layer was dried over anhydrous sodium sulphate, concentrated under reduced pressure to give crude **2**. It was crystallized from methanol and yielded 81% (colorless crystals, mp 161–162 °C).

2.2. Instrumentation

FT-IR spectrum for BPTBMPA was recorded on a Perkin–Elmer FT-IR spectrophotometer at the region of 4000–600 cm^{-1}. ^{1}H and ^{13}C NMR spectra were measured on a Varian Infinity Plus spectrometer at 300 and 75 Hz, respectively. ^{1}H and ^{13}C chemical shifts are referenced to the internal deuterated solvent. The UV–vis absorption spectrum was examined in the range 200–800 nm using a Shimadzu UV-2600 spectrophotometer in dichloromethane solvent.

2.3. X-ray crystal structure determination

The solid-state structure of BPTBMPA has been confirmed by X-ray diffraction analysis. Data have been obtained with Bruker APEX II QUAZAR three-circle diffractometer. Indexing was performed using APEX2 [21]. Data integration and reduction were carried out with SAINT [22]. Absorption correction was performed by multi-scan method implemented in SADABS [23]. The Bruker SHELXTL [24] software package was used for structure solution and structure refinement. All non-hydrogen atoms were refined anisotropically using all reflections with I > 2σ(I). Aromatic C-bound H atoms were positioned geometrically and refined using a riding mode. Crystallographic data and refinement details of the data collection for BPTBMPA are given in Table 1. The selected bond lengths and bond angles are given in Table 2. Final geometrical calculations were performed using PLATON software [25]. MERCURY software [26] was used for visualization of the cif files. The important conditions for the data collection and the structure refinement parameters of BPTBMPA are also given in Table 1.

Table 1
Crystal data and refinement parameters for BPTBMPA.

CCDC	
Empirical Formula	$C_{14}H_{18}BrN_3$
Formula weight (g.mol^{-1})	308.22
Temperature (K)	173 (2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	5.9314(10)
b (Å)	20.050(3)
c (Å)	11.8114(16)
α(°)	90
β(°)	96.169(11)
γ(°)	90
Crystal size (mm)	0.345 × 0.109 × 0.107
V (Å3)	1396.5(4)
Z	4
Density (g/cm3)	1.446
μ (mm−1)	2.930
F(000)	632
θ range for data collection (°)	2.03–26.73
h/k/l	−7/6, −23/25, −14/14
Reflections collected	12537
Independent reflections	2964 [R(int) = 0.0840]
Absorption correction	multi-scan
Data/restraints/parameters	2964/2/173
Goodness-of-fit on F2 (S)	1.038
Final R indices [I > 2σ(I)]	R1 = 0.0358, wR2 = 0.0877
R indices (all data)	R1 = 0.0499, wR2 = 0.0936
Largest diff. peak and hole (e.Å−3)	0.437 and −0.757

Table 2
The experimental and theoretical bond lengths (Å) and angles (°) for BPTBMPA.

Bond lengths	X-ray	HSEH1PBE	Bond angles	X-ray	HSEH1PBE
Br1–C1	1.909(3)	1.898	C6–C1–C2	121.7(2)	120.7
C1–C6	1.369(4)	1.387	C6–C1–Br1	118.7(2)	119.6
C1–C2	1.378(4)	1.389	C1–C2–C3	118.7(3)	119.4
C2–C3	1.384(4)	1.388	C3–C4–C13	122.3(2)	121.4
C3–C4	1.394(4)	1.401	C1–C6–C5	118.9(2)	119.2
C4–C5	1.397(3)	1.402	N2–C7–C10	110.1(2)	109.7
C4–C13	1.474(3)	1.461	N2–C7–C9	108.0(2)	108.8
C5–C6	1.385(4)	1.389	C10–C7–C9	111.7(2)	111.5
C7–N2	1.485(3)	1.480	N2–C7–C8	108.6(2)	109.4
C7–C10	1.518(4)	1.532	N3–C12–C13	111.7(2)	111.3
C7–C9	1.521(4)	1.531	N3–C12–C11	120.0(2)	120.1
C7–C8	1.524(4)	1.526	C14–C13–C12	104.6(2)	104.0
C11–C12	1.490(4)	1.490	C14–C13–C4	126.7(2)	126.6
C12–N3	1.330(3)	1.316	C12–C13–C4	128.7(2)	129.4
C12–C13	1.404(4)	1.418	N2–C14–N1	123.9(2)	124.2
C13–C14	1.384(3)	1.392	N2–C14–C13	107.8(2)	107.3
C14–N2	1.348(3)	1.356	C14–N2–N3	110.9(2)	111.1
C14–N1	1.381(3)	1.390	C14–N2–C7	129.4(2)	129.0
N2–N3	1.381(3)	1.356	C12–N3–N2	105.0(2)	106.3
R^2		0.99202			0.99292

3. Computational details

All of the calculations for BPTBMPA have been performed by using Gaussian 09 Rev: D.01 program [27], and the output files have

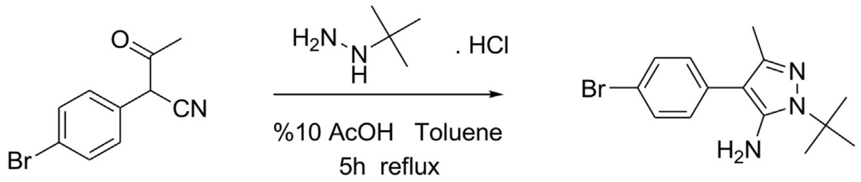

Fig. 1. The synthesis scheme for BPTBMPA.