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Molecular structure and vibrational and chemical shift assignments of 3′-chloro-4-dimethylamino azobenzene by DFT calculations

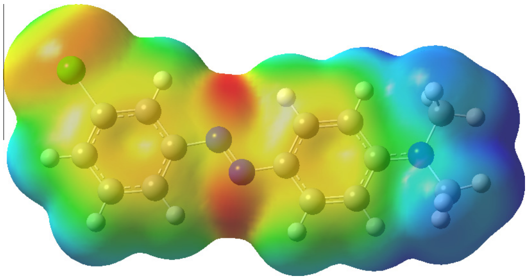
Mehmet Toy [a,*], Hasan Tanak [b]

[a] *Faculty of Education, Department of Science Education, Amasya University, Amasya, Turkey*
[b] *Department of Physics, Faculty of Arts and Sciences, Amasya University, 05100 Amasya, Turkey*

HIGHLIGHTS

- The spectroscopic properties of the compound were examined by FT-IR, NMR and UV techniques and DFT/B3LYP method.
- The DFT theoretical results were compared with the experimental results.
- The TD-DFT calculations lead to a very closer agreement with the experiment.
- The NLO, MEP and HOMO–LUMO are also analyzed.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, a combined experimental and theoretical study on ground state molecular structure, spectroscopic and nonlinear optical properties of azo compound 3′-chloro-4-dimethlamino azobenzene are reported. The molecular geometry, vibrational wavenumbers and the first order hyperpolarizability of the title compound were calculated with the help of density functional theory computations. The optimized geometric parameters obtained by using DFT (B3LYP/6-311++G(d,p)) show good agreement with the experimental data. The vibrational transitions were identified based on the recorded FT-IR spectra in the range of 4000–400 cm^{-1} for solid state. The ^{1}H isotropic chemical shifts with respect to TMS were also calculated using the gauge independent atomic orbital (GIAO) method and compared with the experimental data. Using the TD-DFT method, electronic absorption spectra of the title compound have been predicted, and good agreement is determined with the experimental ones. To investigate the NLO properties of the title compound, the polarizability and the first hyperpolarizability were calculated using the density functional B3LYP method with the 6-311++G(d,p) basis set. According to results, the title compound exhibits non-zero first hyperpolarizability value revealing second order NLO behavior. In addition, DFT calculations of the title compound, molecular electrostatic potential and frontier molecular orbitals were also performed at 6-311++G(d,p) level of theory.

Introduction

Azobenzene and its derivatives have found extensive applicability in areas such as dyestuffs [1], pH indicators [2], photo storage units [3], and triggers for optical switching and actuators [4]. It is well known that azobenzene can exist in two different configurations (trans and cis) in the electronic ground state. The trans-azobenzene can be converted to cis-azobenzene upon UV light (365 nm) irradiation. The cis-to-trans isomerization readily occurs at room temperature and can be stimulated by visible light irradiation [5]. In addition, azobenzene and its derivatives have attracted much attention for their nonlinear optical (NLO) properties [6,7].

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[*] Corresponding author. Tel.: +90 358 252 62 30; fax: +90 358 252 62 22.
E-mail address: mehmettoy05@gmail.com (M. Toy).

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The literature concerning azobenzene derivatives is rich and the papers published cover subjects such as crystal structure determination [8–10], density functional theory (DFT) calculations on the vibrational characteristics, electronic spectra and chemical shifts [11–13], photochemical transformations [14,15], pH indicators [16] and optical properties [17,18]. Many reports have appeared on the synthesis and characterisation of novel azo containing organic [19,20] and metal coordination compounds [21,22].

In a previous publication, IR, ^1H NMR and UV–Vis spectra of 3′-chloro-4-dimethlamino azobenzene had been studied [23]. In spite of its importance, mentioned above, there is no theoretical calculation on 3′-chloro-4-dimethlamino azobenzene published. In this work, we wish to report the spectroscopic and quantum chemical calculation studies carried out on 3′-chloro-4-dimethlamino azobenzene and make a comparison of the calculated results with those of similar compound, 2′-chloro-4-dimethlamino azobenzene, reported earlier by our group [24]. As an extensive study in this area, our aim in this work is to explore the spectral and physico-chemical properties of the azobenzene compound, 3′-chloro-4-dimethlamino azobenzene (Fig. 1), using the DFT calculations. The properties of the structural geometry, vibrational spectra and assignments, NMR spectra, electronic absorption spectra, molecular electrostatic potential (MEP) and NLO properties of the title azobenzene compound have been investigated and reported.

Experimental and computational methods

Synthesis

The title compound was synthesized by published method [23].

Physical measurements

The FT-IR spectrum of the title compound were recorded in the range 4000–400 cm^{-1} region with a Perkin–Elmer 1600 series spectrophotometer using KBr pellets. The ^1H NMR spectra were recorded on a Varian-Mercury 200 MHz spectrometer using TMS as an internal standard and $CDCl_3$ as solvent.

Computational methods

All calculations were performed using the Gaussian 09W program package [25]. Molecular structure was optimized using the B3LYP (Becke's Three parameter Hybrid Functional Using the LYP Correlation Functional) approach in conjunction with the 6-311++G(d,p) basis set. The harmonic vibrational frequencies were calculated at the same level of theory for the optimized structure and the obtained frequencies were scaled by 0.96 [26]. Vibrational band assignments were made using the Gauss-View molecular visualization program [27]. The vibrational frequency calculations at the same level of theory revealed no imaginary frequencies, indicating that an optimal geometry at this level of approximation was found for the title compound. The geometry of the title compound, together with that of tetramethylsilane (TMS) is fully optimized. ^1H NMR chemical shifts were calculated within gauge-independent atomic orbital (GIAO) approach [28] applying the same method and the basis set as used for geometry optimization. The predicted ^1H NMR chemical shifts were derived from the equation $\delta = \sum_0 - \sum$, where δ is the chemical shift, $\sum$ is the absolute shielding and $\sum_0$ is the absolute shielding of the standard (TMS) [29] whose value is 31.97 ppm. For the calculations of the MEP [30], the same level of theory B3LYP/6-311++G(d,p), were used. The mean linear polarizability and mean first hyperpolarizability properties of the title compound were obtained by molecular polarizabilities basing on theoretical calculations [31].

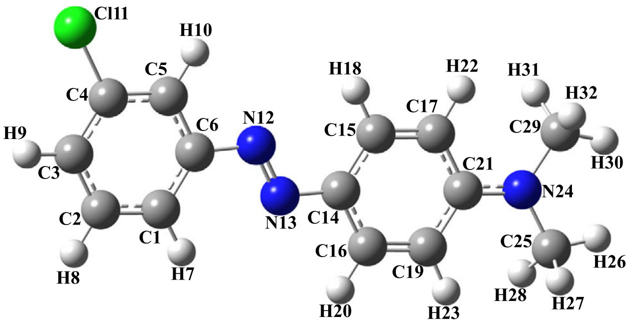

Fig. 1. The theoretical geometric structure of the title compound.

Results and discussion

Molecular structure

The atomic numbering scheme the theoretical geometric structure of the title compound are shown in Fig. 1. The optimized parameters (bond lengths, bond angles and dihedral angles) of the title compound have been obtained using the B3LYP/6-311++G(d,p) method. These results are listed in Table 1.

The molecular structure of the title compound is planar. The dihedral angle between the benzene rings is 0.70°. The dimethylamino group is almost coplanar with the attached ring with C17—C21—N24—C25 torsion angle of 175.10° for B3LYP. The configuration of this molecule is trans with respect to azo bridge. The structure of the title compound is very similar to the structure of 2′-chloro-4-dimethylamino azobenzene studied previously [24]. The N═N distance of the title molecule is essentially identical to that of 2′-chloro-4-dimethylamino azobenzene [24], 1.259 Å, and a little longer than those of 1-{5-[(E)-(4-Propylphenyl)diazenyl]-2-hydroxyphenyl}ethanone [32] and 5-(2-chlorophenyldiazenyl)salicyl-aldehyde [33], 1.2572 (12) and 1.255 (2) Å, respectively. In 4-(2-chlorophenyl-diazenyl)-2-{[tris(hydroxymethyl)-methyl]am inomethylene}cyclohexa-3,5-dien-1(2H)-one, the N═N distance is 1.258 (2) Å [33]. The N12—C6 and N13—C14 bond lengths are 1.417 and 1.401 Å, respectively, for the title compound, and 1.412 and 1.400 Å for 2′-chloro-4-dimethylamino azobenzene [24], consistent with the conventional single C—N bond length (1.450 Å) [34]. In the molecular structure of the title compound, the bond lengths and angles are within normal ranges and they are comparable with those related azo compounds [35–38].

IR spectroscopy

Harmonic vibrational frequencies of the title compound were calculated using the DFT method with the 6-311++G(d,p) basis set. The vibrational band assignments have been made using the Gauss View molecular visualization program. In order to facilitate assignment of the observed peaks we have analyzed vibrational

Table 1
Selected molecular structure parameters.

Bond lengths (Å)		Bond angles (°)	
N12—N13	1.258	C6—N12—N13	114.88
N12—C6	1.417	N12—N13—C14	116.01
N13—C14	1.401	N13—C14—C16	116.41
C4—Cl11	1.761	C21—N24—C29	120.29
C21—N24	1.376	C5—C4—Cl11	119.19
Torsion angles (°)			
N12—N13—C14—C16	179.79	C5—C6—N12—N13	179.60
C1—C6—N12—N13	−0.44	C17—C21—N24—C29	5.35
C6—C5—C4—Cl11	179.97	C19—C21—N24—C25	−5.06