Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 135 (2015) 583–596

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

# Spectroscopic analysis and charge transfer interaction studies of 4-benzyloxy-2-nitroaniline insecticide: A density functional theoretical approach

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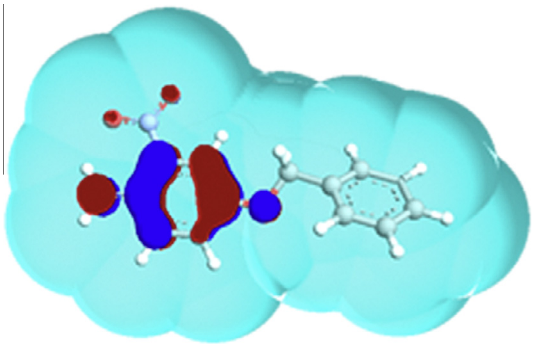
## HIGHLIGHTS

- Spectral investigation has been carried out on insecticide compound BONA.
- Hydrogen bonding and charge transfer interactions are also analyzed.
- The vibrational spectral analysis supports the existence of strong intra- and inter-molecular hydrogen bonding.
- N–H···O hydrogen bonding between the drug molecule and the amino acids of the protein binding site shows bioactive nature.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 2 July 2013
Received in revised form 12 June 2014
Accepted 29 June 2014
Available online 18 July 2014

*Keywords:*
Raman
UV–Vis
NMR
DFT
Molecular docking

## ABSTRACT

A widespread exploration on the intra-molecular charge transfer interaction through an efficient π-conjugated path from a strong electron-donor group (amino) to a strong electron-acceptor group (nitro) has been carried out using FTIR, FT-Raman, UV–Vis, fluorescence and NMR spectra on insecticide compound 4-benzyloxy-2-nitroaniline. Density functional theory method is used to determine optimized molecular geometry, harmonic vibrational wavenumbers and intensities using 6-311G(d,p) basis set by means of Gaussian 09W program suit. A comprehensive investigation on the $sp^2$ to $sp^3$ hybridization and non-planarity property has been performed. Natural bond orbital analysis is used to study the existence of C–H···O, N–H···O and C–H···π proper and improper hydrogen bonds. The HOMO and LUMO analysis reveals the possibility of charge transfer within the molecule. A complete assignment of the experimental absorption peaks in the ultraviolet region has also been performed. Isotropic chemical shifts of $^{13}C$, $^{1}H$, $^{15}N$ and $^{18}O$ NMR and nuclear spin–spin coupling constants have been computed using the gauge-invariant atomic orbital method. The biological activity of substituent amino and nitro groups are evident from the hydrogen bonds through which the target amino acids are linked to the drug as evidenced from molecular docking.

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http://dx.doi.org/10.1016/j.saa.2014.06.137
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## Introduction

The benzothiozole system is a common component of many compounds with a wide range of biological activities [1]. Substituted amines are important intermediates in the synthesis of benzothiozole derivatives. Spectroscopic studies on aniline and its derivatives have been studied extensively [2–4], since they are widely used in commercial and industrial purposes, including pesticide, pharmaceuticals manufacturing and chemical dye industries. Nitro anilines share the common feature of having an electron-rich (donor, $-NH_2$) and an electron-deficient (acceptor, $-NO_2$) substituent, connected by a conjugated $\pi$ electron system. Nitro anilines belong to push–pull molecules due to the intra-molecular charge transfer (ICT) from the electron-donor group through the phenyl ring to the electron-acceptor group. Aniline derivatives can form inter- and intra-molecular hydrogen bonding in solid state which imparts innovative properties in compounds. Inter- and intra-molecular hydrogen bonding interactions [5–7] thus received an increased attention both from practical and theoretical point of view in determining the structure and activity of biological molecule [8].

The change in electron density (E.D) in the $\sigma^*$ antibonding orbitals and $E^{(2)}$ energies were calculated by natural bond orbital (NBO) analysis using the DFT method to give clear evidence about stabilization of various molecular interactions. The B3LYP functional provides an excellent agreement between accuracy and computational efficiency of vibrational spectra of bioactive molecules [9–11]. NMR spectroscopy is the most valuable tool used for structure elucidation in solution [12]. The gauge-invariant atomic orbital (GIAO) method was utilized for calculating nuclear magnetic shielding tensors. Fluorescence spectroscopy is an important investigational tool in many areas of analytical science, due to its extremely high sensitivity and selectivity [13].

Main scope of this work is to analyze the hydrogen bonding capabilities, intra-molecular charge transfer (ICT), non-planarity and $sp^2$ to $sp^3$ hybridization in monomer, dimer, trimer and stacking forms of the insecticide molecule 4-benzyloxy-2-nitroaniline [14] (BONA). The spectroscopic techniques used are UV–Vis, fluorescence, FT-Raman and FTIR spectra. HOMO–LUMO energy gap, natural bond orbital (NBO) analysis together with the $\pi$-conjugation, electron delocalization, hyper conjugation, steric effect, and solvent effect were also analyzed. The experimental results were supported by theoretical predictions, the density functional theory (DFT) and the time-dependent density functional theory (TD-DFT) calculations. This paper also reports the NMR chemical shift ($\delta$) together with nuclear spin–spin coupling constant ($^nJ_{HH}$ and $^nJ_{CH}$).

## Experimental

4-Benzyloxy-2-nitro aniline procured from Sigma–Aldrich (St. Louis, MO, U.S.A) was used without further purification. The UV–Vis absorption spectrum of the sample was recorded in methanol, acetone and water solvents using Varian Cary 100 B10 UV–Vis spectrophotometer. Fluorescence spectrum was recorded by means of F96-fluorospectrophotometer. $^1H$ and $^{13}C$ NMR spectra were taken in BRUKER TPX-400 FT-NMR spectrometer. The IR spectrum of the sample was recorded using a Perkin–Elmer Spectrum One FTIR Spectrometer in the region 400–4000 $cm^{-1}$ with samples in the KBr pellet. The resolution of the spectrum is 1 $cm^{-1}$. NIR FT-Raman spectrum in the range 50–3500 $cm^{-1}$ was recorded using the powdered sample with 1064 nm line provided by Nd: YAG laser as the excitation source and analyzed on Bruker Vertex 70 FT-IR-RAM-II FT-Raman module. The detector was a Ge diode cooled to liquid nitrogen temperature. One thousand scans were accumulated with a total registration time of about 30 min. The spectral resolution after apodization was 2 $cm^{-1}$.

## Computational details

All the electronic structure calculations have been carried out using Gaussian '09 program package [15]. The geometry is fully optimized at the Becke3–Lee–Yang–Parr (B3LYP) level with standard 6-311G(d,p) basis set [16]. The computed wavenumbers were scaled by an empirical scaling factor of 0.97 [17] to fit with the experimental wavenumbers, which accounts for systematic errors caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity. Since the electron correlation effects have been extensively considered in DFT method, a precisely predicted structure of the molecule can be evolved. The Raman activities ($S_i$) calculated by Gaussian '09 are converted to relative Raman intensities ($I_i$) using the relation derived from the basic theory of Raman scattering [18,19].

The natural bonding orbital calculations were done at the B3LYP method in order to investigate the optimized geometry corresponding to hydrogen bonding. The hyperconjugative interaction energy was deduced from the second-order perturbation approach [20]. The frontier molecular orbitals and the HOMO–LUMO energy gap has been computed. The CAM-TD-DFT method is usually found to be a strong and accurate method for describing low-lying excited states of conjugated molecules and has consequently been applied to solve countless chemical and physical problems. Electronic transitions for the molecule were calculated using CAM-TD-DFT method. Solvent effects were considered using the polarizable continuum model (PCM) [21] which takes into account of the solute cavity in a wide range of solvents of different polarity. $^1H$, $^{13}C$, $^{15}N$ and $^{18}O$ NMR chemical shifts together with nuclear spin–spin coupling constants were computed using the GIAO method [22,23]. Average polarizibility, heat of formation and ionization potential were calculated by using MOPAC 09 program [24].

## Results and discussion

### Optimized geometry

Understanding the interaction of aniline with a substituent group in determining the structural and vibrational properties of aniline derivatives [25,26] are of great importance. The optimized molecular structure (Monomer, Dimer, Trimer and stacking) of BONA is shown in Fig. 1. The complete optimized geometrical parameters in monomer, dimer, trimer and stacking form along with experimental values [14] are depicted in Table 1. The asymmetry of the benzene ring is evident from the negative deviation in the bond angles of $C_1–C_2–C_3$, $C_5–C_7–C_8$ and positive deviation of the remaining angles from the normal value of 120° due to the presence of $NO_2$ and $NH_2$ groups. But in the benzyloxy group the ring is symmetric; the CCC angles are not affected from the standard value 120°.

The dihedral angles $H_{27}–N_{25}–C_2–C_1$ ($\simeq -9.7°$) and $H_{26}–N_{25}–C_2–C_3$ ($\simeq 12.8°$) in monomer, dimer and stacking structures show that the amino group is not co-planar with phenyl ring, while in trimer in order to accommodate two more similar molecules to form inter-molecular hydrogen bonding with $NO_2$ and $NH_2$ groups the dihedral angles $H_{89}–N_{88}–C_2–C_1$ (0.0°) and $H_{90}–N_{88}–C_2–C_3$ (0.0°) adopt a perfect co-planar structure. The aromatic ring of the nitrophenylamine group in BONA is twisted with respect to the benzyl ring system, with a dihedral angle of $-46.5°$ ($O_{29}–C_{10}–C_{13}–C_{22}$) between the ring planes [14]. The steric interaction of $H_9$ with $H_{11}/H_{12}$ [$H_9 \cdots H_{12} \simeq 2.323$ Å], the delocalization electron at $C_{10}$ due to the hyperconjugative interaction of $H_{11}/H_{12}$ with benzene ring and the presence of phenoxy group causes deviation from the co-planarity in BONA structure. The inter-atomic distance $H_9 \cdots H_{12} \simeq 2.323$ Å and bond angle $C_8–C_7–O_{29} \simeq 125.6°$ are also the evidence of loss of

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