Indian J. Res. Found., (2015) 4, 1-3. ISSN 2454-6577

INDIAN JOURNAL OF RESEARCH FOUNDATION
www.indianjournal.net

RESEARCH ARTICLE

Computational and experimental spectroscopic study on 4-amino-6-methyl-3phenyl-1,2,4-triazin-5(4H)-one

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Received 6 October, 2015; Accepted 10 November 2015
Available online 10 December 2015

Abstract

Vibrational spectral analysis and quantum chemical computation based on density functional theory (DFT) has been performed on dimerized form of 4-amino-6-methyl-3phenyl-1,2,4-triazin-5(4H)-one. The geometry, inter-molecular hydrogen bond and harmonic vibrational frequencies of the 4-amino-6-methyl-3phenyl-1,2,4-triazin-5(4H)-one molecule have been investigated with the help of B3LYP method. The calculated molecular geometry has been compared with the experimental data. The various intramolecular interactions have been exposed by natural bond orbital analysis (NBO). Mullikan population analysis was performed on the atomic charges and the HOMO-LUMO energies were calculated.

Keywords

DFT

NBO analysis

HOMO-LUMO

Charge transfer

Introduction

4-amino-6-methyl-3phenyl-1,2,4-triazin-5(4H)-one are chemically stable and can penetrate slowly through the soil, causing long-term contamination of underground drinking water resources [1]. Spectral analysis have been carried out using computation and experimental methods. Inter-atomic hydrogen bonding interaction have received much attention from both practical and theoretical values, as they can determine the structure activities of biological molecules. In this study, 4-amino-6-methyl-3phenyl-1,2,4-triazin-5(4H)-one was investigated along with their dimer, to obtain good understanding of their hydrogen bonding capabilities. Vibrational spectroscopic investigation with the help of quantum chemical computation have been recently used as an efficient tool in the structural analysis of triazine compounds [2]. Structural analysis have been successfully used to calculate electronic structures and energies of compounds by Density functional theory (DFT)

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method with the B3LYP/6-311G(D,P) basis set using Gaussian’09 program package. Hence the present investigations aim to interpret the vibrational characteristics of their monomer and dimer using their FT-IR, FT-Raman, HOMO-LUMO energies and NBO analysis.

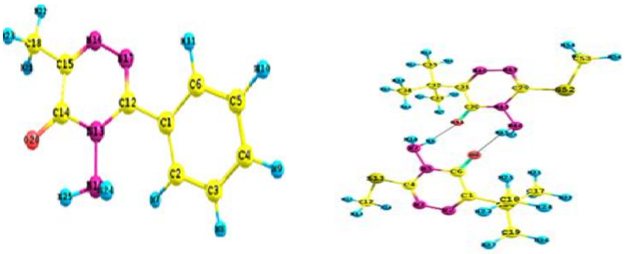

Fig 1 Structure of 4-amino-6-methyl-3phenyl-1,2,4-triazin-5(4H)-one (monomer and dimer)

Computation

The DFT computations for the 4-amino-6-methyl-3phenyl-1,2,4-triazin-5(4H)-one was carried out in the gaussian 09 program package using “ultrafine” integration grids. The calculations were performed at the BLYP level with the standard 6-311 G(D,P) basis set in order to derive the optimized geometry, vibrational wavenumbers and natural bond orbital analysis of 4-amino-6-methyl-3phenyl-1,2,4-triazin-5(4H)-one [3].

Results and discussion

The calculated data of 4-amino-6-methyl-3phenyl-1,2,4-triazin-5(4H)-one are in close agreement [4] with the experimental values (**Table 1**). In the dimer, the molecules are bound together *via* intermolecular hydrogen-bonded interactions. Due to hydrogen bonding, the C=O bond length increases by 0.012Å. The shortening of the N_{16}–N_{17} bonds (0.014), may be due to the increased double-bond character arising from the delocalization of the electrons in the ring. DFT calculation, for the monomers show a shift in bond angle from 120° at the C_{14} position. The bond angle $O_{20}C_{14}N_{13}$ decreases by 0.2°.

For primary amines, the asymmetric NH_2 stretching will give rise to a band in the range 3500–3420 cm^{-1}, while symmetric stretching will appear between 3420 and 3280 cm^{-1} [5]. The calculation shows the asymmetric NH_2 stretching wavenumbers in the monomer and dimer at 3373, 3359cm^{-1}, respectively. Symmetric NH_2 stretching in the monomer and dimer at 3245 and 3249 cm^{-1}.NH stretching shows red shifting due to strong NH…O hydrogen bonding [6] **Fig 2**.

Table 1 Optimized bondlength, bond angle, dihedral angle for 4-amino-6-methyl-3phenyl-1,2,4-triazin-5(4H)-one

Parameter	Monomer	Dimer (d)	XRD (e)
C_{14}-O_{20}	1.236	1.239	1.227
N_{17}-N_{16}	1.371	1.359	1.373
C_{14}-C_{15}	1.461	1.456	1.455
O_{20}-C_{14}-N_{13}	120.1	120.8	120.9
N_{19}-N_{13}-C_{12}	123.3	120.9	122.1
O_{20}-C_{14}-C_{15}	127.3	125.5	125.9

In NBO analysis, the intramolecular hyperconjugative interactions are formed through orbital overlap between π (C–C) and π* (C–C) bond orbitals, which results in an intramolecular charge transfer (ICT) by stabilizing the system. In the monomers, the stabilization energy contributions from the π (C_1–C_2) / π (C_5–C_6)→π* (C_3–C_4) interactions are 77.6 and 89.2 kJ mol^{-1} Similarly, for the dimers, the values are 78.7 and 89.7 kJ mol^{-1} .

Table 2 NBO analysis for 4-amino-6-methyl-3phenyl-1,2,4-triazin-5(4H)-one

Nature	Donor NBO (i)	ED(i) (e)	Acceptor NBO (j)	ED (j) (e)	$E^{(2)}$ (kj/mol)
Monomer	π (C1-C2)	1.647	π * (C3–C4)	0.325	77.6
	π (C5-C6)	1.654	π * (C3–C4)	0.325	89.2
Dimer	π (C1-C2)	1.638	π *(C3–C4)	0.327	78.7
	π (C5-C6)	1.654	π *(C3–C4)	0.327	89.7

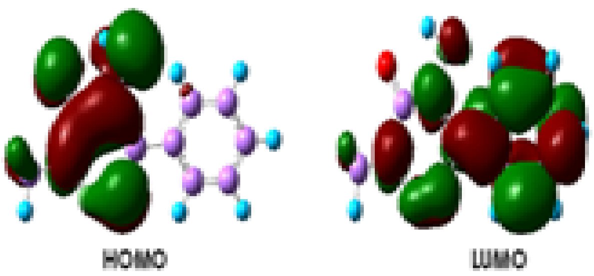

Fig 3 HOMO-LUMO plots for 4-amino-6-methyl-3phenyl-1,2,4-triazin-5(4H)-one

Spatial distribution of molecular orbitals especially those of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are excellent indicators of electron transport in molecular system **Fig 3**. The electron density of the HOMO in the heterocyclic ring is also larger than the LUMO; hence the transition is from the heterocyclic ring to the benzene ring [7]. Due to substantial electron transfer from the HOMO to the LUMO, the N_{13}–N_{14} bond shortens. The energy gap of HOMO-LUMO is 3.054 eV.

Conclusions

The equilibrium geometries of the monomer and dimeric structures of 4-amino-6-methyl-3phenyl-1,2,4-triazin-5(4H)-one were determined and analyzed at the DFT level. The optimized geometry shows due to hydrogen bonding, the C=O bond length increases. Vibrational wavenumbers and Infrared and Raman intensities calculated at B3LYP method agreed well with the experimental data. NBO analysis reveals that the intramolecular hyperconjugative interactions between π (C_5–C_6) $\rightarrow$ π^* (C_3–C_4) bond orbitals. The lowering of HOMO–LUMO energy gap shows the charge transfer interactions taking place within the molecule.

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