Synthesis, spectroscopic (UV–vis and GIAO NMR), crystallographic and theoretical studies of triazine heterocyclic derivatives

Salman A. Khan [a,*], Abdullah Y. Obaid [a], Laila M. Al-Harbi [a], Muhammad Nadeem Arshad [a,b], Onur Şahin [c], Cem Cüneyt Ersanlı [d], R.M. Abdel-Rehman [a], Abdullah M. Asiri [a,b], Michael B. Hursthouse [e]

[a] Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia
[b] Centre of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia
[c] Scientific and Technological Research Application and Research Center, Sinop University, 57010 Sinop, Turkey
[d] Department of Physics, Faculty of Arts and Sciences, Sinop University, 57010 Sinop, Turkey
[e] School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK

HIGHLIGHTS

- Synthesis of triazine heterocyclic derivatives.
- Molecular geometry of compounds in the ground state using the DFT with 6-31G(d,p).
- Crystal structure determination of triazine heterocyclic derivatives.

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ABSTRACT

This work presents the synthesis and characterization of triazine heterocyclic derivatives. The spectroscopic properties like nuclear magnetic resonance [NMR, (^{1}H and ^{13}C)] were recorded in CDCl$_3$ solution and Ultraviolet–Visible (UV–vis) absorption spectrums of compounds, 5,6-diphenyl-[1,2,4]triazin-3-ylamine (**1**), (5,6-diphenyl-[1,2,4]triazin-3-yl)-hydrazine (**2**) and 5,6-diphenyl-4H-[1,2,4] triazine-3-thione (**3**), were recorded in the range of 200–800 nm, using chloroform as base solvent. Molecular geometry of compounds with triazine heterocyclic derivative in the ground state have been calculated using the density functional theory (DFT) with 6-31G(d,p) basis set and compared with the X-ray experimental data. The calculated results show that the optimized geometry can well reproduce the crystal structures. Total static dipole moment (μ), the average linear polarizability (α) and the first hyperpolarizability (β) values of the investigated molecules have been computed using the same methods. The energetic behavior of compounds in solvent media has been examined using B3LYP method with the 6-31G(d,p) basis set by applying the polarizable continuum model (PCM). The total energy of compounds decreases with increasing polarity of the solvent. Frontier molecular orbitals and the molecular electrostatic potential (MEP), ^{1}H NMR, and ^{13}C NMR of three triazine derivatives were investigated using theoretical calculations. The linear polarizabilities and first hyperpolarizabilities of the studied molecules indicate that the compounds **1**–**3** can be used as a good nonlinear optical material (NLO). Isotropic chemical shifts were calculated using the gauge-invariant atomic orbital (GIAO) method. Comparison of the NMR chemical shifts, absorption wavelengths with the experimental values revealed that DFT and time dependent-density functional theory (TD-DFT) method produce generally closer to good results.

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Introduction

The usefulness of organic ligands with heteroatoms N, O, S is well known. However when these ligands are coordinated with a metal atom, they show a remarkable biological activities like anti-microbial, anti-viral and anti-tumor etc. [1–3]. 1,2,4-Triazine derivatives of Pd(II) and Pt(II) show monodentate and bidentate behavior [4] due to their tautomeric and ambidentate nature. Derivatives of triazines were investigated for their antitumor, fungicidal, herbicidal, insecticidal and activities [5]. Wide use of atrazine as herbicidal compounds resulted in alarming threat for

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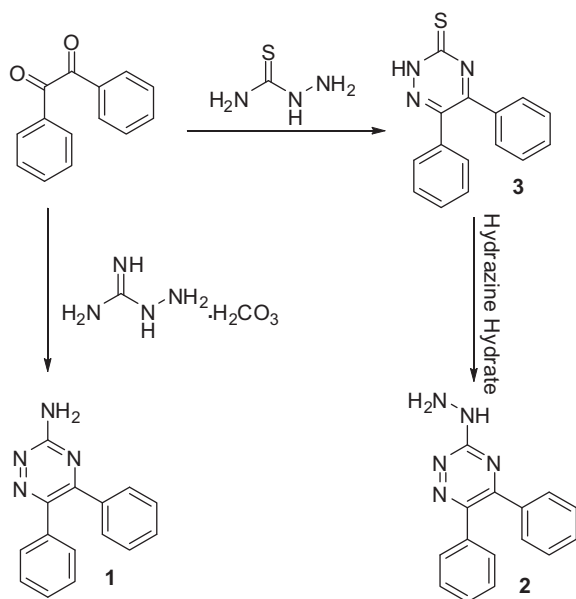
Scheme 1. Representing the synthesis of triazine derivatives.

human health as well as environment [6]. Keeping in view the positive and negative aspects of triazine based molecules Larif et al. reported a detailed research explaining the biological activities of various derivatives of triazines using DFT and quantitative structure activity relationship (QSAR) studies [7]. We have recently reported the synthesis and spectroscopic studies of 1,2,4-triazine complexes with Ru(II) [8].

In recent years, DFT has been a shooting star in theoretical modeling. The development of better and better exchange–correlation functionals made it possible to calculate many molecular properties with comparable accuracies to traditional correlated *ab initio* methods, with more favorable computational costs [9]. Literature survey revealed that the DFT has a great accuracy in reproducing the experimental values of in geometry, dipole moment, vibrational frequency, *etc.* [10–16]. It was noted that the experimental results belong to solid phase and theoretical calculations belong to gas phase. In the solid state, the existence of the crystal field along with the intermolecular interactions have connected the molecules together, which result in the differences of bond parameters between the calculated and experimental values. Despite the differences observed in the geometric parameters, the general agreement is good and the theoretical calculations support the solid state structure.

In this present paper, we report the crystal structures and spectral characterizations of triazine heterocyclic derivatives. Representing the synthesis of triazine derivatives is given in Scheme 1. The properties of the structure geometry, NLO properties, FMO and MEP for compounds **1**–**3** at the DFT/B3LYP/6-31G(d,p) level were studied for the first time. Besides these, the experimental and calculated values are valuable for providing insight into NMR, UV–vis spectrum and molecular parameters. The results obtained from theoretical calculations and experiments were compared.

Experimental and computational method

Materials and methods

All chemicals used in this study were purchased from Fluka and used without further purification. The melting point was recorded on Stuart scientific SMP3 (Bibby, UK) melting point apparatus and is reported as uncorrected. The ^{1}H NMR and ^{13}C NMR experiments were performed in Bruker-AVANCE-III 600 MHz at 300 K. The compounds were dissolved in CDCl₃. Chemical shifts (δ) were reported in parts per million (ppm) relative to tetramethylsilane (TMS) for ^{1}H NMR and ^{13}C NMR spectra. ^{1}H NMR and ^{13}C NMR spectra were obtained at a base frequency of 150 and 600 MHz, respectively. The UV–vis absorption spectrum of the title molecules were examined in the range 200–800 nm using Spectro UV–VIS double beam PC scanning spectrophotometer UVD-2960 Labomed Inc. The UV patterns are taken from 1.69×10^{-4} molar solution of compound **1**, 6.46×10^{-5} molar solution of compound **2**, and 1.39×10^{-4} molar solution of compound **3**, dissolved in chloroform.

Synthesis

5,6-Diphenyl-[1,2,4]triazin-3-ylamine (**1**)

Benzil (4 g, 19.03 mmol) and aminoguanidine bicarbonate (2.58 g, 4.76 mmol) in n-butanol (100 ml) was refluxed for four hours. The reaction was monitored through thin layer chromatography (TLC). The mixture was cooled. The solid obtained was filtered off and recrystallized from ethanol to give yellow crystals [17].

Yield: 4.09 g; 85%; m.p. 160 °C; ^{1}H NMR shifts (CDCl₃, δ ppm): 7.30–7.44 (10H, aromatic), 5.53 (2H, s, NH₂); ^{13}C NMR shifts (CDCl₃, δ ppm): 161.18, 157.24, 150.78, 136.04, 135.97, 130.37, 129.52, 129.38, 129.24, 128.53, 128.38; UV–vis data (nm): λmax = 345.

(5,6-Diphenyl-[1,2,4]triazin-3-yl)-hydrazine (**2**)

A mixture of 5,6-diphenyl-4H-[1,2,4]triazine-3-thione (5 g, 18.84 mmol) and hydrazine hydrate (10 ml) in isopropyl alcohol was refluxed for 4–6 h, until no more H₂S evolved. Acetic acid was added drop wise into mixture to remove the excess of hydrazine till neutralization. The mixture was cooled. The solid obtained was filtered off and crystalized from ethanol to give yellowish crystals [18].

Yield: 4.19 g: 83.8%; m.p. 175–178 °C; ^{1}H NMR shifts (CDCl₃, δ ppm): 7.31–7.49 (10H, aromatic), 6.64 (1H, s, NH), 4.18 (2H, s, NH₂); ^{13}C NMR shifts (CDCl₃, δ ppm): 162.20, 157.12, 151.21, 135.96, 135.92, 130.52, 129.56, 129.25, 128.62, 128.39, 128.38; UV–vis data (nm): λmax = 355.

5,6-Diphenyl-4H-[1,2,4]triazine-3-thione (**3**)

Benzil (6 g, 28.5 mmol) was dissolved in glacial acetic acid (150 ml) and added to the solution of thiosemicarbazide (2.59 g, 28.5 mmol) in hot water (100 ml). The mixture was refluxed for 4 h, the precipitate appeared filtered until hot. The orange filtrate obtained was recrystallized from ethanol to give reddish crystals [18].

Yield: 5.27 g; 87.82%; m.p. 222–224 °C; ^{1}H NMR shifts (CDCl₃, δ ppm): 7.27–7.57 (10H, aromatic). 11.78 (1H, b, NH); ^{13}C NMR shifts (CDCl₃, δ ppm): 179.24, 160.73, 146.66, 132.22, 130.28, 130.10, 129.86, 129.40, 128.74, 128.60, 128.39; UV–vis data (nm): λmax = 440.

Crystal structure determination

Diffraction data of compounds **1**–**3** were collected on Oxford Diffraction SuperNova (single source at offset) Eos diffractometer equipped with a graphite-monochromatic Cu K_α radiation at 296 K. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares method using SHELXL-97 [19]. All non-hydrogen atom parameters were refined