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Spectroscopic, reactivity and NLO analysis of new hydrazone-containing dipyrromethane using experimental and theoretical approaches

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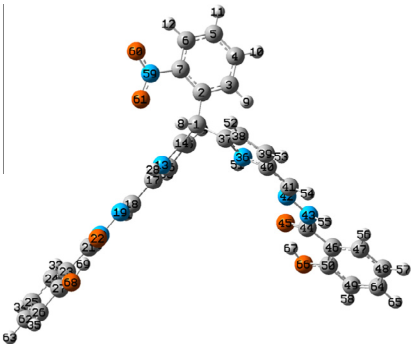
HIGHLIGHTS

- Intramolecular hydrogen bonding is obvious in down field chemical shift, vibrational red shift and NBO.
- The interaction $n_3(O61) \rightarrow \pi^*(N59—O60)$ stabilizes the molecule up to 653.87 kJ/mol.
- QTAIM analysis are performed to determine hydrogen bonding.
- Global electrophilicity index (ω = 5.39 eV) shows that studied compound behaves as a strong electrophile.

GRAPHICAL ABSTRACT



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ABSTRACT

The molecular structure and detailed spectroscopic analysis of a novel synthesized dipyrromethane: 1,9-bis[(2-hydroxybenzoyl)-hydrazonomethyl]-5-(2-nitrophenyl)-dipyrromethane (**3**) have been performed using both experimental techniques and theoretical calculations. Thermodynamic parameters (H, G, S) of reactants and products have been used to investigate the nature of synthesis. The singlet chemical shift at 5.343 ppm of *meso*-proton designates formation of product molecule (**3**). TD-DFT has been used to calculate oscillatory strength (f) and wavelength absorption maxima (λ_{max}) of various electronic excitations and their nature within molecule. The molecular orbital coefficients and molecular plots analysis assign nature of electronic excitations as $\pi \rightarrow \pi^*$. Natural bond orbital (NBO) analysis has been carried out to investigate the intramolecular H-bonding, conjugative and hyperconjugative interactions within molecule. The result of intramolecular hydrogen bonding (O68—H69···O22/O66—H67···O45) is obvious in ^{1}H NMR, FT-IR and NBO due to down field chemical shift, vibrational red shift, and $n_2(O22) \rightarrow \sigma^*(O68—H69)/n_2(O45) \rightarrow \sigma^*(O66—H67)$ interactions energies 105.12/104.91 (kJ/mol), respectively. To investigate the strength and nature of H-bonding, topological parameters at bond critical points (BCP) have been analyzed by 'Quantum theory of Atoms in molecules' (QTAIM). Local reactivity descriptors- Fukui functions(f_k^+, f_k^-), local softnesses (s_k^+, s_k^-) and electrophilicity indices (ω_k^+, ω_k^-) analyses have been performed to find out the reactive sites of the molecule. The computed first hyperpolarizability ($\beta_0 = 14.30 \times 10^{-30}$ esu) evaluates the molecule to be suitable for non-linear optical (NLO) response.

1. Introduction

Dipyrromethanes work as building blocks in syntheses of a variety of calix[n] pyrroles, porphyrins [1–4], polypyrrolic

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macrocycles [5], hexaphyrin [6] and corroles [7,8]. The oxidized dipyrromethanes (dipyrromethenes or dipyrrins) give monoanionic, conjugated, planar ligands that have attracted attention in the metal organic framework and have strong coordinating ability towards different metal ions [9–12]. They are versatile ligands for supramolecular coordination chemistry and self-assembly with various transition metal ions are reported [13,14]. The heteroleptic complexes and coordination polymers of dipyrrin are used for developing novel magnetic and electronic materials [15–19]. The dipyrrinato metal complexes of Ga(III), In(III) have shown luminescent properties [20] and its several metal-organic frameworks (MOFs) with Ag^+ salts generate strong optical absorption materials [21]. Dipyrromethane based amido-imine hybrid macrocycles have shown oxoanions receptor property [22]. Dipyrrins are also used as ligands for the syntheses of boron dipyrromethene (BODIPY) [23–25], which are used extensively as molecular probes and dyes.

Hydrazones are versatile intermediates for the syntheses of *N*-alkyl hydrazides, 1,3,4-oxadiazolines, 2-azetidinones and 4-thiazolidinones [26,27]. Due to the presence of the active pharmacophore (—CO—NH—N═CH—) these compounds show different biological activities as antidepressant [28], antimalarial [29], anticancer [30] and antimicrobial [31]. They have strong coordinating ability towards different metal ions [32,33] and used as prospective new materials for the development of potential chemosensors [34], opto-electronic applications [35].

The development of organic NLO materials for device applications requires a multidisciplinary effort involving both theoretical and experimental studies in the fields of chemistry. Quantum-chemical calculations have made an important contribution to understand the electronic polarization underlying the molecular NLO processes and the establishment of structure–property relationships [36,37]. Organic molecules with large second-order NLO are the subject of substantial research due to their potential applications in optical modulation, molecular switching, optical memory, and frequency doubling [38–43]. Non-linearity in organic molecules can be synthetically modulated by varying the composition or length of conjugated π-systems, and by evaluating the effects of various electron-donor and acceptor groups.

DFT is an effective tool in quantum chemistry for evaluation of the molecular structures, vibrational frequencies, intra-/intermolecular interactions and nature of chemical reactions. It has been used extensively to study H-bond interactions. The existence of H-bond can be determined by the structural parameters and their strength estimated by the elongation or contraction of H-bond length [44–47]. However, in many cases, the H-bond interactions are too complex to understand by the structural parameters. Therefore, quantum theory of atoms in molecules (QTAIM) [40,48] and natural bond orbital (NBO) analyses [49] are used to evaluate the strength and nature of H-bonds in detail. According to QTAIM, the presence of a bond critical point (BCP) between two atoms is a universal indicator of bonded interactions and the electron density (ρ_{BCP}), at the bond critical point is related to the bond strength or bond order. A useful aspect of the NBOs is that it provides an accurate method for studying intramolecular interactions and also gives an efficient basis to investigate charge transfer or conjugative interaction in various molecular systems [50].

In view of above properties and versatile applications of dipyrromethane derivatives the title compound (**3**) has been synthesized and characterized. In present paper, we report the molecular structure and detailed spectroscopic analysis of the title compound using both experimental and theoretical spectroscopic techniques. Furthermore, quantum chemical calculations have been performed to determine the HOMO–LUMO analysis, intramolecular conjugative and hyperconjugative interactions, H-bonding, chemical reactivity and NLO response of the investigated molecule (**3**).

2. Experimental details

2-[(2-Hydroxybenzoyl)-hydrazonomethyl]-1*H*-pyrrole (**1**) was prepared by refluxing the equimolar reaction mixture of pyrrole-2-carboxaldehyde-1*H*-pyrrole and salicylhydrazide in methanol as solvent. 2-nitro benzaldehyde (**2**) was purchased from commercial source. TLC analysis was carried out using glass plates pre-coated with silica gel (Kieselgel 60 F256, 0.2 mm, Merck). The Mass spectrum of (**3**) was recorded on JEOL-Acc TDF JMS-T100LC, Accu TOF mass spectrometer. The ^{1}H NMR spectrum of (**3**) was recorded in MeOD on Bruker DRX-300 spectrometer using TMS as an internal reference. The FT-IR spectrum was recorded in KBr medium on a Bruker spectrometer. The UV–Visible absorption spectrum of (**3**), (1×10^{-5} M in MeOD) was recorded on ELICO SL-164 spectrophotometer.

Synthesis of 1,9-bis[(2-hydroxybenzoyl)-hydrazonomethyl]-5-(2-nitrophenyl)-dipyrromethane (**3**), $C_{31}H_{25}N_7O_6$:

To the solution of 2-[(2-hydroxybenzoyl)-hydrazonomethyl]-1*H*-pyrrole (0.150 g, 0.6548 mmol) and 2-nitro benzaldehyde (0.0494 g, 0.3274 mmol) in 20 mL MeOH, conc. HCl (0.01 mL) was added as catalyst. The reaction mixture was refluxed for overnight giving dark brown color to the reaction mixture and completion of reaction was analyzed using thin layer chromatography (TLC). On completion of reaction, the reaction mixture was treated with saturated aqueous solution of $NaHCO_3$ and the resulting final reaction mixture was extracted with dichloromethane (20 mL × 4). The organic layer was dried over $MgSO_4$ and solvent was removed under reduced pressure. Remaining solid was purified by column chromatography on silica using hexane and ethylacetate as eluent. Thus pure product (**3**) was obtained. Color: dark brown, Yield: 59%.

Mass spectrum and Elemental analysis: The MS for $C_{31}H_{25}N_7O_6$: calc. 591.18663 amu, found m/z 592.26 $[M+H^+]$. Elemental analysis for $C_{31}H_{25}N_7O_6$: calc. C 62.92, H 4.26, N 16.58, obs. C 62.88, H 4.23, N 16.60.

3. Computational details

All the quantum chemical calculations are carried out with Gaussian 09 program package [51] to predict the molecular structure, ^{1}H NMR chemical shifts, vibrational wavenumbers, electronic reactivity descriptors and first hyperpolarizability of the optimized structure using B3LYP functional and 6-31G(d,p) basis set, which invokes Becke's three parameter (local, non-local, Hartree–Fock) hybrid exchange functional (B3) [52], with Lee–Yang–Parr correlational functional (LYP) [53]. The basis set 6-31G(d,p) with 'd' polarization functions on heavy atoms and 'p' polarization functions on hydrogen atoms are used for better description of polar bonds of molecule [54,55]. It should be emphasized that 'p' polarization functions on hydrogen atoms are used for reproducing the out of plane vibrations involving hydrogen atoms. To estimate the enthalpy (*H*) and Gibbs free energy (*G*) values, thermal corrections to the enthalpy and Gibbs free energy are added to the calculated total energies. Time dependent density functional theory (TD–DFT) is used to find the various electronic excitations and their nature within molecule. Natural bond orbital (NBO) analysis is performed using the option implemented in Gaussian (09) to gain a better understanding of the charge distribution within molecule. The optimized geometrical parameters are used in the vibrational wavenumbers calculation to characterize all stationary points as minima and their harmonic vibrational wavenumbers are positive. Potential energy distribution along internal coordinates is calculated by Gar2ped software. Topological parameters are calculated using software AIMALL (Version 10.05.04). The optimized geometries of the molecule are visualized using Gauss-View software.