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Synthesis, molecular structure, hydrogen-bonding, NBO and chemical reactivity analysis of a novel 1,9-bis(2-cyano-2-ethoxycarbonylvinyl)-5-(4-hydroxyphenyl)-dipyrromethane: A combined experimental and theoretical (DFT and QTAIM) approach

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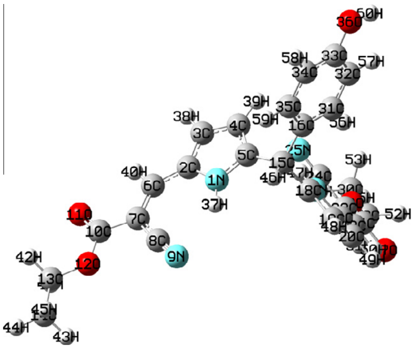
HIGHLIGHTS

- FT-IR spectrum of the studied compound was recorded and compared with the theoretical result.
- All the theoretical calculations were made using DFT/B3LYP/6-31G(d,p) method.
- NBO analysis are performed to determine the hyperconjugative interactions.
- QTAIM analysis are performed to determine hydrogen bonding.
- Chemical reactivity has been explained with the aid of electronic descriptors.

GRAPHICAL ABSTRACT

A detailed spectroscopic analysis of a newly synthesized 1,9-bis(2-cyano-2-ethoxycarbonylvinyl)-5-(4-hydroxyphenyl)-dipyrromethane (**3**) have been carried out using ^{1}H NMR, UV–Visible, FT-IR and Mass spectroscopic techniques. All the quantum chemical calculations (^{1}H NMR, UV–Visible, FT-IR, NBO$_s$, QTAIM) are carried out using DFT level of theory, B3LYP functional and 6-31G(d,p) as basis set. A combined experimental and theoretical vibrational analysis designates the existence of H-bonding between pyrrole N—H as proton donor and nitrogen of cyanide as proton acceptor. To investigate the strength and nature of H-bonding, topological parameters at bond critical points (BCPs) are analyzed by Bader's 'Quantum theory of Atoms in molecules' in detail. Global electrophilicity index ($\omega = 4.5281$ eV) shows that title molecule (**3**) is a strong electrophile. Local reactivity descriptors as Fukui functions (f_k^+, f_k^-), local softnesses (s_k^+, s_k^-) and electrophilicity indices (ω_k^+, ω_k^-) analyses are performed to find out the reactive sites within molecule.



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ABSTRACT

The spectroscopic analysis of a newly synthesized 1,9-bis(2-cyano-2-ethoxycarbonylvinyl)-5-(4-hydroxyphenyl)-dipyrromethane (**3**) has been carried out using ^{1}H NMR, UV–Visible, FT-IR and Mass spectroscopic techniques. All the quantum chemical calculations have been carried out using DFT level of theory, B3LYP functional and 6-31G(d,p) as basis set. Thermodynamic parameters (*H*, *G*, *S*) of all the reactants and products have been used to determine the nature of the chemical reaction. The chemical shift of pyrrolic NH in ^{1}H NMR spectrum appears at 9.4 ppm due to intramolecular hydrogen bonding. TD-DFT calculation shows the nature of electronic transitions as $\pi \rightarrow \pi^*$ within the molecule. A combined experimental and theoretical vibrational analysis designates the existence of H-bonding between pyrrole N—H as proton donor and nitrogen of cyanide as proton acceptor, therefore, lowering in stretching

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Reactivity descriptors

vibration of NH and CN. To investigate the strength and nature of H-bonding, topological parameters at bond critical points (BCPs) are analyzed by 'Quantum theory of Atoms in molecules' (QTAIMs). Natural bond orbitals (NBO_s) analysis has been carried out to investigate the intramolecular conjugative and hyperconjugative interactions within molecule and their second order stabilization energy ($E^{(2)}$). Global electrophilicity index (ω = 4.528 eV) shows that title molecule (**3**) is a strong electrophile. The maximum values of local electrophilic reactivity descriptors (f_k^+, s_k^+, ω_k^+) at vinyl carbon (C6/C22) of (**3**) indicate that these sites are more prone to nucleophilic attacks.

Introduction

Dipyrromethane and its derivatives are the building blocks for the syntheses of a variety of calix[n] pyrroles, porphyrins [1–4], polypyrrolicmacrocycles [5], hexaphyrin [6] and corroles [7,8]. The oxidized dipyrromethanes named as 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 as Li(I), Zn(II), Ni(II), Pd(II/III), Cu(II) and Sn(II) [9–12]. They are reported as versatile ligands for coordination chemistry and supramolecular self-assembly with various transition metal ions [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.

Hydrogen bonds are of versatile importance in fields of chemistry and biochemistry, as they govern chemical reactions, supramolecular structures, molecular assemblies and life processes. Intra and intermolecular hydrogen bonds are classified in two categories depending upon the nature of changes in bond length during the hydrogen bridges formation [26–28].

Cyanovinyl was employed first by Fisher [26,29] as protecting group for formyl in pyrrole for the synthesis of 2,5-diformyl-3,4-dimethylpyrrole and later by Woodward [30] in the synthesis of chlorophyll. The *C*-vinylpyrrole fragment is found to be reactive for the target synthesis of conjugated and fused heterocycles similar to natural pyrrole assemblies [31,32]. The functionalized *C*-vinylpyrroles are prospective new materials for molecular optical switches, nanodevices, photo- and electro-conducting applications and also used as ligands for new photo catalysts, biologically active complexes [33–35].

In observation of above applications of cyanovinyl containing dipyrromethane**-**1,9-bis(2-cyano-2-ethoxycarbonylvinyl)-5-(4-hydroxyphenyl)-dipyrromethane (**3**) has been synthesized and characterized using ^{1}H NMR, UV–Visible, FT-IR and Mass spectroscopic techniques. Quantum chemical calculations have been carried out using DFT to determine the thermodynamic parameters and the nature of the reaction. The ^{1}H NMR chemical shifts and vibrational analysis indicated the existence of intramolecular H-bonding. To investigate the strength and nature of intramolecular H-bonding, topological and energetic parameters at bond critical points (BCPs) have been analyzed using QTAIM. NBO_s analysis has been carried out to investigate the intramolecular conjugative and hyperconjugative interactions within molecule and their second order stabilization energy. The nature of chemical reactivity and site selectivity of this molecule has been determined on the basis of Global and Local reactivity descriptors [36–41].

Experimental details

*Synthesis of 1,9-bis(2-cyano-2-ethoxycarbonylvinyl)-5-(4-hydroxyphenyl)-dipyrromethane **(3)***

Ethyl 2-cyano-3-(1*H*-pyrrol-2-yl)-acrylate **(1)** was prepared by an earlier reported method. To the solution of ethyl 2-cyano-3-(1*H*-pyrrol-2-yl)-acrylate (0.200 g, 1.0522 mmol) and 4-hydroxybenzaldehyde (0.0642 g, 0.5261 mmol) in 20 ml dichloromethane, p-toluene sulfonic acid (0.0002 g) as catalyst was added. The reaction mixture was refluxed for 8 h, the color of reaction was changed to dark brown and completion of the reaction was analyzed by thin layer chromatography (TLC). Reaction mixture was washed with saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2 (15 ml × 3). 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 ethyl acetate and pure product (**3**) was obtained. Dark brown color compound yielded: 0.1839 g, 72.20%; m.p.: 132–136 °C; DART Mass for C27H24N4O5: Calc. 484.1748 amu, Found *m*/*z* 485.25 [M+H$^+$].

Quantum chemical calculations

All the quantum chemical calculations were carried out with Gaussian 03 program package [42] using B3LYP functional and 6-31G(d,p) basis set [43–45]. Potential energy distribution along internal coordinates was calculated by Gar2ped software. Topological parameters were calculated using software AIM2000 [46].

Results and discussion

Thermochemistry

Optimized geometry of the reactants ethyl 2-cyano-3-(1*H*-pyrrol-2-yl)-acrylate (**1**) and 4-hydroxybenzaldehyde (**2**) and product 1,9-bis(2-cyano-2-ethoxycarbonylvinyl)-5-(4-hydroxyphenyl)-dipyrromethane (**3**) and byproduct water (**4**) involved in chemical reaction are shown graphically in Scheme 1. The calculated thermodynamic parameters – Enthalpy (*H*/a.u.), Gibbs free energy (*G*/a.u.) and Entropy [*S*/(cal/mol K)] of **(1), (2), (3), (4)** and their change for **Reaction**, at 25 °C are listed in Table 1. The calculated negative values of enthalpy change (ΔH) and entropy change (ΔS) show that energy factor is favorable, whereas Gibbs free energy (*G*) factor is unfavorable. The calculated positive value of (ΔG) shows that this reaction is non-spontaneous. At 25 °C, thermodynamic equilibrium constant (K_T) for this reaction is calculated as 2.7883×10^{-7} i.e. $K_{eq} \ll 1$ indicating that the reaction will require elevation of temperature and presence of catalyst.

Molecular geometry

Optimized geometry for the ground state lower energy conformer of (**3**) is shown in Fig. 1. Selected optimized geometrical parameters of (**3**) are listed in S Table 1 of Supplementary material.