

Facile synthesis, structural elucidation and spectral analysis of pyrrole 4-imidazole derivatives



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ABSTRACT

In this work pyrrole 4-imidazole derivatives (**3A-3D**): benzimidazoles and pyrrole 4-imidazoline have been synthesized by condensation, cyclization and oxidation of ethyl 4-formyl-3,5-dimethyl-1*H*-pyrrole carboxylate and phenylene diamine derivatives/ethylene diamine. The structure of these biheterocyclic compounds have been derived by elemental and spectroscopic - IR, UV, MS, ¹H and ¹³C NMR analysis as well as theoretical study. The static first hyperpolarizability, β_0 values for pyrrole 4-imidazole derivatives, (**3A-3D**) have been calculated as 10.901×10^{-31} , 19.607×10^{-31} , 40.323×10^{-31} , 5.686×10^{-31} esu, respectively. The gradual increase in β_0 value of synthesized pyrrole-benzimidazole derivatives from **3A** to **3C** is due to addition of acceptors -Cl atom in **3B** to -NO₂ group in **3C** on benzimidazole side. The experimental absorption spectra found to be in UV region and the high β_0 values show that the synthesized pyrrole-imidazoles are suitable as non-linear optical (NLO) materials.

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1. Introduction

The chemistry of heteroatoms constitutes the broadest and complex branches of chemistry [1–8]. The diversity of synthetic methods utilized in this field, coupled with the immense physiological and industrial significance make the general heterocyclic arena of central importance to organic chemistry [9]. Azole systems represent one of the most important classes of five-membered heterocyclic species. The pyrrole and imidazole are aromatic azole. In azoles the numbering of ring atoms starts with the heteroatom that is not part of a double bond, and then proceeds towards the other heteroatom [10]. The pyrrole is most simple azole containing single nitrogen whereas imidazole consists of two nitrogen and two double bonds at alternative position along with three carbons. The partially reduced form of imidazole is imidazoline that has one double bond; completely reduced form is imidazolidine, is without double bond, and oxidized form is imidazolone [11]. Imidazole on fusion with benzene form benzimidazole is class of heterocyclic aromatic compound. Imidazoles have been found to be present in a number of natural products and pharmacologically active compounds, whereas pyrrole fragment is a constituent of many biological systems [12–14]. Benzimidazole is

an important pharmacophore and honoured structure in medicinal chemistry. Benzimidazole derivatives possess antihypertensive [15], anti-inflammatory [16], antimicrobial [17,18], antioxidant [19], antitumor [20–22], antifungal [23,24], anti-parasitic, anti-depressant [25], antibacterial activity [26] and other properties. There is less reported work on pyrrole containing imidazole derivative and that is also limited to synthetic and their biological activities. In this work, the pyrrole-imidazole derivatives have been synthesized and characterized. In the present paper we report the structure of synthesized compounds using experimental spectroscopic findings and quantum chemical calculations. Furthermore, quantum chemical calculations have been performed to find NLO property, electronic properties correlation, vibrational frequencies and chemical reactivity analysis of synthesized compound.

2. Computational details

The synthesized compounds have been optimized using hybrid B3LYP [27]; functional of DFT and 6-31G(d,p) basis set. The NMR chemical shifts, electronic transitions were calculated employing Gauge Induced atomic orbital (GIAO) and time dependent DFT (TD-DFT) method respectively. The calculated frequencies are scale down by using single scaling factor 0.9608 [28] in order to improve the agreement with the experimental values. All calculations were performed by using the Gaussian 09 [29] program package on a personal computer.

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3. Results and discussion

3.1. Molecular structure and calculated thermodynamics parameters

Scheme 1 shows the formation of pyrrole-imidazole derivatives and Fig. 1 shows mechanism of formation of pyrrole-imidazoles (3A–3D). Fig. 2 shows optimized geometries of all derivatives with atom numbering. The asymmetry has been observed in the pyrrole ring between the bonds N1–C2 and N1–C5 due to the presence of electron withdrawing ethoxycarbonyl group. This observations also shown in the quantum calculation and crystal structures of the ethyl-3,5-dimethyl-1H-pyrrole-2-carboxylate [30], methyl 4-p-tolyl-1H-pyrrole-2-carboxylate [31] and other pyrrole derivatives [6,7,32–39]. The ground state geometries show that imidazole ring and pyrrole ring are near to plane or in plane. They are slightly deviated from the plane around C3–C4–C7–N21, C3–C4–C7–N20, C3–C4–C7–N16 by 0.0056°, 0.0000, –0.0228° and 12.2409° in molecule 3A, 3B, 3C and 3D, respectively. The calculated bond lengths, bond angles and selected dihedral angles for most stable conformer of pyrrole 4-imidazole derivatives 3A, 3B, 3C and 3D are given in Supplementary Table 1. The calculated thermodynamics parameters of all reactants and products were performed to determine the feasibility of the reaction at room temperature and their values are listed in Table 1. The negative value of enthalpy ($\Delta H_{\text{Reaction}}$) and Gibbs free energy ($\Delta G_{\text{Reaction}}$) indicates that all reactions are exothermic and spontaneous at all temperature. The calculated ($\Delta H_{\text{Reaction}}$), ($\Delta G_{\text{Reaction}}$) and ($\Delta S_{\text{Reaction}}$) are found to be (–0.09, –0.10 a.u. and 6.76 cal/mol-K, for (reaction 1A), –0.10, –0.11 a.u. and 7.82 cal/mol-K for (reaction 1B), –0.10, –0.12 kcal/mol and 8.81 cal/mol-K for (reaction 1C) and –0.10, –0.12 kcal/mol and 8.22 cal/mol-K for (reaction 1D).

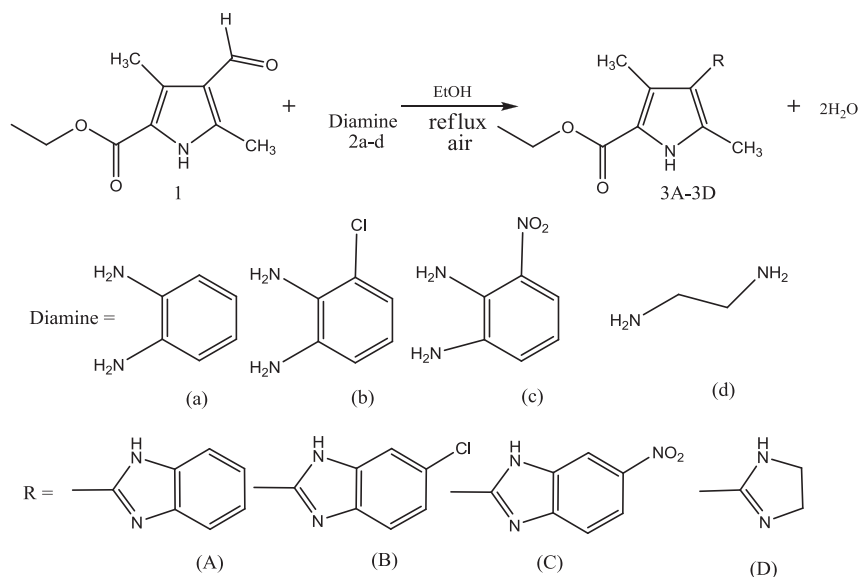
3.2. Structure elucidation with the help of spectroscopy

The combined experimental $^1\text{H}/^{13}\text{C}$ NMR and calculated chemical shifts for the stable conformers of pyrrole 4-imidazole derivatives 3A, 3B, 3C and 3D are given in Tables 2 and 3. The experimental spectra of all synthesized compounds are given in Supplementary Fig. S1. The ^1H chemical shift for N–H proton of pyrrole in pyrrole 4-imidazole derivatives 3A, 3B, 3C and 3D were

found experimentally at δ 11.701, δ 9.450, δ 9.977 and δ 9.273 ppm, with respect to calculated values at δ 8.412, δ 8.787, δ 8.706 and δ 9.0463 ppm. The differences or discrepancy between experimental and theoretical ^1H NMR data are due to the intermolecular hydrogen bonding with highly polar solvent DMSO. The ^1H NMR spectrum of 3A, 3B, 3C and 3D shows two singlet signals assigned to the –CH₃ protons present at pyrrole ring. The chemical shifts assigned at δ 2.461 (3H) and δ 2.486 (3H) for 3A, δ 2.336 and δ 2.375 for 3B, δ 2.437 and δ 2.458 for 3C and δ 2.283 and δ 2.205 ppm for 3D, respectively. The signal assigned to the ester protons (–CH₂–) at the δ 4.268, δ 4.205, δ 4.328, δ 4.299 and for –CH₃ at δ 1.318, δ 1.292, and δ 1.454, δ 1.307 ppm for the molecules 3A, 3B, 3C and 3D, respectively. The GIAO-computed values were very similar for rest of the protons present in the molecules. Additional support for the formation of products has been confirmed by ^{13}C NMR spectra. All experimental and calculated values correlate well. The UV–visible spectra of pyrrole 4-imidazole derivatives have been studied by the time-dependent density functional theory (TD-DFT). The observed and calculated electronic transitions of high oscillatory strength for pyrrole 4-imidazole molecules 3A, 3B, 3C and 3D are given in Table 4 and shown in Fig. 3. Fig. 4 shows the distributions of electrons and energy levels in the molecular orbitals for molecules 3A, 3B, 3C and 3D. The absorption maxima observed for molecule 3A, λ_{max} at 275 (252), for 3B at 304 (318), and 227 (230), for 3C at 284 (306), 236 (262), 223 (218) and for molecule 3D at 254 (254), 234 (234) nm. The differences or discrepancy between experimental and theoretical UV–Visible data due to the intermolecular hydrogen bonding with DMSO solvent. These transition are assigned as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ in nature.

3.3. Vibrational assignment

The experimental IR spectra of imidazole derivatives (3A–3D) in the region 400–4000 cm^{-1} are shown in Supplementary Figs. S9–S12. Combined theoretical (scaled) and experimental vibrational wavenumbers (in cm^{-1}) with their assignment are given in Table 5. The calculated vibrational wavenumbers are scaled down by a single factor 0.9608 [28], to discard the anharmonicity present in real system. In FT-IR spectrum of 3A, 3B, 3C and 3D, the N–H stretch of pyrrole ($\nu_{\text{N-H}}$) were observed at 3289, 3259, 3308 and 3281 cm^{-1} , whereas these were calculated as 3504, 3499, 3502 and 3504 cm^{-1} . The observed stretching mode of carbonyl group



Scheme 1. Representing synthesis of pyrrole-imidazole derivatives (3A–3D).

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