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Spectroscopic and quantum chemical correlation for structural evaluation, chemical reactivity and non-linear optical property investigation of two chalcone having pyrrole moiety: A comparative study

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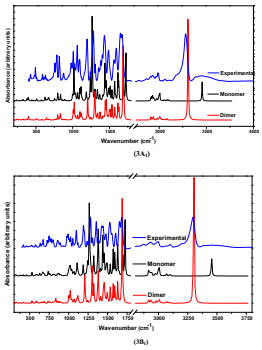
HIGHLIGHTS

- The computational calculations have been performed using DFT methods.
- FT-IR spectra of the studied compounds were recorded and compared with the theoretical results.
- Experimental and calculated ^{1}H NMR chemical shifts have been compared with theoretical results.
- Chemical reactivity has been explained with the aid of global and local electronic descriptors.

GRAPHICAL ABSTRACT



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ABSTRACT

As part of study of pyrrole–chalcone, ethyl 4-[3-(4-chloro-phenyl)-acryloyl]-3,5-dimethyl-1*H*-pyrrole-2-carboxylate (ECADPC) and ethyl 3,5-dimethyl-4-[3-(3-nitro-phenyl)-acryloyl]-1*H*-pyrrole-2-carboxylate (EDNAPC) have been synthesized by Claisen–Schmidt condensation using chloro- and nitro- substituted aromatic aldehyde and ethyl 3,5-dimetyl-4-acetyl-1*H*-pyrrole-2-carboxylate. The products were characterized by ^{1}H NMR, UV–Visible, FT-IR spectroscopic methods and Quantum chemical calculations. Conformational analysis, normal mode frequencies and corresponding vibrational assignments based on potential energy distribution study revealed that ECADPC and EDNAPC exist in dimer form in solid state. 'Quantum theory of Atoms in molecules' (QTAIM) analysis has been performed to know the strength of intra- and intermolecular interactions. The UV–Visible spectra study reveals that the compounds are almost transparent in the visible region. Angular distribution of the probability density for population conformational analysis of ECADPC and EDNAPC are determined by analysis of the potential energy surface (PES). The calculated static first hyperpolarizability (β_0) value for monomers of ECADPC and EDNAPC are 17.078×10^{-30} and 2.344×10^{-30} esu respectively, infers ECADPC to be more suitable for non-linear optical (NLO) response than EDNAPC. The electronic descriptors analysis predicts the nature of local reactive sites within the molecule.

Introduction

Chalcones form an important class of compounds having various properties and applications. Chalcones are chemically open chain flavonoids consisting two aromatic rings linked by α,

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β-unsaturated carbonyl groups or with propanone chain. Chalcones are widely present in fruits and vegetables and are the prominent secondary metabolites of flavonoids and isoflavonoids in plants. They possess wide varieties of biological activities [1–6]. They are used as versatile starting materials for the synthesis of a variety of N, O containing heterocyclic compounds such as pyrazoline [7], oxazoline [8] and pyrimidine [9].

Derivatives of chalcones are prospective new materials for optical sensors [10], ultrafast optical nonlinearities [11], UV-absorption filters [12] and nonlinear optical (NLO) response [13]. NLO materials have been attractive in recent years with respect to their future potential applications in the field of optoelectronic such as optical communication, optical computing, optical switching, and dynamic image processing [14]. A nonlinear optical (NLO) property has been the subject of intense research due to their application in a wide range of technologies such as optical computing and optical communication [15,16]. To have strong second-order NLO properties, the compound must possess a large first-order molecular hyperpolarizability and must crystallize in a non centrosymmetric structure to have a nonzero χ. Besides the strong NLO response, the NLO materials must also fulfill some other technological requirements for practical applications such as wide transparency extending down to UV region, fast response, thermal stability, chemical stability, mechanical stability and high laser damage threshold [17]. The intramolecular charge-transfer feature available in the chalcone allows the researcher to design new molecules substituted for donor or acceptor groups, which gives an understanding of structure–property relationship.

Nowadays, theoretical conformational study, structural and spectral interpretation is quite useful in understanding the relationship between the molecular structure and properties of the compound. It also provides a guideline to the experimentalists for the design and synthesis of new organic materials. These above various applications have attracted experimentalists and theoretician to investigate the spectroscopic and structural properties of chalcones [16,17] and their derivatives [18]. Looking at the importance of pyrrole nucleus and chalcone, we are working and our research group has published paper on ortho-chloro derivative as ethyl 4-[3-(2-chloro-phenyl)-acryloyl]-3,5-dimethyl-1*H*-pyrrole-2-carboxylate (ECPADMPC) [19] and ortho-nitro derivative as ethyl 3,5-dimethyl-4-[3-(2-nitro-phenyl)-acryloyl]-1*H*-pyrrole-2-carboxylate (EDNPAPC) [20].

In order to understand and obtain results as effect of substituent on aromatic part of chalcone, new pyrrole–chalcones ECADPC and EDNAPC have been synthesized and comparative study about physiochemical nature has been performed even using our earlier results published on (ECPADMPC) [19] and (EDNPAPC) [20] chalcones. The ECADPC and EDNAPC have been characterized by different spectroscopic techniques (FT-IR, ^{1}H NMR, UV–Vis). The static first hyperpolarizability as well as reactivity has also been calculated. The interest in this study also provides opportunity for synthesis of new heterocyclic compounds that may have considerable pharmacological activities and material applications.

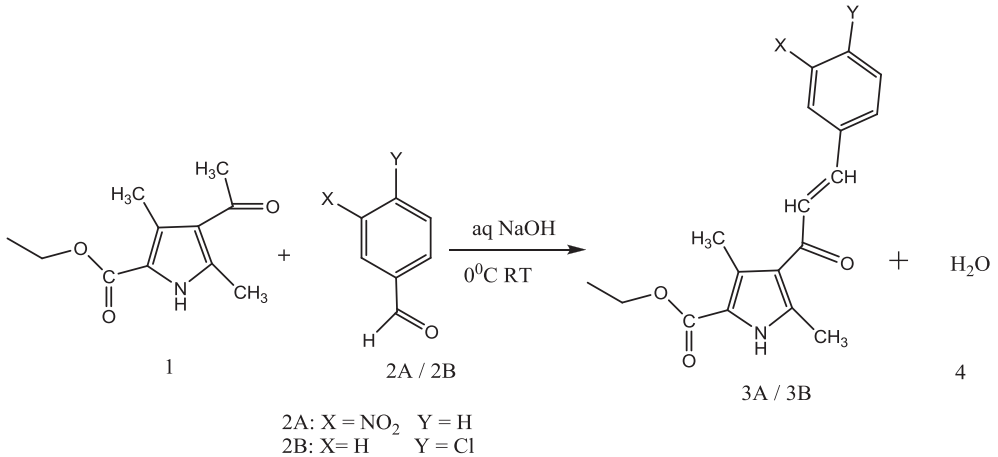
Materials, physical measurements, synthesis of ECADPC and EDNAPC

All chemicals used were of analytical grade. The solvent methanol was dried and distilled before use according to the standard procedure. Ethyl 4-acetyl-3,5-dimetyl-1*H*-pyrrole-2-carboxylate was prepared by an earlier reported method [21]. The FT-IR, ^{1}H NMR,UV–Vis absorption spectra were recorded on Bruker spectrometer, Bruker DRX-300 and ELICO SL-164 spectrophotometer, respectively.

A synthetic route for the formation of products is shown in Scheme 1. An equimolar mixture of ethyl 4-acetyl-3,5-dimethyl-1*H*-pyrrole-2-carboxylate (0.209 g, 1.00 mmol) and corresponding aldehyde ((4-chloro-benzaldehyde (0.3358 g, 1.00 mmol), 3-nitrobenzaldehyde (0.151 g, 1.001 mmol)) in 20 ml ethanol were stirred for 30 min in a round bottom flask placed in ice bath. To these NaOH solution (10 mL, 60%) were added dropwise with continuous stirring for 30 min. The reaction mixtures were stirred for overnight at room temperature. The completion of the reaction was monitored by thin layer chromatography (TLC). After completion of reaction, the reaction mixture was neutralized with dil. HCl, The mixtures were kept in a refrigerator for overnight to precipitate out the products. Then ice-cold distilled water (40 mL) was added, filtered, washed well with cold water, dried in air and recrystallized from ethanol. After recrystallization, the creamy color (ECADPC) and yellow color (EDNAPC) precipitate were obtained. The precipitate was filtered off, washed with ethanol and dried in air. Yield: 60%, mp 178 °C (ECADPC); 58.42%, mp 175 °C (decompose, EDNAPC).

Quantum chemical study

All computational calculations have been performed on personal computer using the Gaussian 09 program package [22] in gas phase at B3LYP/6-31G(d,p) and B3LYP/6-311 + G(d,p) level [23–25]. IEFPCM model with DMSO solvent (relative permittivity (ε) 46.7) was used for both NMR and UV–Visible spectra calculation. The calculated wavenumbers are scaled down using



Scheme 1. Represents the synthesis of ECADPC (3A) and EDNAPC (3B).