



Evaluation of molecular assembly, spectroscopic interpretation, intra-/inter molecular hydrogen bonding and chemical reactivity of two pyrrole precursors



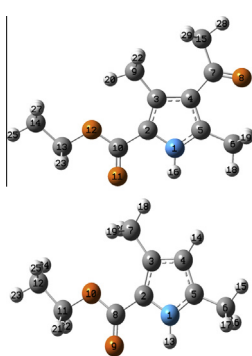
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HIGHLIGHTS

- The computational calculations were done using DFT/B3LYP/6-31G(d,p) and B3LYP/6-311+G(d,p) methods.
- FT-IR spectra of the studied compounds were recorded and compared with the theoretical results.
- Intra- and intermolecular charge transfer have been evaluated using NBO analysis.
- Chemical reactivity has been explained with the aid of global and local electronic descriptors.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper describes the evaluation of conformational, spectroscopic, hydrogen bonding and chemical reactivity of pyrrole precursor: ethyl 3,5 dimethyl-1*H*-pyrrole-2-carboxylate (EDPC) and ethyl 3,4-dimethyl-4-acetyl-1*H*-pyrrole-2-carboxylate (EDAPC) for the convenient characterization, synthetic usefulness and comparative evaluations. All experimental spectral values of ¹H NMR, UV-Vis and FT-IR spectra coincide well with calculated values by DFT. The orbital interactions in EDPC and EDAPC are found to lengthen their N–H and C=O bonds and lowers their vibrational frequencies (red shift) resulting to dimer formation. The QTAIM and NBO analyses provide the strength of interactions and charge transfer in the hydrogen bonding unit and stability of dimers. The binding energy of EDPC and EDAPC dimer are found to be 9.92, 10.22 kcal/mol, respectively. In EDAPC and EDPC dimer, hyperconjugative interactions between monomer units is due to $n_1(\text{O}) \rightarrow \sigma^*(\text{N-H})$ that stabilize the molecule up to 9.7 and 9.3 kcal/mol, respectively. On evaluation of molecular electrostatic potential (MEP) and electronic descriptors for EDPC it has been found that it is a good precursor for synthesis of formyl and acetyl derivatives whereas EDAPC has been found to be a good precursor for synthesis of schiff base, hydrazones, hydrazone-hydrazones and chalcones.

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Introduction

Synthetic pyrrole derivatives have been receiving great attention and gaining extraordinary importance due to

recognition of their range of properties – organoleptic, organic semiconductor, optoelectrical, non-linear optical and applications – pharmaceuticals, conducting polymers, organic light-emitting diodes [1], organic photovoltaic (OPVs) [2], organic field-effect transistors (OFETs) [3,4], sensory materials [5,6], photo-electrochemical solar cells, anticorrosion materials and catalysts [7,8].

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With increasing demand for number of pyrrole based compounds, attempts are being made in directions of simplifying the synthetic strategies of known precursors, synthesis of new pyrrole based precursors and derivatives as well as detailing out their spectral analysis, structural elucidation and chemical reactivity. The crystal structure of ethyl 3,4-dimethyl-4-acetyl-1H-pyrrole-2-carboxylate (EDAPC) and ethyl 3,5 dimethyl-1H-pyrrole-2-carboxylate (EDPC) have been reported [9,10].

Hydrogen bonds are of versatile importance in the fields of chemistry and bio-chemistry [11], which governs solvation, atmospheric chemistry [12], molecular assemblies, molecular recognition, organic synthesis, supramolecular structures, biochemical phenomena and life processes.

In DFT the energy of the molecule is determined from the electron density instead of a wavefunction and has emerged as an important inexpensive quantum chemical tool for studying various chemical problems [13]. The Quantum theory of atoms in molecules (QTAIM) efficiently describes H-bonding and its concept without border. With respect to change of both method and basis set reliability and stability of values of QTAIM parameters have been studied and found that they almost remain independent of basis set in case of used functional B3LYP in DFT [14]. The NBOs provides an accurate method for studying interaction among intra- and intermolecular bonding and an efficient basis for investigating charge transfer or conjugative interaction in various molecular systems [15].

In order to have the convenient characterization, comparative evaluations and synthetic usefulness for vast number of compounds with range of properties for variable applications and vast exploitation, there is need to evaluate the structural, spectral and reactivity of the known precursors. Using the experimental spectral data and quantum chemical calculations these aspects have been evaluated. Vibrational, QTAIM and NBO analyses are important for characterization of hydrogen-bonding and other weak interactions, whereas molecular electrostatic potential (MEP) and electronic descriptors are used for the chemical reactivity descriptions of molecule. Evaluation of chemical reactivity finds their suitability as precursor for synthesis of certain compound and class of compounds suiting pharmacological activities and material applications.

Experimental details

Preparation and spectral recording

The EDPC and EDAPC were easily and economically prepared by a Knorr-type reaction from the condensation of ethyl oximinoacetate and acetylacetone, and ethyl oximinomalonate and acetylacetone, respectively [9,10] and recrystallized using ethanol. FT-IR spectra were recorded in KBr disk on a Nicolet MX-1 FT IR spectrophotometer, ¹H NMR spectra were recorded at 300 MHz (CDCl₃) on a Bruker spectrometer and the chemical shifts are reported in (parts per million) units with respect to TMS as internal standard and the ultraviolet absorption spectrum was examined in the range 200–800 nm using Shimadzu UV 2100, UV-Vis recording spectrophotometer equipped with a 10-mm quartz cell. The UV pattern is taken from 10⁻⁵ molar solution in methanol at 20 °C.

Computational details

All calculations (geometry optimization, IR vibrational frequencies, ¹H NMR chemical shifts and UV-Vis) have been performed using Gaussian 09 program package [16] at B3LYP/6-31G(d,p) and B3LYP/6-311+G (d, p) basis set [17]. The optimized structures were compared with experimental results in CHEM3D by

superimposing them minimizing the root square distance between selected atoms. The ¹H NMR chemical shifts [18] and electronic absorption spectrum were also calculated. The calculated vibrational wavenumber at B3LYP/6-31G (d, p) and B3LYP/6-311+G (d, p) have been scaled down using single scaling factor 0.9608 and 0.9613, respectively [19,20]. The potential energy distribution along internal coordinates system recommended by Pulay et al. [18] has been used for FT-IR assignment. AIM calculation was performed by AIM2000 program [21] and the wavefunction generated from the electron density of single crystal.

The interaction potential (the negated binding energy) of two molecules A and B is defined by

$$\Delta E = E_{AB} - E_A - E_B \quad (1)$$

where the total energies of the dimer E_{AB} and of the two isolated molecules E_A and E_B are obtained from separate calculations and structural relaxation of the molecules upon formation of the dimer is neglected [22,23].

The BSSE quantity was obtained using the Boys–Bernardi method [24] as

$$(BSSE) = [E_A^{CP} + E_B^{CP}] - [E_{AB}] \quad (2)$$

where the superscripts denote counterpoise-corrected energy of monomer A and B in the full basis set of the dimer. Finally the corrected counterpoise-energy to the interaction energy is obtained as the differences between Eqs. (1) and (2).

The reorganization energy (E_{reorg}) is the deformation energy due to the dimerization. The reorganization energy, the energy associated with the transition from the optimized geometry of monomer to the geometry of the monomer in the dimer, should be also included in the correction of BSSE [25–27]. The electronic descriptors have been calculated by standard procedures [28–35]. For visualization Gauss View [36] program package was used.

Results and discussions

Geometry optimizations and conformational study

The structure concerns the way in which atoms are bonded together into stable molecular structure, and the way in which these structure change in the course of interaction with radiation and chemical transformations (reaction). The initial geometry were taken from X-ray crystal structure [9,10] and the geometries were optimized (yielding no imaginary frequency) by the DFT method, employing B3LYP/6-31G (d, p) and B3LYP/6-311+G (d, p) basis set using Gaussian 09 program [15] without any constraint to the potential energy surface. The other conformers (II, III and IV) of EDAPC were generated by rotation of acetyl and ester functional groups and for EDPC by rotation of ester functional group. The optimized structures are given in Fig. 1. The respective energies of all EDPC conformers are –708.68542 (IA), –708.68517 (IIA), –708.68366 (IIIA) and –708.68228 (IVA) a.u. The conformer IA is 0.156 kcal/mol lower in energy than conformer IIB. The energy difference between conformers (IA & IIB) and (IA & IVA) are 1.104 and 1.197 kcal/mol, respectively. The energies of EDPC conformers are –556.03363 (IB) and –556.03262 (IIB) a.u. The energy difference between conformer IB and IIB of EDPC is found to be 0.633 kcal/mol. The conformer IA of EDPC and IB of EDPC have lowest energy than other conformers. Conformer IA and IB have suitable geometry by having pyrrolic N–H and carbonyl C=O of ester on same side, thereby, favoring dimer formation. The conformer IA and IB forms centrosymmetric dimer by hydrogen bonds, as shown in Fig. 2 and often observed in related compounds [37–42]. The dimer of EDPC and EDPC pyrrole derivatives were

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