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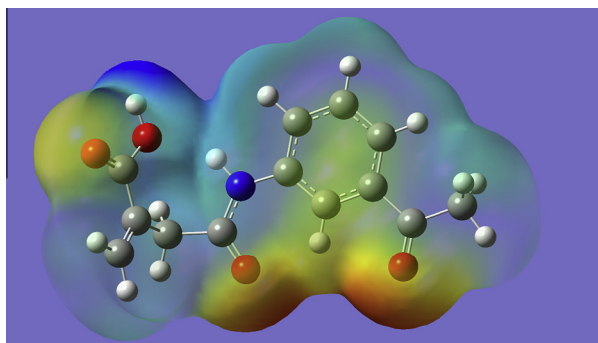
FT-IR, molecular structure, first order hyperpolarizability, MEP, HOMO and LUMO analysis and NBO analysis of 4-[(3-acetylphenyl)amino]-2-methylidene-4-oxobutanoic acid

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HIGHLIGHTS

- IR, XRD and NBO analysis were reported.
- The wavenumbers are calculated theoretically using Gaussian09 software.
- The wavenumbers are assigned using PED analysis.
- The geometrical parameters are in agreement with XRD data.

GRAPHICAL ABSTRACT



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ABSTRACT

4-[(3-Acetylphenyl)amino]-2-methylidene-4-oxobutanoic acid is synthesized and the structure of the compound was confirmed by IR, ¹H NMR and single crystal X-ray diffraction studies. FT-IR spectrum of 4-[(3-acetylphenyl)amino]-2-methylidene-4-oxobutanoic acid was recorded and analyzed. The crystal structure is also described. The vibrational wavenumbers were computed using HF and DFT methods are assigned with the help of potential energy distribution analysis. The NH stretching frequency is red shifted in the IR spectrum with a strong intensity from the computed frequency, which indicates the weakening of the NH bond resulting in proton transfer to the neighboring oxygen atom. The first hyperpolarizability and infrared intensities are also reported. The stability of the molecule arising from hyper-conjugative interaction and charge delocalization has been analyzed using NBO analysis. The HOMO and LUMO analysis are used to determine the charge transfer within the molecule. Molecular electrostatic potential map was performed by the DFT method. The geometrical parameters of the title compound obtained from XRD studies are in agreement with the calculated (DFT) values.

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Introduction

Copolymers containing both hydrophilic and hydrophobic segments are drawing considerable attention because of their possible use in biological systems. N-substituted itaconamic acids are strongly amphiphilic molecules [1]. Itaconic anhydride is an unsaturated dicarboxylic organic anhydride with one carbonyl group conjugated to the methylene group. It can be regarded as a substituted acrylic or methacrylic derivatives. In addition it can be obtained from renewable resources [2,3]. Anhydride derivatives are used extensively as reactive starting material for the preparation of cinnamates as flavoring agents and components in perfumes and of cinnamic amides with such applications as sun blocking ingredients in cosmetics [4,5] and compounds of medicinal usefulness [6,7]. Itaconic anhydride is produced from the pyrolysis of citric acid or through the fermentation of carbohydrates forming itaconic acid followed by its dehydration to form the anhydride [8]. Itaconic anhydride can be polymerized [9] or copolymerized with various other monomers [10,11] by free radical reactions. Because it forms highly reactive tertiary radicals [12,13], itaconic anhydride is more reactive than maleic anhydride and is an alternative monomer for introducing polar functionality into polymers. It can be also useful for the synthesis of various biodynamic derivatives such as imides

[14], pyridazine [15], oxazepine [16] and oxobutanoic acid [17] derivatives. In the present study, IR spectrum of 4-[(3-acetylphenyl)amino]-2-methylidene-4-oxobutanoic acid was reported both experimentally and theoretically. The energies, degrees of hybridization, populations of the lone pairs of oxygen, nitrogen atoms, energies of their interaction with the anti-bonding orbital of the benzene ring and the electron density distributions and $E(2)$ energies have been calculated by NBO analysis using DFT method to give clear evidence of stabilization originating from the hyper-conjugation of various intra-molecular interactions. There has been growing interest in using organic materials for nonlinear optical devices, functioning as second harmonic generators, frequency converters, electro optical modulators, etc., because of the large second order electric susceptibilities of organic materials. Since the second order electric susceptibility is related to first hyperpolarizability, the search for organic chromophores with large first hyperpolarizability is fully justified.

Experimental

Itaconic anhydride (0.112 g, 1 mmol) dissolved in a 30 mL acetone and it was stirred at ambient temperature and 3-aminoaceto-

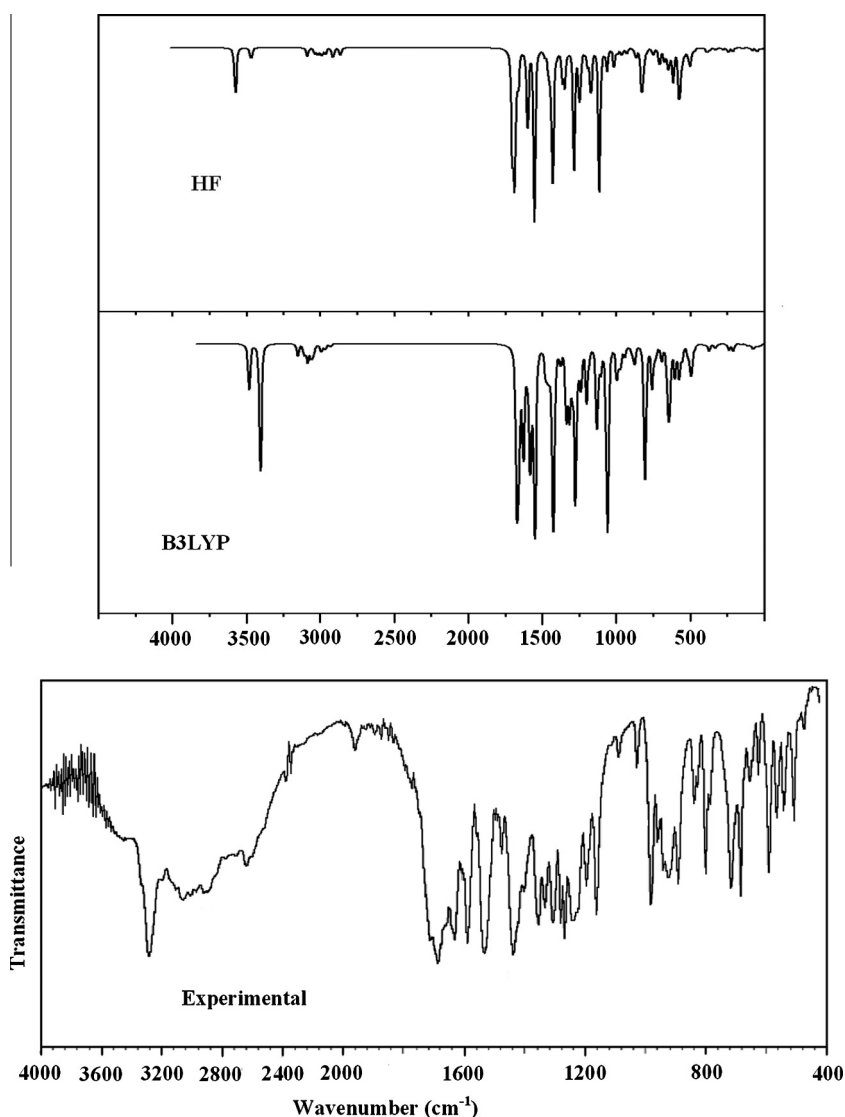


Fig. 1. FT-IR spectrum of 4-[(3-acetylphenyl)amino]-2-methylidene-4-oxobutanoic acid.

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