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Molecular structure, FT-IR, first order hyperpolarizability, NBO analysis, HOMO and LUMO analysis of 2-(4-chlorophenyl)-2-oxoethyl 3-methylbenzoate by HF and density functional methods

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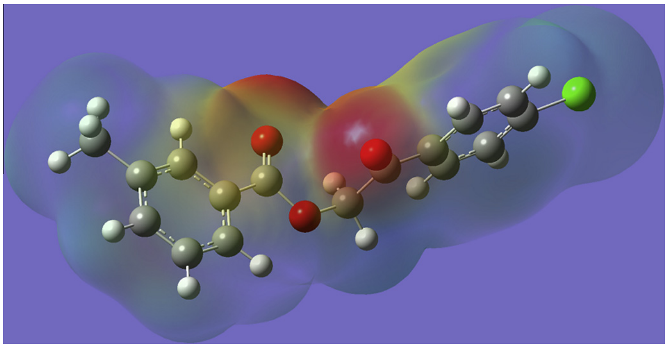
HIGHLIGHTS

- IR, single crystal 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 that XRD data.

GRAPHICAL ABSTRACT



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ABSTRACT

2-(4-Chlorophenyl)-2-oxoethyl 3-methylbenzoate is synthesized by reacting 4-chlorophenacyl bromide with 2-methylbenzoic acid using a slight excess of potassium or sodium carbonate in DMF medium at room temperature. The structure of the compound was confirmed by IR and single-crystal X-ray diffraction studies. FT-IR spectrum of 2-(4-chlorophenyl)-2-oxoethyl-3-nitrobenzoate was recorded and analyzed. The crystal structure is also described. The vibrational wavenumbers were computed using HF and DFT methods and are assigned with the help of potential energy distribution method. The first hyperpolarizability and infrared intensities are also reported. The geometrical parameters of the title compound obtained from XRD studies are in agreement with the calculated (DFT) values. 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. MEP was performed by the DFT method.

Introduction

Phenacyl bromide derivatives have found vital applications from decades in the field of synthetic chemistry [1] such as in

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the synthesis of oxazoles and imidazoles [2] as well as benzoxazepine [3]. In organic chemistry, phenacyl benzoate is a derivative of an acid which is formed by the reaction between an acid and a phenacyl bromide. They play a key role as protecting groups for carboxylic acids in organic synthesis and biochemistry [4–6]. The advantage of using these photosensitive blocking groups in general is that, they can easily be cleaved under completely neutral and mild conditions [4–6] and therefore were used for the identification of organic acids. Chlorophenyl derivatives are used as industrial chemical because they are lipid soluble and resistant to metabolism. These compounds accumulate in adipose tissue. These derivatives are used as the major metabolite of DDT, and PCBs (Polychlorinated biphenyls) with an increased risk of breast cancer. The methyl benzoates have very pleasant odors and indeed are the major components of the flavor and odor aspects of a number of fruits. The compounds of natural odors are often used in the food industry for artificial flavors and fragrances [7]. Muthu et al. [8] reported the vibrational spectroscopic study of a chlorophenyl derivative. Tasal and Kumalar [9] reported the ab initio HF, DFT and experimental study of a derivative containing oxoethyl group. In the present study, single crystal XRD and IR spectrum of 2-(4-chlorophenyl)-2-oxoethyl-3-methylbenzoate was reported both experimentally and theoretically. The energies, degrees of hybridization, populations of the lone electron pairs of oxygen, 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 intramolecular 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

Synthesis of 2-(4-chlorophenyl)-2-oxoethyl 3-methylbenzoate

The reagents and solvents for the synthesis were obtained from the Aldrich Chemical Co., and were used without additional purification. 2-Bromo-1-(4-chlorophenyl)ethanone (0.002 mol) was reacted with 3-methylbenzoic acid (0.003 mol) in presence of potassium carbonate in dimethyl formamide (10 ml) at room temperature for about 2 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was poured into ice-cold water. The solid product obtained was filtered, washed with water and re-crystallized from ethanol. Crystals suitable for X-ray diffraction studies were grown in a mixture of acetone/ethanol (1:1 *v*/*v*) by the slow evaporation technique. Melting point (126–128 °C) was determined by Stuart Scientific (UK) apparatus. The purity of the compound was confirmed by thin layer chromatography using Merck silica gel 60 F254 coated aluminum plates. X-ray analysis was done using Bruker SMART Apex II DUO CCDC diffractometer. The data were processed with SAINT and corrected for absorption using SADABS [10]. The structure was solved by direct method using the program SHELXTL [11], and were refined by full-matrix least squares technique on F^2 using anisotropic displacement parameters. The non-hydrogen atoms were refined anisotropically. In the title compound, all the H atoms were calculated geometrically with isotropic displacement parameters set to 1.2 (1.5 for methyl groups) times the equivalent isotropic *U* values of the parent carbon atoms. For methyl groups, a rotating group model was applied.

The title compound, ($C_{16}H_{13}ClO_3$), crystallizes in monoclinic space group $P2_1/c$ and the molecular structure of the compound is shown in Fig. 1. The crystal data and parameters for structure refinement of the title compound are given in Table S1 as supporting information. In the compound, methyl-substituted benzene ring is twisted from the chloro-substituted benzene ring with a dihedral angle 67.81(13)°. In the crystal packing (Fig. 2), the molecules are linked into centrosymmetric dimers *via* intermolecular $C_{15}—H_{15A}\cdots O_3$ hydrogen bonds (supporting material Table S2) with R_2^2 (10) graph-set motifs (Fig. 2) [12]. H—bonding interactions are listed in Table S2. The dimers are further connected by intermolecular $C_8—H_{8B}\cdots O_3$ hydrogen bonds (Table S2) to form a ladder-like-pattern along the *a*-axis as illustrated in Fig. 2. Further stabilization is provided by weak C—H···π interactions, involving the C_{16} atom and the centroid of the benzene ring ($C_1—C_6$).

Crystallographic data for the compound has been deposited at the Cambridge Crystallographic Data Centre with the CCDC No.: 939880. FT-IR spectrum (Fig. 3) of the compound was recorded as KBr pellets, in the ratio 1:3 by the mass of the sample to that of KBr, in the region of 4000–400 cm^{-1} with Perkin–Elmer spectrum GX with a spectral resolution of 4 cm^{-1}.

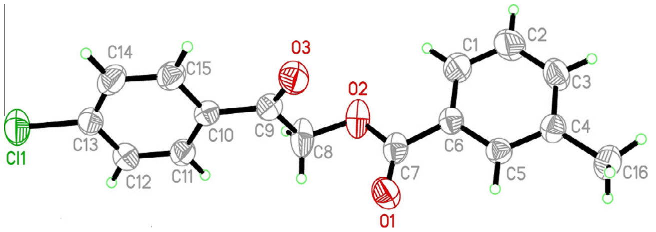

Fig. 1. Molecular view of 2-(4-chlorophenyl)-2-oxoethyl-3-methylbenzoate showing 30% probability displacement ellipsoids and atom labeling scheme.

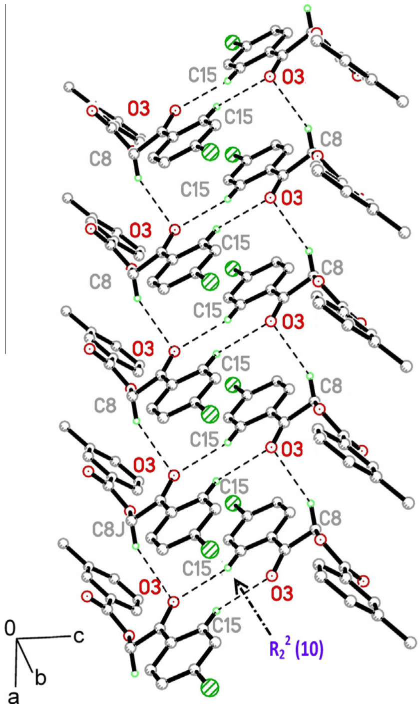

Fig. 2. Crystal structure of 2-(4-chlorophenyl)-2-oxoethyl-3-methylbenzoate with intermolecular hydrogen bonding patterns shown as dashed lines. Hydrogen atoms not involved in intermolecular interactions have been omitted for clarity.