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Vibrational spectroscopy, intramolecular CH···O interaction and conformational analysis of 2,5-dimethyl-benzyl benzoate

Rommel B. Viana [a], [*], Gabriela L.O. Ribeiro [a], Leidy J. Valencia [b], Jaldyr J.G. Varela Jr. [c], Anderson B. Viana [d], Albérico B.F. da Silva [a], Rodolfo Moreno-Fuquen [b]

[a] *Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, SP, Brazil*
[b] *Departamento de Química, Facultad de Ciencias, Universidad del Valle, Santiago de Cali, Colombia*
[c] *Laboratório de Química Quântica Computacional, Departamento de Química, Universidade Federal do Maranhão, São Luís, MA, Brazil*
[d] *Departamento de Engenharia Oceânica, Centro de Tecnologia (Bloco C, Sala 203), Instituto Alberto Luiz Coimbra de Pós Graduação e Pesquisa de Engenharia (COPPE), Universidade Federal do Rio de Janeiro (UFRJ), Rio de Janeiro, RJ, Brazil*

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ABSTRACT

The aim of this study was to report the spectroscopic and electronic properties of 2,5-dimethyl-benzyl benzoate. FT-IR and Raman vibrational spectral analyses were performed, while a computational approach was used to elucidate the vibrational frequency couplings. The electronic properties were predicted using the Density Functional Theory, while the G3MP2 method was employed in the thermochemical calculation. A conformational analysis, frontier orbitals, partial atomic charge distribution and the molecular electrostatic potential were also estimated. Concerning to the dihedral angles in the ester group, a conformational analysis showed a barrier energy of 10 kcal mol^{-1}, while other small barriers (below 0.6 kcal mol^{-1}) were predicted within the potential surface energy investigation. Insights into the relative stability among the different positions of methyl groups in the phenyl ring demonstrated that the energy gaps were lower than 1 kcal mol^{-1} among the regioisomers. In addition, the Quantum Theory of Atoms in Molecules (QTAIM) was used to understand the intramolecular CH···O interaction in the title compound, while various methodologies were applied in the atomic charge distribution to evaluate the susceptibility to the population method.

1. Introduction

Benzyl benzoate and its derivatives can be used in several applications [1–11]. Benzyl benzoate is an important constituent of repellents applied on honey beens at canola and alfalfa fields [1] and it was also used in the reduction of dust mite allergens in carpet [2,3]. Additional application of benzyl benzoate was also seen in the treatment of scabies, an endemic ectoparasitic infection in Africa [4–6]. Moreover, benzyl benzoate derivatives showed oestrogenic [7], anti-larvicidal [8], anti-acaricidal [9,10] and anti-hypertensive activities [11].

The aim of this study was to perform a spectroscopic and a quantum chemical investigation of 2,5-dimethyl-benzyl benzoate. Although 2,5-dimethyl-benzyl benzoate has been structurally characterized [12], to our knowledge, no spectroscopy investigation of this compound involving detailed vibrational analyses or quantum chemical characterization have been reported. Therefore, this study will provide a description of the 2,5-dimethyl-benzyl benzoate geometry and its conformational aspects, as well as an elucidation of vibrational frequencies and their couplings and details of the electronic properties that cannot be assessed by experimental results. Taken together, these data should provide a deep understanding of this system. Additional analyses were also devoted to estimate the heat of formation, the partition coefficient, the frontier orbitals, the molecular electrostatic potential, as well as the atomic charge distribution of the title compound. Natural Bond Orbital (NBO) and Quantum Theory of Atoms in Molecules (QTAIM) were also performed in order to elucidate the electronic properties.

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[*] Corresponding author. Av. Trabalhador São Carlense, 400 (caixa-postal: 780), Bairro: Centro, CEP: 13560970, São Carlos, SP, Brazil.
E-mail address: rommelbv@yahoo.com.br (R.B. Viana).

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2. Materials and methods

2.1. Experimental details

2,5-dimethyl-benzyl benzoate was synthesized using the procedure of Gowda et al. [12]. The FTIR spectrum was performed between KBr windows from 4000 to 400 cm^{-1} on a FTIR GX1 spectrophotometer (resolution of 1 cm^{-1} and 64 scans). The Raman spectrum (2000–200 cm^{-1}) was measured with a Bruker IFS 66 and a FRA 106 accessory (resolution of 1 cm^{-1} and 100 scans, employing an excitation line of 1064 nm with 800 mW). These spectroscopic analyses were performed in a monocrystalline solid sample while the crystal packing was already determined by Gowda et al. [12].

2.2. Computational methodology

The electronic calculations were performed with the GAUSSIAN 09 program [13]. The PBE1PBE functional [14,15] was used to optimize the structure employing the 6-311G(3df,3pd) basis set [16,17], where the absence of imaginary frequencies indicates that the optimized structure is a true minimum. A tight convergence was applied in the self-consistent field and in the optimization procedure, as well as in an *ultrafine* grid. The relaxed scan at the dihedral angle C-O-O-C was performed using the PBE1PBE/6-31G(2df,2pd) method. In the atomic charge distribution, we applied the Mulliken, Löwdin, generalized atomic polar tensor (GAPT) [18], natural population analysis (NPA) [19], Chelp [20], ChelpG [21] and Merz-Singh-Kollman (MK) [22,23] methodologies. Natural bond orbital (NBO) analysis was carried out using the NBO 6.0 program [24]. Topological analysis with Quantum Theory of Atoms in Molecules (QTAIM) [25] was performed using the AIMALL program [26].

3. Results and discussions

3.1. Geometry and structure prediction

Fig. 1 shows the potential energy surface (PES) relaxed scan performed in the O-C-O-C dihedral angle. The relaxed scan was performed with a step of 3° leading into a total number of 120 coordinate points and the full geometry was optimized in each coordinate point. The PBE1PBE/6-31G(2df,2pd) method was used only for this task. The starting point in the PES analysis presents a 0° dihedral angle, and it was selected five points (**ia**, **ib**, **ic**, **id** and **ie**) along the surface in order to show the changes between the dihedral angle and the relative energy. In this respect, **ib** represents the largest barrier energy within the potential surface energy (10 kcal mol^{-1}), while the others coordinate points are smaller than 1 kcal mol^{-1}. These data are similar with those reported by Druzbicki et al. [27] and Wlodarska [28], however, our results are higher than the values predicted by Metsala et al. [29] for hydroxyphenyl benzoates. In contrast, **ic** shows the smallest energy gap among the selected coordinate points which was chosen to be subsequently optimized with PBE1PBE/6-311G(3df,3pd), as can be seen in Fig. 2. This final structure was used in further analyses and in Table 1 is showed several properties of the title compound.

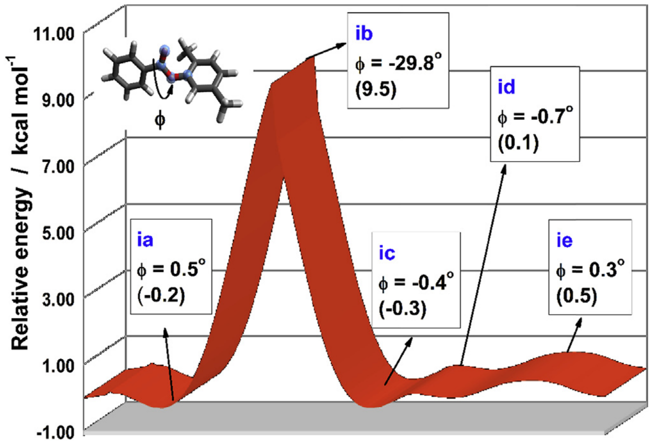

Fig. 1. The potential energy surface (PES) relaxed scan performed in the O-C-O-C dihedral angle (ϕ) of 2,5-dimethyl-benzyl benzoate. The relative energies (in kcal mol-1) are presented in parentheses. The relaxed scan was performed with a step of 3° leading into a total number of 120 coordinate points and the full geometry was optimized in each coordinate point employing PBE1PBE/6-31G(2df,2pd). The starting point presents a dihedral angle with 0°, and it was selected five points (ia, ib, ic, id and ie) along the PES in order to show the relation between the relative energy and the changes in dihedral angle.

Comparing our DFT results with experimental ones are seen a good agreement for bond lengths and angles. A similar picture is also seen when we look at the dihedral angles. The experimental [12] and predicted C_{12}-O_{14}-C_{15}-C_{16} dihedral angles are 90.19° and 106.22°, respectively. There was also good agreement between the C_3-C_2-C_{12}-O_{14} torsional angles, which were −10.13° and −0.11° for the experimentally-determined [12] and predicted values respectively. These data are also similar with other benzyl-benzoate structures, such as dimethyl- [30–32], dichloro- [33] and trinitro-structures [34], demonstrating that these dihedral angles are not susceptible to the substituent effects.

3.2. Electric dipole moment, partition coefficient and frontier molecular orbitals

In Table 1 was described the electric dipole moment, the octanol/water partition coefficient (Log P), the surface area, the volume, the refractivity and the mean polarizability. The predicted electric dipole moment of the title compound is 1.79 Debye with PBE1PBE/6-311G(3df,3pd). Applying a NBO analysis, we estimated that the major contribution to the dipole moment comes from the oxygen lone pair electrons [$_{lp}$(O)] in the ester group, followed by the contribution of the σ(C-H) and π(C-C) bonds in the phenyl groups.

The octanol/water partition coefficient (Log P) was also estimated here, which indicates the hydrophobicity of the compound.

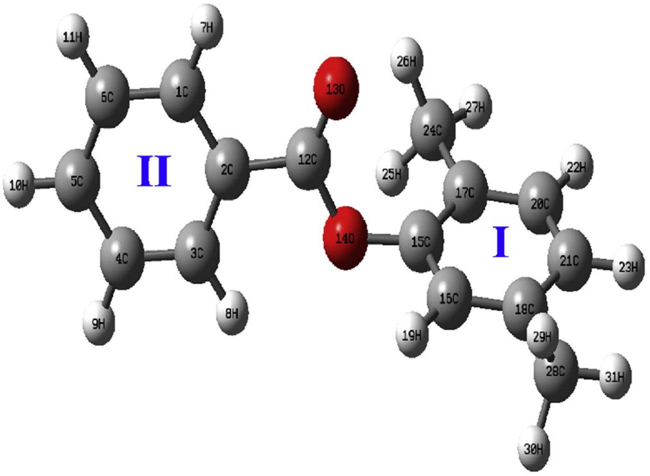

Fig. 2. 2,5-dimethyl-benzyl-benzoate structure optimized with PBE1PBE/6-311G(3df,3pd).