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Research paper

Theoretical study on the third-order nonlinear optical properties and structural characterization of 3-Acetyl-6-Bromocoumarin

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ABSTRACT

Coumarin derivatives exist widely in nature and show a wide range of biological activities such as anti-inflammatory, anti-oxidative and anti-cancer. The structure of $C_{11}H_7BrO_3$ has been redetermined using 3330 measured reflections with 1666 unique [Rint = 0.0088] with final indices $R1 = 0.0128$ [$I > 2\sigma(I)$] and $wR_2 = 0.0347$ (all data). The bromocoumarin molecule is almost planar and has three planar dimers stabilized by interaction of type C—H···Br and C—H···O, which form parallel layers connected via several π–π interactions [centroid–centroid distances = 3.958(1) Å]. To provide a view of the non-linear optical behavior of third order of the crystal bromocoumarin in both cases static and dynamic, we calculate the linear polarizability (α) and the second hyperpolarizability (γ) using a new supermolecule approach combined with an iterative electrostatic scheme where the neighboring molecules are represented by point charges. The results of calculations of the HOMO and LUMO energies show the occurrence of charge transfer inside the molecule. The computational results of the second (static and dynamics) hyperpolarizabilities show the molecule exhibiting second hyperpolarizability with values different of zero, which implies a third order microscopic behavior.

1. Introduction

The study of the effects (hyper) polarizabilities in organic materials constitutes an interesting topic that is considered by researchers in the last 30 years, e.g., by Champagne and Bishop [1]. The interest in molecules with great hyperpolarizability, especially the organic and polymeric, have attracted considerable interest because of their usefulness as nonlinear optical materials [2]. The fascination with new organic-based materials in nonlinear optical (NLO) emerged in the 1970s, when Davydov and colleagues reported a strong second harmonic generation (SHG) in organic samples [3]. The relative ease of synthesis, manipulation, and possibly its greater efficiency in NLO, put the organic structures on the research frontier and technological applications that has raised a lot of attention, and even today many researches are devoted to the rational synthesis of chromophores to optimize particular properties in NLO [4,5]. Theoretical researches have played an invaluable role in helping us to understand experimental datas, e.g, concerning the microscopic origin of molecular responses in NLO. The design of new chromophores with improved properties in NLO, obtained by adjusting the molecular parameters which optimizes a desired property. For example, Oliveira et al. investigated the static and dynamic effects of the first hyperpolarizability of azo-enaminones obtained from the approximation methods HF and MP2; the authors observed the mentioned property increasing with the donor group [6–8].

The polarizabilities and hyperpolarizabilities characterize the degree of distortion of the molecular electron cloud that results from the application of an external electric field. These are dynamic electrical properties respectively related to optical phenomena as absorption and refraction, and nonlinear optical phenomena. The determination of these properties is essential, among others, for a better understanding of dispersion forces and long range intermolecular inductions. Using the supramolecular method in

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an iterative process one can simulate the effect of the polarized medium upon the electrical properties of organic molecules. In this way, one obtains the dipole moment, the linear polarizability and second hyperpolarizability constituting the asymmetric unit of the crystal, surrounded by a polarized domain due to other molecules treated as point charges.

This polarization procedure is based on the fact that the dominant intermolecular interactions are electrostatic in nature and it takes into account the long-range electrostatic effects [9–11]. In addition, a dimer model was used to study in which way the incorporation of polarization effect in the material medium modifies the action of intermolecular interactions upon the electrical properties [12]. Moreover, the effects of the formation of dimers (in different configurations) have already been studied [13,14]. Reliable relations of structural properties are required for the rational design of materials optimized for photonic devices such as modulators electrooptic and all optical switches. Here the properties refer to the linear polarizability (α) and second hyperpolarizability (γ). It was recently proposed that an unconventional blockade may allow emission of antibunched light to reach passive devices made of materials with high susceptibility χ^3, such as silicon [15,16]. In the recent works by Seidler and co-workers, the authors have developed a general embedding/local field theory scheme to calculate χ^1 and χ^2, of molecular crystals [17–21] and another recent work by Santos et al. [22] the authors have used the present technique of polarization to estimate the calculation of χ^1 and χ^2 of molecular crystals, with results close to the experiments.

In the present work, the average linear polarizability α and second hyperpolarizability γ were studied both in the static and dynamic cases and the energy of the HOMO and LUMO were also investigated through the MP2 method. Also, the molecular parameters of hardness (η) and electronegativity (ζ) were obtained via the use of molecular frontier orbital energies. For background to related compounds and synthesis approach see [23–25]. The structure of 3-Acetyl-6-Bromocoumarin (ABC) $C_{11}H_7BrO_3$ has been previously determined [26], but the present redetermination, provides more accurate data, which are available in the Cambridge Structural Database (deposit@ccdc.camac.uk) under accession number 1,432,625.

2. Methodology

2.1. Synthesis and crystallization

The compound 5-bromo-2-hydroxybenzaldehyde was synthesized as described previously by Bhatnagar et al. [27] with slight modifications. To a solution of 5-bromo-2-hydroxybenzaldehyde (2 mmol) and methyl acetoacetate (2.2 mmol) in 3.0 mL of ethanol, an amount of 0.2 mL of diethylamine was added. After stirring overnight at room temperature, the solid was filtered, washed with cold ethyl ether and recrystallized from ethanol to afford the crystalline solid.

2.2. Crystallographic characterization

The single-crystal X-ray diffraction data Table 1 of the ABC ($C_{11}H_7BrO_3$) were collected at 293(2) K using a APEX2 [28] diffractometer with MoKα radiation (λ = 0.71073 Å). The cell refinement and data reduction were carried out also using the software SAINT [29]. The structure Fig. 1 was solved by direct methods using SHELXT [30,31] and anisotropically refined with full-matrix least-squares on F^2 using SHELXL [31,32]. The hydrogen atoms on the carbon atoms were positioned geometrically and refined applying the riding model [C—H 0.93 Å for C sp^2 and C—H 0.96 Å for C sp^3] with $U_{iso}(H) = 1.2U_{eq}(C)$ for C sp^2 and $U_{iso}(H) = 1.5U_{eq}(C)$ for C sp^3. All non-hydrogen atoms were refined with anisotropic displacement parameters. Number of restraints – 0, number of constraints – 0. Molecular representation, tables and pictures were generated by WinGX [33], ORTEP-3 [33], MERCURY 3.5 [34,35], Mogul [34,36] and POV-RAY [37] programs. The intermolecular interactions of the title compound were quantified using PARST [38] and PLATON [39,40] programs. The intermolecular contacts in the crystal structure were analyzed using Hirshfeld surfaces [41] and the associated 2D fingerprint plots [42]. This approach is a graphical tool used for visualization of intermolecular interactions. Such surfaces were generated from the CIF using the program CrystalExplorer 3.1 [43], which is performed by constraining these calculations [DFT/6-311G(d,p)] to experimental X-ray diffraction data via Tonto [44].

Table 1
Crystal data and refinement parameters of the $C_{11}H_7BrO_3$.

Empirical formula	$C_{11}H_7BrO_3$	
Formula weight	267.08 g/mol	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P – 1	
	a = 3.958(2) Å	α = 82.784(2)°
Unit cell dimensions	b = 11.048(1) Å	β = 79.940(2)°
	c = 11.125(6) Å	γ = 89.212(2)°
Volume	475.221(1) Å^3	
Z	2	
Calculated density	1.866 g/cm^3	
Absorption coefficient	4.305 mm^{-1}	
$F(000)$	264	
Crystal size	0.189 × 0.128 × 0.051 mm	
θ range for data collection	1.858–24.997°	
Limiting indices	$-4 \leqslant h \leqslant 4$, $-13 \leqslant k \leqslant 13$, $-13 \leqslant l \leqslant 13$	
Reflections collected/unique	3330/1666 [R(int) = 0.0088]	
Data completeness to θ = 25.242°	97.3%	
Data/restrictions/parameters	1666/0/164	
Solution	Direct methods	
Refinement	Full-matrix least-squares on F^2	
S (Goodness-of-fit) on F^2	1.084	
Final R indices [$I > 2\sigma$(I)]	$R1$ = 0.0125; wR_2 = 0.0345	
R indices (all data)	$R1$ = 0.0128; wR_2 = 0.0347	
$\Delta\rho$max. and $\Delta\rho$min. (e.Å^{-3})	0.282e–0.208e. Å^{-3}	

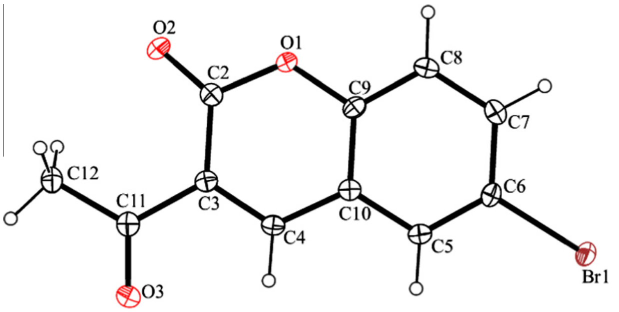

Fig. 1. The molecular structure of $C_{11}H_7BrO_3$ with atomic numbering system. Displacement of ellipsoids are drawn at the 50% probability level. The hydrogen atoms are spheres with arbitrary radii.

2.3. Computational details

To determine this method we used an experimental geometry of the asymmetric unit of ABC, see Fig. 2. The effects of the ABC crystal packing were modeled considering the nearest core units, each unit cell ABC composed by two molecules, each molecule consisting of 22 atoms. Each atom of the configuration around the ABC molecule was treated as point charge, in a 3 × 3 × 3 configuration