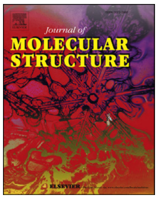
Journal of Molecular Structure 1157 (2018) 210–221

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc



Molecular structure of hybrid imino-chalcone in the solid state: X-ray diffraction, spectroscopy study and third-order nonlinear optical properties

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A R T I C L E I N F O

Article history:
Received 1 November 2017
Received in revised form
6 December 2017
Accepted 6 December 2017

Keywords:
Non-linear optical properties
Hirshfeld surface
Chalcones

A B S T R A C T

A comprehensive structural study of the compound (2E)-1-((E)-4-(4-methoxybenzylideneamino) phenyl)-3-(4-methoxyphenyl)prop-2-en-1-one was carried out in this work. Single crystal X-ray diffraction (SCXRD), X-ray powder diffraction (XRPD), NMR, Raman and Infrared spectroscopies, and DFT calculations were performed for characterization of this iminochalcone hybrid. Intermolecular interactions were described by Hirshfeld surface analysis derived from crystal structure. Reactivity and intramolecular charge transfer were investigated using the frontier molecular orbitals and molecular electrostatic potential. In addition, we have calculated the Nonlinear Optical Properties at the CAM-B3LYP/6−311+g(d) level of theory in the presence of different solvents (gas-phase, acetone, chloroform, dichloromethane, dimethyl sulfoxide, ethanol, methanol, and water), being found meaningful NLO parameters for our compound. At last, there is a good agreement between calculated and experimental IR spectrum, allowing the assignment of some of normal vibrational modes of the iminochalcone hybrid.

1. Introduction

Chalcones are α,β-unsaturated ketones in which two phenyl rings are linked to carbonyl and β carbons. Concerning their origin, chalcones are plant secondary metabolites structurally related to flavonoids, which are precursors of heterocyclic compounds owing biologic importance, such as benzodiazepines, pyrazolines, and flavones [1–3]. Besides their natural origin, chalcones can be synthesized by some classical routes, like the Claisen-Schmidt Condensation [3]. Such route consist of a catalysed condensation of aldeydes and ketones in the presence of an acid or basis as catalyst [4–6]. The growing interest in the study of these compounds is due to their relatively simple structure and synthesis route, besides several pharmacological activities. Their biological profiles are intrinsically related to the substituents at phenyl rings and α,β-carbons. For instance, Xia et al. [7] reported antiproliferative activities in amino-substituted chalcones, while chemotherapy and antibacterial activities are assigned to α-methylated and nitrofuryl-substituted chalcones, respectively [8]. In view of so many activities, it is evident that the need for getting structural knowledge of this compound class, since their physical, chemical and biological characteristics depend on their three-dimensional arrangement.

The design of crystal structures with desired properties is an important area of crystal engineering, and chalcones have been subject of these studies, which were devoted to the understanding of intermolecular interactions and identification of supramolecular synthons [9]. In recent years, considerable attention has been given

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https://doi.org/10.1016/j.molstruc.2017.12.023
0022-2860/

to the synthesis and designs of the chalcone molecules with specific properties such as non-linear optical ones, especially those with third-order properties [10]. Design of new second order nonlinear optical (NLO) materials requires a fundamental understanding of the structure and bonding features [11]. The NLO properties are mainly governed by molecular alignment and supramolecular interactions in organic solids. Therefore, it is of fundamental importance to understand, at the molecular level, the relationship between the molecular structure and electronic and optical properties of novel NLO-active molecular materials [12].

In this sense, in recent decades, in view of their large number of applications in spectroscopy, photonics, optoelectronics, etc., the NLO property of crystalline materials have attracted attention of several researchers from diversified scientific fields [13–17]. For instance, theoretical chemists are used to working with the *ab initio* description of NLO to understand in detail the structural and electronic properties of the crystalline environment [18,19].

Thus, this paper presents the structural elucidation of (2E)-1-((E)-4-(4-methoxybenzylideneamino)phenyl)-3-(4-methoxyphenyl)prop -2-en-1-one (MBA-MP) in terms of bond lengths and angles, molecular interactions and supramolecular arrangement. The chemical composition and intra and intermolecular interactions of the sample were confirmed by powder X-ray diffraction and spectroscopic (IR, NMR and Raman) analyses, whereas theoretical calculations allowed us to approach reactivity, charge transfer and NLO parameters of the studied compound.

2. Experimental and computational procedures

2.1. Synthesis and crystallization

The compound MBA-MP was synthesized by Claisen-Schmited condensation [20] and imine formation [21] reactions, with 1-(4-aminophenyl)ethanone and 4-methoxybenzaldehyde as reagents. In a 50 mL flask were added 15 mL of ethanol and 10% NaOH solution, followed by 0.2701 g of 1-(4-aminophenyl)ethanone (2 mmol). After the dissolution of ketone, it was added 0.2721 g of 4-methoxybenzaldehyde (2 mmol). The resulting solution was stirred at room temperature for 24 h, after this time the medium reaction was neutralized with 50% HCl solution. The resulting precipitate was filtered and washed with water, and finally purified by recrystallization from ethanol. Yellow single crystals of iminochalcone hybrid MBA-MP was obtained by the slow evaporation of ethanolic solution at 25 °C (Fig 1).

2.2. Crystallographic characterization

The X-ray diffraction data of MBA-MP were collected at room temperature using the Bruker APEX II CCD diffratometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). The imino-chalcone hybrid MBA-MP crystallized in the monoclinic non-centrosymetric space group *Pc* [22], which is a requirement for a crystalline material to exhibit NLO property. The main crystallographic parameters are shown in Table 1. The cell refinement and data reduction were carried out by the Bruker software SAINT. The structure was solved by direct methods and refined by least square methods throughout SHELX2014 softwares [23]. All hydrogen atoms were placed in calculated positions and refined with fixed individual displacement parameters [Uiso(H) = 1.2Ueq or 1.5Ueq] according to the riding model (CeH bond lengths of 0.97 Å and 0.96 Å, for aromatic and methyl groups, respectively). The structural information (molecular representation, tables and figures) was prepared with the programs WinGX [24], Ortep 3 [24] and Mercury [25]. The possible interactions and hydrogen bonds were checked by PARST [26] software and analyzed from Hirshfeld surface [27]. Hirshfeld surfaces and fingerprints show intermolecular interactions of MBA-MP and were calculated by Crystal Explorer software [28]. The crystallographic information files of the $C_{24}H_{21}NO_3$ molecule were deposited in the Cambridge Structural Data Base [29,30] under the code CCDC 1503286. Copies of the data can be obtained, free of charge, via www.ccdc.cam.ac.uk.

2.3. Hirshfeld surface analysis

The potential intermolecular interactions of MBA-MP were visualized and interpreted using Hirshfeld surface analysis. This graphical tool investigates in a straight way the molecular packing and supramolecular arrangement [28]. The first properties to be mapped on this surface were d_e and d_i, the distances of an atom external or internal to the generated Hirshfeld surface, respectively [9]. These interactions are examined within the context of the whole system and the colored map describes specific properties of the surface facilitating the visual inspection of intermolecular interactions. Fingerprint plots can summarize all contact distances to the Hirshfeld surface (d_i, d_e) and express their relative contribution [31]. Thus, interactions found in MBA-MP were mapped as a function of d_e (the distance from the surface to the nearest atom in the molecule itself) and d_i (distance from the surface to the nearest atom in another molecule) by Crystal Explorer 3.1 software [28], with the fingerprint plots being generated using the standard distances ranging from 0.6 to 2.8 Å for d_e/d_i.

2.4. Powder diffraction

XRPD patterns of MBA-MP were recorded at room temperature on a XPERT PANalytical diffractometer, equipped with X'Celerator detector and using filtered Kα1 radiation of a Cu tube operating with at 40 kV and 45 mA. Further measurements were performed at XRD1 beamline of Brazilian Synchrotron using 7 and 12 keV photons at room temperature and 100 K. All measurements were carried out in transmission mode using 0.7 mm glass capillary. The procedures for the structural determination were carried out using DASH [32] and the molecular structure was given by Nuclear Magnetic Resonance (NMR). Rietveld analyses of patterns were performed using GSASEXPGUI [33] and TOPAS 4.2 version (Bruker AXS GmbH, Karlsruhe, Germany). Many attempts to find a structural solution using powder diffraction data with DASH and the molecular structure from NMR gave no unequivocal solution, but a molecular conformation was obtained considering the same space group determined by single crystal experiments. Then, the Rietveld analyses were performed using GSAS-EXPGUI and TOPAS 4.2 by considering the initial model from CIF obtained from single crystal data analysis and the CIF gotten from DASH (Fig. 3). The satisfactory fitting was achieved with both CIFs, confirming the molecular structure of MBA-MP (Table 1).

2.5. Infrared and Raman spectroscopies

The experimental absorption spectrum in the solid state was measured in the region 4000–400 cm^{-1} and obtained in a spectrophotometer FT-IR/IRAffinity-1 Shimadzu. The sample was analyzed as a KBr pellet and the main absorbent groups were characterized. Raman spectra of different regions of a single crystal sample surface were collected with 20× objective lens at room temperature using a PeakSeeker 785 (RAM – PRO – 785). Raman system with a diode laser of 785 nm and 50 mW at the source were employed. The backscattered Raman radiation was dispersed with a grating and focused on a Peltier-cooled charge-coupled device CCD detector allowing us to obtain a spectral resolution of 6 cm^{-1}. All spectra were recorded in the spectral window from 200 to