



# Synthesis, spectroscopic characterization, electronic and optical studies of (2Z)-5,6-dimethyl-2-[(4-nitrophenyl)methylidene]-2,3-dihydro-1-benzofuran-3-one

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## ARTICLE INFO

### Article history:

Received 13 October 2014

Received in revised form

15 November 2014

Accepted 18 November 2014

Available online 16 December 2014

### Keywords:

Crystal structure  
Molecular geometry  
Optical properties  
Band structure

## ABSTRACT

The title compound, (2Z)-5,6-dimethyl-2-[(4-nitrophenyl) methylidene]-2,3-dihydro-1-benzo furan-3-one, has been synthesized and characterized using experimental (XRD) and theoretical methods (FTIR, NMR, electronic and optical studies). The compound crystallizes in monoclinic space group  $P2_1/c$  with  $a = 7.527(7) \text{ \AA}$ ,  $b = 15.9397(15) \text{ \AA}$ ,  $c = 13.5106(10) \text{ \AA}$ ,  $\beta = 117.649(4)^\circ$  and  $Z = 4$ . The initial coordinate geometry obtained by XRD is further used to obtain the optimized ground state geometry of the title compound using DFT/B3LYP/6-311++G (2d,2p) level of theory. Geometrical parameters, vibration frequencies, Gauge invariant atomic orbital (GIAO)  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts of the title compound have been calculated theoretically using the optimized ground state geometry. Apart from this, density of states of different atoms, band gap studies and optical properties have also been studied successfully using theoretical models.

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## 1. Introduction

Combining crystallography with molecular modelling has gained popularity in the recent years for characterization of molecules and to explore their physical and chemical properties. DFT, HF and MP2 along with other modelling methods are widely used in the theoretical modelling of molecules to understand the physical and chemical properties. We have explored the title compound by both experimental and theoretical methods to throw light on some of its properties which can be used for development of advanced applications. The title compound is an aurone type. Claisen–Schmidt reaction is one of the most important reactions for the synthesis of donor–acceptor conjugated dienes, known as chalcones [1]. Chalcones are precursors of open chain flavonoids and isoflavonoids, which are abundant in edible plants. It is

generally synthesized by the reaction of acetophenone and benzaldehyde in acidic [2] and basic medium [3,4]. Chalcones are the class of active compounds that have displayed a broad spectrum of pharmacological activities such as anti-oxidant [5], anti-inflammatory, antibacterial, anticancer, anti-allergic, antimalarial, antiviral and antifungal agents. In recent years, chalcones have been used in the field of material science as non-linear optical (NLO) material because chalcone derivatives are notable materials for their second harmonic generation (SHG). Researchers have reported different synthetic methods, such as, refluxing in an organic solvent [6], the solvent-free solid-phase reaction [7], ultra sonication [8], photosensitization [9] and microwave radiation [10]. Minor changes in their skeletal structure have offered a high degree of diversity that has proven useful for the development of new antioxidants having improved potency and lesser toxicity. In addition, the nucleus has been found to be used as antioxidant in a wide range of formulations targeting for the anti-aging activity. Aurones, (Z)-2-benzylidenebenzofuran-3-(2H)-ones, constitute a less studied subclass of flavonoids, which occur rarely in nature: to date a few aurones have been reported that were obtained from natural sources, mainly flowering plants, and a few ferns, mosses and

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marine brown algae [10]. They are also responsible for the bright yellow colour of some ornamental flowers such as snapdragon, cosmos and dahlia which are biosynthesized from chalcones by the key enzyme aureusidin synthase [11]. The naturally occurring aurones are aureusidin [12], sulfuretin [13] and maritimetin [14] possessing various hydroxylation patterns. A few natural aurones bearing methoxy substituent(s) on either or both rings have been reported [15–21]. Many synthetic routes have been proposed to synthesize aurones from 2-hydroxychalcone [22–27].

Encouraged with the above findings, an optically active aurone derivative: (2*Z*)-5,6-dimethyl-2-[(4-nitrophenyl)methylidene]-2,3-dihydro-1-benzofuran-3-one is synthesized successfully, spectroscopic characterization, its electronic and optical properties are discussed in detail.

## 2. Experimental and theoretical methods

### 2.1. Synthesis of the title compound

The reagents and solvents for the synthesis were obtained from the Sigma–Aldrich Chemical Co., and used as such without further purification. Melting point was determined by Stuart Scientific (UK) apparatus. The synthesis of the title compound was carried out according to the procedure reported earlier [3,4]. 4-Nitrobenzaldehyde (0.1 mol) was reacted with 1-(2-hydroxy-4,5-dimethylphenyl)ethanone (0.1 mol) in presence of catalytic amount of sodium hydroxide in methanol (10 mL). The reaction mixture was stirred at room temperature for about 5 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 obtained was filtered and washed successively with distilled water. The dried product was recrystallized with ethanol to get.

### 2.2. Crystallography study

A yellowish, block-shaped single crystal of the title compound, with dimensions of 1.00 mm × 0.36 mm × 0.22 mm was selected and mounted on a Bruker APEX-II CCD diffractometer with a fine-focus sealed tube graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) at 297 K in the range of  $2.6 \leq \theta \leq 32.3^\circ$ . The data were processed with SAINT and corrected for absorption using SADABS [28]. A total of 37,134 reflections were collected, of which 5201 were independent and 3460 reflections with  $I > 2\sigma(I)$ . The structure was solved by direct method using the program SHELXTL [29] and was refined by full-matrix least squares technique on  $F^2$  using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were positioned geometrically [C–H = 0.93–96 Å] and refined using riding model with isotropic displacement parameters set to 1.2 or 1.5 (methyl group) times the equivalent isotropic  $U$  values of the parent carbon atoms. A rotating group model was used for methyl groups. The final full-matrix least squares refinement gave  $R = 0.054$  and  $wR = 0.185$  ( $w = 1/[\sigma^2(F_o^2) + (0.0954P)^2 + 0.15897P]$  where  $P = (F_o^2 + 2F_c^2)/3$ ,  $S = 1.06$ ,  $(\Delta/\sigma)_{\max} = 0.001$ ,  $\Delta\rho_{\max} = 0.32 \text{ e}\text{\AA}^{-3}$  and  $\Delta\rho_{\min} = -0.20 \text{ e}\text{\AA}^{-3}$ . A summary of crystal data and parameters for structure refinement details are given in Table 1. Hydrogen bonding geometries are listed in Table 2. The ORTEP diagram of the compound (I) with atom labelling scheme drawn at 50% probability ellipsoids is depicted in Fig. 1.

### 2.3. Computational details

Ground state geometry using B3LYP/DFT/6-311+G(2d,2p) level of theory has been used for calculation of geometrical parameters, vibrational frequencies and NMR (GIAO) chemical shifts as employed in Gaussian 09 package (G09 Rev:D.01) [30] and Gauss

**Table 1**

Crystal data and parameters for structure refinement of the title compound (I).

Compound	(I)
CCDC	934224
Molecular formula	C <sub>17</sub> H <sub>13</sub> NO <sub>4</sub>
Molecular weight	295.28
Temperature (K)	297
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
<i>a</i> (Å)	7.5257 (7)
<i>b</i> (Å)	15.9397 (15)
<i>c</i> (Å)	13.5106 (10)
$\alpha$ (°)	90
$\beta$ (°)	117.649 (4)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	1435.6 (2)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.366
Crystal dimensions (mm)	1.00 × 0.36 × 0.22
$\mu$ (mm <sup>-1</sup> )	0.10
Radiation $\lambda$ (Å)	0.71073
Reflections measured	37134
Ranges/indices ( <i>h, k, l</i> )	–11, 11; –24, 24; –19, 20
$\theta$ limit (°)	2.6–32.3
Unique reflections	5201
Observed reflections ( $I > 2\sigma(I)$ )	3460
Parameters	201
Goodness of fit on $F^2$	1.06
$R_1, wR_2$ ( $I \geq 2\sigma(I)$ )	0.054, 0.189

**Table 2**

Hydrogen-bond geometry (Å, °).

D–H...A	D–H	HA	DA	D–H...A
C5–H5A...O4 <sup>i</sup>	0.93	2.55	3.394 (2)	151
C12–H12A...O2 <sup>ii</sup>	0.93	2.38	3.163 (2)	142
C15–H15A...O1	0.93	2.35	2.9889 (16)	125

Symmetry codes: (i)  $x, y, z + 1$ ; (ii)  $x, -y - 1/2, z - 3/2$ .

view (version 5) molecular visualization software [31]. The molecular geometry of the title compound has been fully optimized by using tight convergence criteria along with redundant inter-nuclear coordinates and Bery's optimization algorithm. Using GIAO (Gauge-Invariant Atomic orbital) approach [32,33] and DFT/6-311+G(2d,2p) level of theory, we herewith report the NMR (<sup>1</sup>H and <sup>13</sup>C) chemical shifts of the compound. The theoretical vibrational spectrum of the compound is investigated by means of VEDA 4 program. For calculations of electronic bands, density of states and optical properties of the compound, CASTEP package [34] as implemented in MATERIAL STUDIO program has been used. The geometry of the compound is again optimized in CASTEP package and this optimized geometry is further used in the calculations of the electronic bands, density of states and optical properties of the title compound. Geometry of the compound for optical, electronic and DOS calculations have been optimized using BFGS algorithm. The BFGS scheme uses a starting hessian which is recursively updated during the optimization process Scheme 1.

## 3. Results and discussion

### 3.1. Molecular geometry

The structures of (I) as predicted from X-ray analysis and DFT/6-311G+(2d,2p)/BLYP level of theory are shown in Fig. 1(a and b), respectively. X-ray analysis reveals that (I) crystallizes in monoclinic system with space group P2<sub>1</sub>/c with  $a = 7.527$  (7) Å,  $b = 15.9397$  (15) Å,  $c = 13.5106$  (10) Å,  $\beta = 117.649$  (4)°,  $Z = 4$  and  $V = 1435.6$  (2) Å<sup>3</sup>. To the best of our knowledge, the experimental and theoretical molecular parameters for the title compound have been calculated for the first time. In the compound (I), C<sub>17</sub>H<sub>13</sub>NO<sub>4</sub>,

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