Synthesis, spectral characterization, optical and crystal structure studies of (2E)-1-(4'-bromobiphenyl-4-yl)-3-(2-methoxyphenyl)prop-2-en-1-one

Vinutha P R¹, Jayarama A², Kaliprasad C S³, Narayana Y³, Suresh Kumar M R⁴

¹Dept. of Physics, Bearys Institute of Technology, Innoli, Mangalore, India.
²Dept. of Physics, Sahyadri College of Engg. and Management, Mangalore, India.
³Dept. of Physics, Mangalore University, Mangalagangotri, India.
⁴Dept. of Physics, Alliance University, Bengaluru, India.
*Corresponding author

Abstract

The title compound, (2E)-1-(4'-bromobiphenyl-4-yl)-3-(2-methoxyphenyl)prop-2-en-1-one (BDCP) was synthesized, characterized using UV-Visible, FT-IR, FT-Raman, Mass spectrometry and ¹H NMR. In addition, powder XRD and thermal studies of the BDCP was carried out. The optical studies of the compound using SHG method are performed. The crystal has shown good SHG property with SHG conversion efficiency 1.36 times that of Urea.

Keywords: NLO crystal, Optical property, Chalcone, SHG, Hydrogen bond. NMR spectroscopy

1. INTRODUCTION

Nonlinear optical (NLO) materials play a major role in fast developing fields like photonics and optoelectronics [1-2]. The NLO properties like second harmonic generation (SHG) and third harmonic generation (THG) exhibited by many materials have been reported in the literature. Among many materials, organic materials are highly attractive due to their high damage resistance, high nonlinearities and ultra fast response [3-4]. The advantages of using organic molecules as NLO materials are that they can be designed to optimize the desired NLO property by having different donor and acceptor groups in the molecules [5-6]. A number of organic materials have been identified and synthesized, showing considerable NLO effects. However only a few of
them could be crystallized and investigated for second order NLO applications. The search for new NLO materials has been increasing as a result of growing demand for such materials. The obligatory requirement for observing second-order NLO response in materials is that it should have a non-centrosymmetric crystal structure.

Chalcones are a class of cross conjugated NLO chromophores that is reported to exhibit good SHG efficiency, transparency and are easily crystallizable [5–6]. Zhao et al. [7] and Uchida et al. [8] have reported that most number of chalcone derivatives shows significantly high SHG conversion efficiency compared to the urea. From the past investigations it is found that carbonyl group alone is sufficient to induce large polarization in chalcone molecules to obtain high SHG conversion efficiency in chalcones [9]. In this article, we describe the synthesis, single-crystal growth of \((2E)-1-(4'-bromobiphenyl-4-yl)-3-(2-methoxyphenyl)prop-2-en-1-one\) (BDCP) and its characterization by IR, DTA, UV Vis and X-ray diffraction techniques.

2. EXPERIMENTAL PROCEDURE

A. Synthesis and crystal growth

In the present study Claisen–Schmidt condensation reaction method was followed to synthesize the title compound. The required chalcone \((2E)-1-(4'-bromobiphenyl-4-yl)-3-(2-methoxyphenyl)prop-2-en-1-one\) synthesized by aldol condensation of equimolar quantities of \(4'-(4\text{-bromophenyl})\) acetophenone with \(2\text{-methoxybenzaldehyde}\) using methanol as solvent of about \(66\) ml [10]. The reaction was carried out at room temperature with gradual addition of NaOH solution. The progress of the reaction was monitored using thin layer chromatography. After continuous stirring for \(1.5\) h, the reaction was complete. The reaction mixture was poured on to \(250\) g of crushed ice with vigorous stirring. The precipitate formed was filtered, dried and recrystallized from ethanol. A dirty white slimy product is obtained which upon refrigerating overnight yielded a yellow powder product. By slow evaporation at constant temperature method grown the good quality single crystals of BDCP. The purified BDCP powder sample was soluble in acetone. A saturated solution of BDCP in acetone was prepared at room temperature. The solution was filtered and kept at room temperature for slow evaporation. The synthesized title compound is shown in Figure 1.

\[
\text{Br} \quad \text{O} \quad \text{OCH}_3
\]

\((2E)-1-(4'-bromobiphenyl-4-yl)-3-(2\text{-methoxyphenyl})\text{prop-2-en-1-one}\)

**Figure 1.** Synthesis of Title compound.
**B. Mass spectrometry**
Mass spectrometry is one of the sophisticated analytical methods to find the unknown compounds within a sample and quantify known materials and elucidate the structure and chemical properties of different molecules. In the present study LCMS-8050 Triple Quadrupole Liquid Chromatograph Mass Spectrometer (LC-MS/MS) was used to measure the mass of synthesized compound.

**C. Second Harmonic Conversion efficiency**
The SHG intensity of the crystals was measured using the powder technique, developed by Kurtz and Perry [11]. The crystal was powdered and densely packed in a capillary. An Nd: YAG laser beam of wavelength 1064 nm, pulse width 8ns and repetition rate 10 Hz was made to fall normally on the sample in the capillary tube. The second harmonic signal was detected by a photo multiplier tube (Hamamatsu R2059) and displayed on a storage oscilloscope Tektronix (TDS 3052B).

**D. FTIR and FT-Raman spectrum**
Fourier Transformation Infrared spectrum is used to analyze the presence of functional groups in the newly synthesized BDCP crystal. The FTIR spectrum was recorded in the region 400 to 4000 cm\(^{-1}\) using the NICOLET 6700, USA spectrometer. The sample used was mixed with a known amount of KBr to make a pellet. The characteristic absorption peaks are observed in the range from 400 to 4000 cm\(^{-1}\) is shown in Fig.4. Laser Raman spectra for BDCP were recorded in the range 400 to 4000 cm\(^{-1}\) using NICOLET NXR, USA Raman spectrometer.  

**E. UV-Visible spectral studies**
The UV-Visible absorption spectrum of the crystal was recorded using a UV-1800 SHIMADZU UV-Visible spectrophotometer in the wavelength range of 200-800 nm. Crystals with parallel surfaces and thickness of 1 mm were used for this purpose.

**F. Differential thermal (DT)/thermogravimetric (TG) analysis**
Differential thermal (DT)/thermogravimetric (TG) analysis were carried out on the NBG samples to look for possible phase transitions and to determine the melting point. TG/DTA studies for NBG were made using Universal V4.5A TA Thermal analyzer at a heating rate of 10 °C min\(^{-1}\) under nitrogen atmosphere.
G. Powder x-ray diffraction study
Powder X-ray diffraction data was collected for the title compound using Rigaku X-ray diffractometer with CuKα radiation (λ = 1.5405 Å) with an applied operating voltage 30 kV and current 20 mA. The sample in the form of powder was mixed with binder and smeared on the surface of a glass slide. The sample was mounted on the centre of a diffractometer table.

3. RESULTS AND DISCUSSIONS
The mass spectrum was record of relative ion abundance versus m/z as shown in Figure 2. The measured value (m/z = 393.05) of title compound is nearly equal to the theoretically calculated mass 393.27. Therefore the synthesis of the compound was confirmed. The \(^1\)H NMR spectra of BDCP are shown in Fig. 3. The \(^1\)H NMR (DMSO, 400 MHz): δ(ppm); 2.67 (s, 3H), 3.359 (s, 1H, CH), 7.464-8.247 (m, 11H, Ar H). The SHG efficiency of newly grown crystal was measured by Kurtz and Perry method [12] and presented in table 1. The KDP was used as reference material to measure the SHG efficiency. SHG conversion of the newly grown crystal was found to 1.36 times that of Urea and 13.6 times that of KDP. The high value of SHG is due to the non-centrosymmetric structure of the title compound. The reported results shows that bromine attached to the benzene ring improves the donor acceptor group which is responsible for SHG conversion efficiency of the material [13-15]. This is also one of the reasons for increase in SHG conversion efficiency of the Title compound.

<table>
<thead>
<tr>
<th>Name of the compound</th>
<th>SHG efficiency (Urea = 1)</th>
</tr>
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<tbody>
<tr>
<td>(2(E))-1-(4(^{\prime})-bromobiphenyl-4-yl)-3-(2-methoxyphenyl)prop-2-en-1-one (title compound)</td>
<td>1.36</td>
</tr>
<tr>
<td>Potassium di phosphate (KDP)</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 1. SHG efficiency of the title compound.
FTIR and FT Raman Spectra for the title compound are shown in Figs. 4 and 5 respectively. The bands exhibited in the region around 3000 cm⁻¹ can be immediately assigned to be due to aromatic C-H stretchings [16]. In this view the vibrational frequencies exhibited at 2924 cm⁻¹ in the FTIR and 3080 cm⁻¹ in FT Raman are C-H stretching. The IR spectrum of wave number at 1670 cm⁻¹ and 1680 cm⁻¹ in FT-Raman attributable to the C=O stretch of α, β-unsaturated ketone, confirming the formation of chalcone. The Frequencies in 1599 to 1515 cm⁻¹ in FT IR and 1590 cm⁻¹ in FT-Raman consider to be a C-C stretching. The present sample shows the strong peak at 3080 cm⁻¹ in FT Raman confirms the benzene ring. The band region 1262 cm⁻¹ in FTIR and 1270 cm⁻¹ in FT Raman assigned to C-N Vibrations. The C-O stretching observed in the band region of 1002 to 1078 cm⁻¹ in FTIR and 1090 cm⁻¹ in FT Raman. The band at 738 cm⁻¹ in FTIR and 777 cm⁻¹ in FT Raman spectrum are C-C asymmetric bending.

![FTIR spectrum of BDCP crystal.](image)

**Figure 3.** NMR spectra of BDCP

**Figure 4.** FTIR spectrum of BDCP crystal.
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Figure 5. FT Raman of BDCP crystal.

The UV-Vis spectrum of BDCP is shown in Fig 6. It is clear from the graph that the BDCP has a lower optical cut-off at 428 nm and is transparent almost in the entire visible region. The crystal has strong absorption band in the UV-region. The absence of the absorption in the visible region can be exploited for NLO applications in the room temperature. The thermal analysis was carried out in the temperature range between 30 °C and 600 °C and the response curve of BDCP sample is shown in Fig. 5. The DTA curve shows a major endothermic peak, which corresponds to the melting point of the material at 124 °C and it shows exothermic peak at 552 °C, after that the compound decomposes. The BDCP compound decomposition between 195 °C to 290 °C with a maximum weight loss of 75%.

Using powder XRD, the sample was scanned over 2θ range from 10° to 70° at a range of 2° per minute. From the data collections, the spectra shows many sharp peaks. These sharp peaks indicate that these are highly crystalline in nature. The powder diffraction patterns for all the title compounds are presented in the Figure 8. The lattice parameters of the all the compounds are calculated and summarized in Table 2. The maximum counts are obtained at 26.8 degree with the count rate of 3190. The maximum number of hkl values 110 indicates the BCC crystal.

Figure 6. UV absorption spectra Figure 7. TG and DTA curves of BDCP.
The title compound BDCP has been synthesized, spectrally characterized using UV-Vis, FT-IR, FT Raman, and $^1$H NMR and physically characterized using powder XRD. The thermal studies were carried out using TGA and optical studies using SHG. The title compound is stable at lower temperature and it shows good NLO property as compared to the Urea (1.36 times). The crystal has strong absorption band in the UV-region and therefore it can be used for used for NLO applications at room temperature.
REFERENCE


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