



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, spectral, thermal, optical and theoretical studies of (2E,6E)-2-benzylidene-6-(4-methoxybenzylidene)cyclohexanone



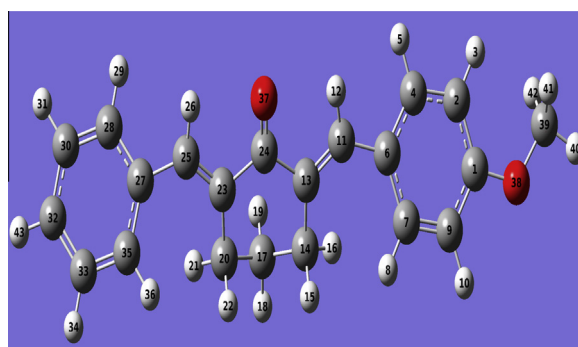
V. Meenatchi, K. Muthu, M. Rajasekar, SP. Meenakshisundaram*

Department of Chemistry, Annamalai University, Annamalainagar 608 002, Tamilnadu, India

HIGHLIGHTS

- Synthesis and characterization of novel chalcone derivative is reported.
- Product formation was confirmed by FT-IR and NMR spectral studies.
- First-order molecular hyperpolarizability is estimated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 June 2013

Received in revised form 28 September 2013

Accepted 2 October 2013

Available online 11 October 2013

Keywords:

Chalcone

Nuclear magnetic resonance spectroscopy

FT-IR

First-order molecular hyperpolarizability

Theoretical studies

ABSTRACT

Single crystals of (2E,6E)-2-benzylidene-6-(4-methoxybenzylidene)cyclohexanone are grown by slow evaporation of ethanolic solution at room temperature. The characteristic functional groups present in the molecule are confirmed by Fourier transform infrared and Fourier transform Raman analyses. The scanning electron microscopy study reveals the surface morphology of the material. Thermogravimetric/differential thermal analysis study reveals the purity of the material and the crystal is transparent in the visible region having a lower optical cut-off at ~ 487 nm. The second harmonic generation efficiency of as-grown material is estimated by Kurtz and Perry technique. Optimized geometry has been derived using Hartree–Fock calculations performed at the level 6-31G (*d,p*) and the first-order molecular hyperpolarizability (β) is estimated. The specimen is further characterized by nuclear magnetic resonance spectroscopy.

Crown Copyright © 2013 Published by Elsevier B.V. All rights reserved.

Introduction

The cytotoxic, anticancer, chemopreventative and mutagenic properties of a number of chalcones have been received [1]. 2,6-Bis(arylidene)cyclohexanone is a useful precursor for the construction of biologically important heterocycles. In addition,

2,6-bis(benzylidene)cyclohexanone was discovered as perspective nonlinear optically (NLO) active chromophore in the crystal state and it is used in second harmonic generation (SHG) applications [2]. Recently, we have investigated the synthesis, structure, growth and characterization of 1,5-diphenylpenta-1,4-dien-3-one [3] and 1,5-diphenylpenta-2,4-dien-1-one [4]. Molecular structure investigations of 1,5-diphenylpenta-1,4-dien-3-one have been reported [5]. As a part of our investigations on the growth and characterization of chalcones, the title study was undertaken. (2E,6E)-2-benzylidene-6-(4-methoxybenzylidene)-cyclohexanone (BMBC) was synthesized, crystals grown and characterized.

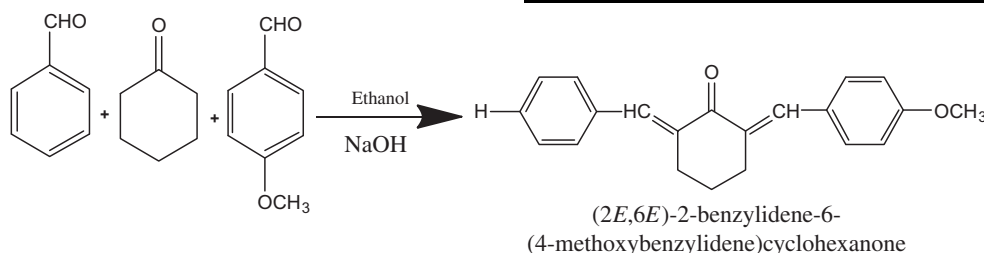
* Corresponding author. Tel.: +91 4144 221670.

E-mail addresses: meenass1957@gmail.com, aumats2009@gmail.com (SP. Meenakshisundaram).

Experimental

Synthesis and crystal growth

BMBC is synthesized by mixing stoichiometric amounts of cyclohexanone, benzaldehyde and *p*-methoxy benzaldehyde in the molar ratio of 1:1:1. The reactants were dissolved in ethanol, thoroughly mixed using a magnetic stirrer (10 min) and 20% NaOH solution was added drop by drop at 25 °C for 30 min [6]. After stirring for 3 h the contents of the flask were poured into ice-cold water. The resulting crude solid was collected by filtration, dried and purified by recrystallization process using ethanol as a solvent. Purity of the compound was checked by thin layer chromatography and melting point techniques.



Single crystals were grown from an ethanolic solution by slow evaporation solution growth technique at room temperature. A saturated solution of BMBC in ethanol was prepared and the solution stirred for 3 h at room temperature to obtain a homogenous solution. The solution was tightly covered with a perforated polythene sheet and kept at a constant temperature in dust free environment. Numerous tiny crystals were formed at the bottom of the beaker due to spontaneous nucleation. Yellow colored crystals of chalcones are harvested in a period of 7–9 days. Photograph of as-grown BMBC crystal is shown in Fig. 1.

Results and discussion

FT-IR and FT-Raman

FT-IR and FT-Raman spectra of BMBC recorded using AVATAR 330 FT-IR by KBr pellet technique and BRUKER RFS 100/S Instrument are shown in Fig. 2. The absorption bands at $\sim 1601\text{ cm}^{-1}$ in FT-IR and 1596 cm^{-1} in FT-Raman are aromatic C=C stretching frequencies of BMBC. The absorption bands



Fig. 1. Photograph of as-grown BMBC crystal.

~ 1654 (FT-IR) and 1661 cm^{-1} (FT-Raman) are assigned to C=O stretching vibrations [7]. The α,β -unsaturated carbonyl and aromatic C=C bending modes are observed at ~ 1508 and $\sim 1442\text{ cm}^{-1}$ respectively [8]. The aliphatic C–H stretching frequencies are observed at ~ 2843 and 2931 cm^{-1} . The observed FT-IR and FT-Raman (Fig. 2b) vibrational bands of BMBC are listed in Table 1.

NMR

^1H NMR and ^{13}C NMR spectra were recorded on BRUCKER AVIII 400 MHz NMR spectrometer operating at 400.13 MHz for ^1H and 100.61 MHz for ^{13}C using standard parameters. BMBC is dissolved in 0.5 ml of CDCl_3 solvent and TMS (tetramethylsilane) was used as an internal standard.

Fig. 3 shows the ^1H NMR spectrum of BMBC. A sharp singlet at 3.84 ppm corresponds to methoxy proton of the phenyl group and the doublet at 2.93 ppm, corresponding to four protons, are due to methylene (H-3, H-5) protons of the cyclohexyl ring. Sharp singlet at 1.80 ppm, corresponding to two protons, is due to para methylene (H-4) protons of the cyclohexyl ring. α,β -Unsaturated protons appeared as a triplet at 7.40 ppm. The multiplets in the range of 6.93–7.80 ppm are due to nine aromatic protons of the phenyl ring.

Fig. 4 shows the ^{13}C NMR spectrum of BMBC. Weak signals at 190 and 160 ppm are due to carbonyl carbon and ipso carbon of the methoxy substituted phenyl ring respectively. The signals at 28.5 and 23.1 ppm are due to methylene carbon of the cyclohexyl ring. α,β -Unsaturated carbons appeared at 137.0 ppm. The aromatic carbons appeared in the range of 113.9–136.6 ppm. The signal at 55.4 ppm represents the methoxy carbon of the phenyl ring.

UV-visible study

UV-vis spectrum of BMBC was recorded using CARY 5E UV-vis spectrophotometer. The purpose of this investigation is to find out the transmission region and the lower optical cut-off wavelength. The optical absorption spectrum (Fig. 5) shows good transmission in the visible region and the lower cut-off wavelength is $\sim 487\text{ nm}$ [9].

Thermal analysis

TG/DTA analysis of BMBC was carried out using NETZSCH STA 449F3 thermal analyzer in nitrogen atmosphere. TG/DTA curve of BMBC is shown in Fig. 6. There is no physically adsorbed water in the molecular structure of the crystal. In DTA, a sharp endothermic peak at $\sim 95\text{ }^\circ\text{C}$ is due to the melting point of the material and it was confirmed by using Sigma instrument melting point apparatus ($\sim 94\text{--}95\text{ }^\circ\text{C}$). The sharpness of the peak shows good degree of crystallinity and purity of material. TG curve shows a single stage weight loss at $\sim 350\text{--}475\text{ }^\circ\text{C}$ and it is due to decomposition of BMBC into fragments and its subsequent volatilization. In DTA curve the exo and endothermic peaks observed at ~ 375 and $\sim 425\text{ }^\circ\text{C}$ could be due to decomposition of the material.

Download English Version:

<https://daneshyari.com/en/article/1230826>

Download Persian Version:

<https://daneshyari.com/article/1230826>

[Daneshyari.com](https://daneshyari.com)