



Synthesis, crystal structures, spectroscopic and nonlinear optical properties of chalcone derivatives: A combined experimental and theoretical study

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ABSTRACT

A set of chalcone compounds were prepared by reacting *p*-bromoacetophenone with various substituted aromatic aldehyde in ethanol using sodium ethoxide as base. The synthesized molecules were well characterized using spectroscopic techniques like UV–Vis, fourier transform infrared (FT-IR) and nuclear magnetic resonance (¹H & ¹³C) spectroscopy. The compounds were crystalized and their final structures were confirmed after diffracting these on single crystal X-ray diffractometer. The spectroscopic and molecular information were compared with simulated properties calculated via density functional theory (DFT). Geometries of all chalcone compounds have been optimized by density functional theory (DFT) at B3LYP level with 6-311 + G(d,p) basis set combination. Theoretical investigations about UV–Vis and FT-IR spectra of chalcone derivatives were reported using time dependent TD/DFT/B3LYP/6-311 + G(d,p) and B3LYP/6-311 + G(d,p) level respectively. The current study revealed that the theoretical findings complement the experimental results. Nonlinear optical properties of chalcone systems were calculated to gain insights the possibility of designing these compounds as NLO materials. The findings suggested that the first order hyperpolarizability of all the molecules except 1-(4-bromophenyl)-3-(1-methyl-1*H*-pyrrol-3-yl)prop-2-en-1-one is also greater than the value of urea ($\beta = 0.372 \times 10^{-30}$ esu). These high values might be produced because of the dipole, molecular alignment and also from the non-covalent interactions. The domination of a particular component indicates a substantial delocalization of charges in that direction.

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1. Introduction

Chalcones are compounds from the family of organic chemistry having acceptor and donor groups in them which enhance their importance in various fields. Different methods have been adopted for the synthesis of chalcones [1]. The aromatic ketone and enone

groups in chalcones are the parts of central core for highly functionalized and vital biological and industrial compounds. This class of compounds has been explored due to their broad spectrum. Other factors which make them important are include their extra chemical stability and applications as intermediate for the synthesis of important heterocyclic compounds with high stability and biological properties too.

The various biologically active heterocycles which can be prepared from the chalcones are aurone [2], flavone [3], pyrazole [4], pyrazoline [5], pyridines [6], benzodiazepine [7] and pyrimidines [8]. Usually nucleophilic addition reactions were followed during the synthesis of given heterocycles. These are also precursors in the biosynthesis of flavonoids [9] and isoflavonoids [10]. Biologically,

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chalcones have been studied as anti-cancer agents *in vivo* and *in vitro* methods [11,12]. Even studies described that chalcones with the almost similar structures differ in the mechanism to kill the abnormal cells [13]. The availability of different functional groups on both of the aromatic rings is also one of the reasons to make them biologically active against a large cell lines; fluoro substituted chalcones showed promising activity against five different cancer cell lines [14]. Antifilarial activity was envisaged for a series of chalcone derivatives which were synthesized for a special task and also have sulfonamide functional group in them [15]. Chalcones have also extensively been studied as anti-inflammatory [16], anti-invasive [17], antifungal [18], anti-leishmanial [19], and antioxidant [20]. Functionalized organometallic chalcones were synthesized and explored for their electrochemical and physical properties [21]. Another point which makes the importance of chalcones is the availability of donor and acceptor groups. Different studies described that these type molecules can be used in organic light emitting diodes (OLEDs) [22]. The nonlinear optical properties of conjugated organic compounds have been the prime focus of various computational and experimental studies because of their promising applications in photonics [23] and optoelectronics [24], integrated optics [25], high-speed optical communications and optical data processing and storage [26]. The chalcone compounds have achieved much consideration because of their excellent NLO properties [27–29]. Usually, an intra-molecular charge transfer process is acquired in NLO chalcone derivatives, where π conjugated framework acts as a center which gets appended by electron acceptor at one side and an electron donor group at the other side, which designs a D- π -A sort framework and is characterized by an intense electronic charge transfer transition in the frontier molecular study [30–32].

The calculations *via* quantum chemistry techniques on the basis of density functional theory (DFT) help us to correlate and compare our experimental values [33]. We have already been involved in synthesis and computational studies of various organic molecules [34–37]. Here we describe the synthesis of six chalcones derivatives. CCDC search describe that their crystal structure has never been reported before this, except 4. The crystal structure of molecule 1 is being reported here as a new orthorhombic-

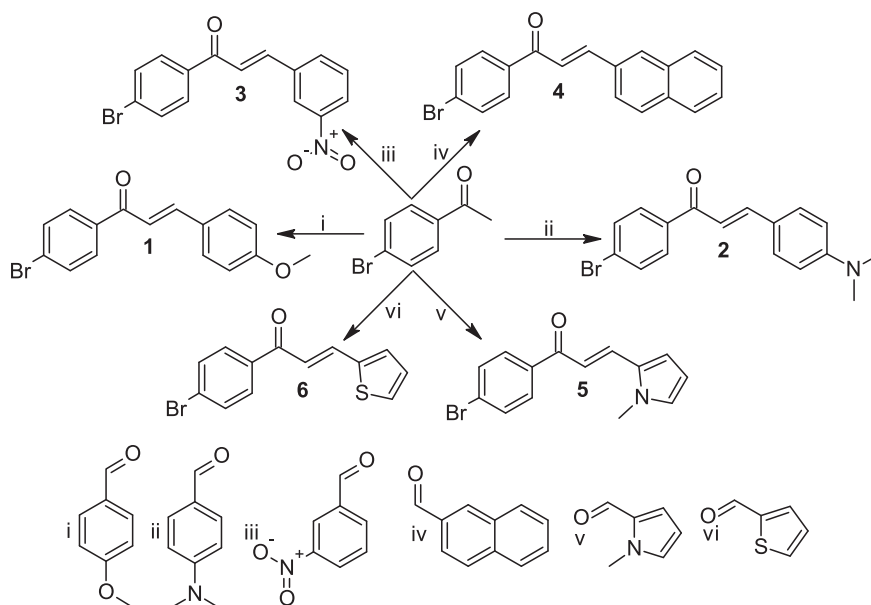
polymorph. We kept constant *p*-bromoacetophenone and varies the aldehydes having electron withdrawing or donating groups, Scheme 1. The spectroscopic studies have been carried out to find the chemical shifts of protons and carbon in each molecule. These values were counterchecked by DFT calculations in addition to this the X-ray single crystal data sets were also compared. Based on DFT, non-linear optical properties of synthesized molecules were investigated. The literature search describes that NLO properties of these compound never been reported before this.

2. Materials and methods

All the chemicals were purchased from well-known international chemical companies and used as it is without further purifications. Melting points were recorded on Stuart Scientific SMP3, version 5.0 melting point apparatus (Bibby Scientific Limited, Staffordshire, UK) and the reported melting points are uncorrected. ^1H NMR spectra were recorded on an AVANCE-III 400 MHz instrument (Bruker, Fallanden, Switzerland) at 300 K, and chemical shifts are reported in δ ppm with reference to the residual solvent signal. FT-IR spectra were recorded as neat on a Thermo Scientific NICOLET iS50 FT-IR spectrometer (Thermo Scientific, Madison, WI, USA). UV–Vis. studies were performed by using Evolution 300UV/VIS spectrophotometer (Thermo Scientific). Silica gel pre-coated aluminum sheets (Type60 GF254, Merck) used for TLC purpose and the spots were detected by exposure UV-lamp at 254 nm or 360 nm.

2.1. Crystallography

A single crystal with suitable size was picked out under microscope for each sample, fixed on glass tip supported by copper rod and magnetic base. This was mounted on Agilent Super Nova (Dual source) Agilent Technologies Diffractometer, equipped with graphite-monochromatic Cu/Mo $K\alpha$ radiation for data collection. The data collection was accomplished using CrysAlisPro software [38] at 296 K under the Cu $K\alpha$ radiation. The structure solution was performed using SHELXS-97 [39] and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [39], in-built with



Scheme 1. Synthesis of derivatives of chalcones.

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