Crystal structure, spectroscopic and third-order nonlinear optical susceptibility of linear fused ring dichloro-substituent chalcone isomers

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A B S T R A C T

Two new anthracenyl chalcone isomers namely (E)-1-(anthracen-9-yl)-3-(2,4-dichlorophenyl)prop-2-en-1-one and (E)-1-(anhracen-9-yl)-3(2,6-dichlorophenyl)prop-2-en-1-one were successfully synthesized using Claisen Schmidt condensation method. The compounds were then characterized by using IR, ^{1}H and ^{13}C NMR and UV–Vis methods. The dichloro anthracene chalcone isomers have been solved and refined using X-ray single crystal diffraction data and optimized at the ground state using density functional theory (DFT) method with B3LYP/6-311G + + (d,p) level. The experimental spectroscopic data were compared with the calculated TD-DFT spectra, where the values are in good agreement. The most stable conformer of the chalcones is identified from the computational results. Both compounds also show a good HOMO-LUMO energy gap values of 2.96 and 3.14 eV. The dipole moment at the different *ortho-para* and *ortho-ortho* position are 2.71D and 4.58D, respectively. The difference in orientation of the *ortho-para* and *ortho- ortho* position results affect the dipole moments and NLO properties response of the compounds. The analyses of nonlinear optical (NLO) properties were performed by calculating the third-order nonlinear polarizabilities. Both compounds show reasonably good NLO responds with the magnitude and sign of the third order optical susceptibility was determined. Based on the measured nonlinear susceptibility χ^3 both structures offers great potential in applications such as optical switching and other optoelectronics devices.

1. Introduction

The need for nonlinear optical (NLO) materials with large optical nonlinearities and fast response time are essential for applications in optical signal processing, optical data storage, optical phase conjugation, optical limiting and optical switches [1,2]. The large third-order nonlinear optical susceptibilities resulting from the nonlinear response of organic molecules has attracted much attentions [2]. Third-order nonlinear optical properties of variety of materials such as organic dyes [3–5], metal complexes of thiourea [6], gold nanoparticles [7], single crystals of organic molecules [8], etc., have been reported in the recent past. Every class has its own intrinsic advantages and disadvantages during their potential use in NLO applications.

There are three essential features for high nonlinear activity in an organic compound which are, a strong electron donor, a highly polarizable π-conjugated bridged and a strong electron acceptor [9]. A chalcone molecule with a π-conjugated system provides a large transfer axis with appropriate substituent groups on the two terminal aromatic rings. Recently, we found that the presence of anthracene fused ring system and the halogen phenyl substituent at the terminal ring derivatives is useful in getting good quality single crystal with easy-synthesizable method. Chalcones and their derivatives are organic "push-pull" molecules and satisfy the criteria given where it can be manipulated with a wide range of substitutions. In addition, the strong "push-pull" configurations in the compounds lead to their significantly larger dipole amplitudes. Systematic studies have shown that increasing the conjugations by adding functional group with electron-acceptor and –donating character at the ends of the conjugated bridge, promotes the charge-transfer processes [10]. Furthermore, organic molecules possessing an electron donor group and an electron acceptor group contribute to large third order optical nonlinearity arising from the intramolecular charge transfer (ICT) between the two groups of opposite nature [11]. In addition, these modifications decrease the HOMO-LUMO energy gap and enhancing the nonlinear responses of such

molecular systems. The polyaromatic hydrocarbons or π-conjugated materials also provide significant property for conductivity that led to tremendous advancements in the field of organic electronics [12]. Additionally, the Naphthoquinone derivatives such as 1,4-naphthoquinone, 5-hydroxy-1, 4-naphthoquinone (Juglone) and 4-naphthoquinone (Lawsone) that have the conjugated π-electrons are likely reported to be good NLOphores [13].

In continuation of our research on anthracenyl chalcones [14–17], we synthesized and reported the new crystal structure of two dichloro anthracene chalcone isomers including (*E*)-1-(anthracen-9-yl)-3-(2,4-dichlorophenyl)prop-2-en-1-one with *o, p*-dichloro phenyl group and (*E*)-1-(anhracen-9-yl)-3-(2,6-dichlorophenyl)prop-2-en-1-one with *o, o*-dichloro phenyl group. The spectroscopic properties of the compounds such as Infrared (IR) vibrational, Nuclear Magnetic Resonance (NMR) and UV–Visible are also presented. The comparison between the theoretical calculation [DFT/B3LYP 6-311 + +G (d,p)] and experimental data are also reported. To determine the compound most stable conformers and the dipole moment values, Potential Energy Surface (PES) and Mulliken studies are also described. The third-order nonlinear optical susceptibility are discussed to determine its optical properties.

2. Methodology

2.1. Synthesis and crystal growth

A mixture of 9-acetylanthracene (0.5 mmol) and corresponding aldehydes (0.5 mmol)) for compound **I** was used 2,4-dichlorobenzaldehyde (0.5 mmol) and for compound **II** was used 2,6-dichlorobenzaldehyde, was dissolved in methanol (20 mL). Catalytic amount of NaOH (10 ml, 20%) was added to the solution drop-wise with vigorous stirring. The reaction mixture was stirred for about 5–6 h at room temperature. The resultant crude products were filtered, washed successively with distilled water and recrystallized from acetone to get the corresponding chalcones (Scheme 1). Crystals suitable for X-ray diffraction study were obtained by the slow evaporation technique using acetone solvent. The yellow plate shaped crystals for both compounds are shown in Fig. 1.

(E)-1-(anthracen-9-yl)-3-(2,4-dichlorophenyl)prop-2-en-1-one (**I**): IR (ATR-FTIR,cm^{-1}):3157(Ar-H), 1638 (C=O), 1616 (−CH=CH−), 605 (C−Cl). ^{1}H NMR(DMSO-d_6) ppm: 7.48 (d, 2H, *J* = 10 Hz, H17A), 7.52 (d, 2H, *J* = 10 Hz, H16A), 7.57–7.59 (m, 3H, phenyl), 7.65 (s, 1H, anthracene), 7.83 (d, 2H, anthracene), 8.08 (s, 1H, anthracene), 8.21 (t, 2H, anthracene), 8.80 (s, 1H, anthracene). ^{13}C NMR (DMSO-d_6) ppm: 199.30 (C=O), 125.05 (C16), 140.78 (C = 17), 126.25, 127.64, 128.04, 128.59, 129.15, 129.29, 129.99, 130.39, 131.03, 131.06, 132.11, 134.35, 135.39, 136.68 (C-aromatic).

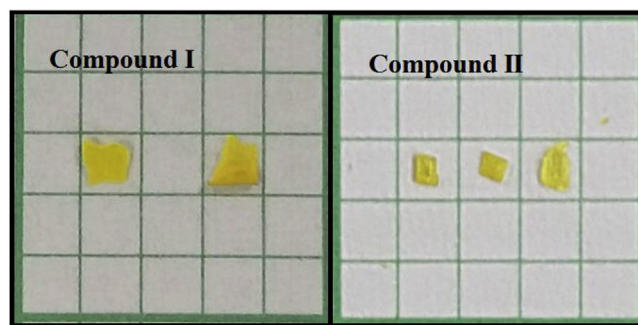*(E)-1-(anhracen-9-yl)-3(2,6-dichlorophenyl)prop-2-en-1-one* (**II**): IR
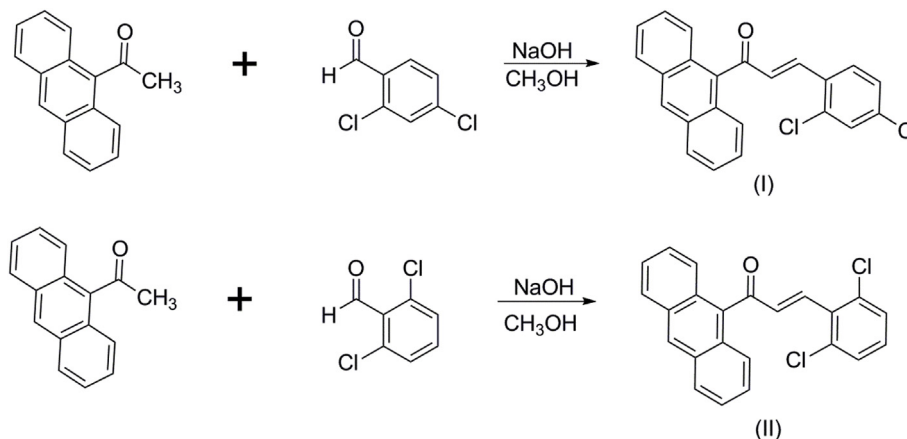
Fig. 1. The single crystals of the compound **I** and **II**.

(FTIR-ATR,cm^{-1}): 3054(Ar-H), 1652 (C=O), 1629(−CH=CH−), 675 (C−Cl). ^{1}H NMR(DMSO-d_6) ppm: 7.23 (d, 2H, *J* = 10 Hz, H17A), 7.51 (d, 2H, *J* = 10 Hz, H16A),7.59–7.61 (m, 3H, phenyl), 7.38 (d, 1H, anthracene), 7.86 (d, 2H, anthracene), 8.20 (t, 3H, anthracene), 8.81 (s, 1H, anthracene). ^{13}C NMR (DMSO-d_6) ppm: 199.48 (C=O), 124.96 (C16), 141.40 (C17), 137.04, 134.28, 133.53, 132.02, 131.53, 131.02, 129.59, 129.41, 129.32, 128.18, 126.28, 124.96 (C-aromatic).

2.2. Spectroscopy analyses

The sample of chalcone was analyzed using Fourier transform infrared-attenuated total reflectance spectroscopy (FTIR-ATR) (Perkin Elmer Spotlight 2000 FT-NIR) equipped with a diamond crystal accessory. For this analysis, 2 mg sample were recorded in the frequency range of 4000–600 cm^{-1} and 40 scans were recorded at a resolution of 4cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded at 500 MHz and 125 MHZ, respectively, in DMSO-d_6, on Bruker 500 MHz Avance III spectrometer. ^{1}H NMR chemical shifts (δ_H) and ^{13}C NMR chemical shifts (δ_C) are quoted in parts per million (ppm) downfield from trimethylsilane (TMS) and coupling constants (J) are quoted in Hertz (Hz). The UV–Vis absorption spectrum of the sample was recorded in DMSO solution with quartz cell of 1.0 cm path length, using a Shimadzu UV-1800 Spectrophotometer in the spectral region of 200–800 nm.

2.3. X-ray single crystal anaysis

Single crystal X-ray diffraction study was performed on ApexII Duo CCD area-detector diffractometer using MoKα radiation (λ = 0.71073 Å). Data collection was performed using the APEX2 software [18], whereas the cell refinement and data reduction were performed using the SAINT software [18]. The crystal structure was solved by direct method using the program SHELXTL [19] and refined by full-matrix least squares technique on F^2. Absorption correction was

Scheme 1. The synthesis of the compound.