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Second- and third-order nonlinear optical properties of bis-chalcone derivatives

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ABSTRACT

Bis-chalcone derivatives: 2,5-bis(benzylidene)-cyclopentanone (CP-DBA), 2,5-bis(4-methoxy-benzylidene)-cyclopentanone (CP-POME), 2,5-bis(4-isopropyl-benzylidene)-cyclopentanone (CP-ISO) and 2,5-bis(cinnamylidene)-cyclopentanone (CP-CAL) are synthesized by Claisen–Schmidt reaction and characterized using, FT-IR, ^{1}H NMR, ^{13}C NMR, and mass spectroscopic techniques. The second- and third-order nonlinear optical properties of these samples are studied using second harmonic generation and nanosecond open-aperture Z-scan methods. CP-POME has shown a very high second harmonic generation (SHG) efficiency (5.3 times that of urea). These molecules reveal a strong third-order nonlinear absorption (NLA) that is of optical limiting type, due to their peculiar D–π–A–π–D structure that leads to high polarization of the delocalized electron cloud. CP-CAL exhibits highest NLA activity with a β coefficient of 1×10^{-10} m/W. Through numerical simulations, the mechanism of NLA is found to be a two-photon absorption process in the case of all the samples.

1. Introduction

The development of nonlinear optical (NLO) molecules has attracted the spotlight of modern research in view of their impending applications in photonic technologies [1–3]. Organic compounds possessing conjugated π electron system connected to a donor (D) and an acceptor (A) have been receiving much attention for optical limiting (OL) applications. They possess high nonlinearity coupled with ultra-fast response which are tunable through structural modification [4].

Chalcones, a class of organic materials, are attractive for their large SHG efficiencies [5,6]. In chalcone type organic molecules, the π-electrons are delocalized all along the length of the molecule and are easily polarizable. To enhance the nonlinear absorption (NLA) in these organic molecules, researchers have developed numerous design strategies such as donor–acceptor–donor (D–A–D), acceptor–donor–acceptor (A–D–A) and donor–pi–donor (D–π–D) architectures [7,8]. Three essential components required for a high non-linear active organic molecule are a strong π-electron donor (D), a polarizable π-bridge, and a strong π-electron acceptor (A). The key molecular features determining the structure of a highly active two-photon absorbing (2PA) chromophore are the extent of conjugation and the presence of charge transfer (π-donor and π-acceptor) groups to increase the charge transfer from end of the molecule to the centre [9–12].

In recent years, tremendous attention has been drawn towards chalcone derivatives as they have varied photonic applications. In addition, they are also used for the synthesis of flavonoids and for a number of biological activities [13–15]. In the present study, we report the synthesis, characterization, second harmonic generation (SHG) applications and third order nonlinear 2PA properties of CP-DBA, CP-POME, CP-ISO and CP-CAL.

2. Experimental

2.1. Synthesis

The above mentioned compounds were synthesized according to Claisen–Schmidt reaction [16]. To a stirred solution of sodium hydroxide (6.25 g) in 62.5 ml of water and 62.5 ml of ethanol at 298 K, one half of the previously prepared mixture of 0.25 mol of substituted aldehyde and 0.125 mol of cyclopentanone was added. After 15 min, the remaining solution was added and stirring was continued for further 45 min at 298 K. The precipitated product was filtered and washed with cold water, till the washings were free of alkali. The final products were recrystallized from hot methanol/ethanol.

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2.2. Nonlinear optical measurements

2.2.1. Powder SHG measurement

The powder SHG measurement which was developed by Kurtz and Perry [17,18] enables one to measure the SHG efficiency of new materials relative to standard urea or potassium dihydrogen phosphate (KDP).

The experimental set up consists of Q-switched laser, filters, photomultiplier tube, oscilloscope and beam splitter. The laser beam falls on the sample unfocused. The second harmonic is detected by the photomultiplier after removal of fundamental beams by filters and displayed on oscilloscope .The reference beam is obtained by using beam splitters placed in front of the sample. This can be used to monitor the intensity of second harmonic generated by reference samples by displaying both the signals simultaneously on a dual-beam microscope.

The SHG measurement was made using 8 ns pulses of 1064 nm from Nd:YAG laser working at a repetition rate of 10 Hz. Laser pulses of energy 3.1 mJ/pulse were smeared on to the microcrystalline powdered samples taken in glass capillary. The second harmonic wave of 532 nm produced from the sample was detected by a photomultiplier tube and the resultant signal was fed into an oscilloscope. Urea crystals were used as reference material.

2.2.2. Open aperture Z-scan measurement

To investigate third-order NLO properties of the samples, Z-scan technique is an important experimental method due to its simplicity and sensitivity. A solution of 1 mg/ml of each derivative dissolved in methanol was prepared for carrying out the open aperture Z-scan. For excitation we used 5 ns Gaussian pulses of 532 nm from a Q-switched frequency-doubled Nd:YAG laser. The concentrations of all sample solutions were adjusted such that their linear transmittance is 85 at the excitation wavelength. A beam splitter was placed that divides the laser pulses into two parts. The reflected part was treated as the reference representing the incident light energy while the transmitted part was allowed to pass through the sample via a converging lens to attain gradual variation in the incident intensity along the sample position axis (z-axis). The sample was placed atop an automated translation stage to position the sample along the z-axis with respect to the focal point ($z = 0$). By maintaining constant incident laser energy, the transmitted light through the sample was evaluated as a function of sample position i.e. incident intensity.

3. Results and discussion

3.1. Characterization

Structural characterization of the samples was done using ^{1}H NMR, ^{13}C NMR, mass spectra (see supplementary section for the spectra) and FT-IR. The results and complete assignment of the spectral data are compiled in Table 1. The absorption spectra of these compounds are shown in Fig. 2.

3.1.1. Characterization of 2,5-bis(cinnamylidene)-cyclopentanone (CP-CAL)

This compound was obtained as a bright yellow solid. It was recrystallized from ethanol, M.P. 182–184 °C, yield 96%.

It showed UV λ_{max} at 408 and 271 nm. The presence of C=O group in the compound was identified by strong IR peak at 1672 cm^{-1} and signal at δ195.10 in the ^{13}C NMR spectrum. The presence of two double bonds at α and γ positions is inferred by IR absorption at 1616 cm^{-1}, ^{13}C signals at δ141.45 (2C, C6), δ139.96 (2C, C2, C5), δ132.82 (2C,C8) and δ124.91 (2C,C7). This is also supported by PMR signals at δ7.51 (d, H-6), δ7.39 (d, H-8) and δ7.25 (t, H-7). Phenyl groups presence is indicated by IR bands [19,20] at 1577 cm^{-1} ($\nu_{C=C}$ Ar), 844 cm^{-1} (C—H oop), this is further supported by PMR signals at δ7.37 (dd, H-2′, H-6′), 7.31 (tt, H-4′) and 6.97 (t, H-3′, H-5′) and also ^{13}C NMR data as given in the Table 1. In the mass spectrum the peak at m/z 312 corresponds to the molecular ion. Thus all the data confirm the structure in Fig. 1a to CP-CAL.

3.1.2. Characterization of 2,5-bis(4′-isopropylbenzylidene)-cyclopentanone (CP-ISO)

CP-ISO was recrystallized from ethanol. It melted at 132–134 °C, yield 82.8%.

UV λ_{max} were observed at 369 nm and 261 nm. IR absorption at 1691 cm^{-1} (s) and 1625 cm^{-1} (m) indicate the presence of C=O and C=C bonds, respectively. Peaks at 1598 ($\nu_{C=C}$ Ar), 825 cm^{-1} (C—H oop) indicate the presence of aromatic groups and 1465 cm^{-1} band corresponds to CH_2 group of cyclopentanone ring. The presence of two isopropyl groups is indicated by PMR signals at δ2.97 (septet, 2H, H-7′), δ1.25 (d, 12H, H-8′) and ^{13}C signals at δ34.23 (2C, C-7′) and δ23.92 (4C, C-8′). The molecular ion at m/z 344 and other daughter ions seen in the mass spectrum support the structure of CP-ISO in Fig. 1b.

3.1.3. Characterization of 2,5-bis(4′-methoxybenzylidene)-cyclopentanone (CP-POME)

This was a yellow solid, recrystallized from $CHCl_3$-MeOH mixture, M.P. 214–216 °C, yield 87.5%.

It showed UV λ_{max} at 388 nm, 239 nm. The IR spectrum indicated the presence of C=O (1697 cm^{-1}, s), C=C (1633 cm^{-1}, m) and aromatic-groups (1591 cm^{-1} (s) and 837 cm^{-1}). In its PMR spectrum the signals at δ7.56 (d, 4H, H-2′, H-6′), 6.97 (d, 4H, H-3′, H-5′) confirm the presence of two p-di-substituted benzene rings. The presence of two methoxyl groups (OCH_3) is indicated by the PMR signal at δ3.85 (s, 6H) and ^{13}C NMR signal at δ55.44 (2C). Other signals in the carbon NMR spectrum and mass data with m/z 320[M] $^+$ (see Table 1) confirm the structure in Fig. 1c to CP-POME.

3.1.4. Characterization of 2,5-bis(benzylidene)-cyclopentanone (CP-DBA)

This crystallized as yellow solid from ethyl acetate-methanol mixture. Yield 94.6%, M.P. 186–188 °C.

In its UV spectrum it showed absorption bands at 352 nm and 230 nm. In the IR spectrum the carbonyl stretching band was observed at 1689 cm^{-1}. The peak at 1625 cm^{-1} is assigned to alkene C=C stretch. The presence of aromatic units is inferred from peaks at 1602 cm^{-1} (aromatic C=C stretch) and 765 cm^{-1} C—H out of plane bending. Absorption at 1469 cm^{-1} is due to CH_2 bend. In the proton NMR spectrum alkene protons gave peak at δ7.61 (s, 2H, H-6). Two mono substituted benzene rings are indicated by signals at δ7.60 (d, 4H, H-2′, H-6′), δ7.44 (t, 4H, H-3′, H-5′) and δ7.38 (t, 2H, H-4′). The protons of the cyclopentanone ring resonated at δ3.12 (s, 4H, H-3, H-4). ^{13}C NMR spectrum showed signals at δ196.4 (1C) for the C=O group; δ139.79 (4C, C-2′, C-6′), δ135.85 (2C, C-1′), δ129.42 (2C, C-4′) and δ128.81 (4C, C-3′, C-5′) for the two aromatic ring carbons. Other signals as expected were also observed (see Table 1). The molecular ion in the mass spectrum was observed at m/z 260. Daughter ions due to fragmentation are observed at m/z183, 116 and 91.On the basis of the above data the structure of CP-DBA is confirmed as in Fig. 1d.

3.2. Nonlinear optical properties

3.2.1. Second-order NLO measurements

In general, a material with high SHG efficiency should have extensive π conjugation within the system. Both electron donating and withdrawing groups play a major role in enhancing this type of conjugation. In the present compounds studied, the benzene π-electrons are in cross conjugation with the carbonyl group.