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Synthesis, characterization and nonlinear optical properties of symmetrically substituted dibenzylideneacetone derivatives

N. Sunil Kumar Reddy[a], Rajashekar Badam[a], Romala Sattibabu[b], Muralikrishna Molli[b], V. Sai Muthukumar[b], S. Siva Sankara Sai[b], G. Nageswara Rao[a,*]

[a] Department of Chemistry, Sri Sathya Sai Institute of Higher Learning, Prasanthi Nilayam, Andhra Pradesh 515134, India
[b] Department of Physics, Sri Sathya Sai Institute of Higher Learning, Prasanthi Nilayam, Andhra Pradesh 515134, India

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ABSTRACT

We report here the nonlinear optical (NLO) properties of eight bis-chalcones of D-π-A-π-D type. These dibenzylideneacetone (DBA) derivatives are synthesized by Claisen–Schmidt reaction. The compounds are characterized by UV–vis, FTIR, ^{1}H NMR, ^{13}C NMR, mass spectroscopy and powder XRD. By substituting different groups (electron withdrawing and electron donating) at 'para' and 'meta' positions of the aromatic ring, we observed an enhancement in second harmonic generation with substitution at 'para' position. These compounds have also showed higher two-photon absorption compared to other chalcones reported in literature. These compounds, exhibiting both second and third order NLO effects, are plausible candidate materials in photonic devices.

1. Introduction

The curiosity of scientists in synthesizing organic molecules for nonlinear optical (NLO) applications such as optical switches, THz wave generation [1], electro-optic modulators [2–5], passive optical limiters and frequency conversion [6,7] has exponentially increased in recent years. The organic molecules have overpowered inorganic materials due to their high optical nonlinearity, ultrafast response and versatile ability to tune the optical properties through structural modifications [8]. All these characteristics make them unique and attractive for applications in organic photonic devices. Various types of organic compounds have been investigated for their second and third order NLO properties. These include chalcones [1,7], stilbazolium compounds [9], fullerene based compounds [10], inorganic–organic hybrids [11,12] and many more. Optical limiters based on nonlinear optical absorption (NLA) have been reported using phthalocyanines, organometallic cluster compounds [13], complexes [14,15] and several other inorganic compounds like metal nanoparticles, semiconductor quantum dots [16]. Generally nonlinear absorption in these materials arise from effects like saturable absorption, two-photon or multiphoton absorption, free-carrier absorption, excited state absorption, etc. [14].

The enhanced NLO response of organic chromophores could be mainly attributed to effective tuning and alteration of intermolecular and intramolecular interactions. The intramolecular charge transfer between strong donor and acceptor groups aids in enhancing hyperpolarizabilties at molecular level. For example, conjugated TTF-Quinone molecules have exhibited higher third order NLO response owing to increase in dipole moment arising from intramolecular charge transfer [17]. Similarly, the intermolecular interaction like hydrogen bonding favour head to tail alignment of molecules that leads to formation of non-centrosymmetric crystal structures which ultimately results in efficient second harmonic generation. An optimized NLO chromophore is expected to possess (i) an extended conjugated system, (ii) a large dipole moment difference between excited state and ground state electronic configuration (charge asymmetry). The charge asymmetry is achieved by introducing different functional groups substituted in the molecule. The presence of appropriate strong electron donor and strong acceptor groups can improve the polarizability in either or both ground and excited electronic states leading to large molecular hyperpolarizabilities and good crystallizability [18]. The extensive delocalization of π-electrons which favours easier polarizability is achieved by the presence of strong electron donor (D) and strong acceptor (A) groups with a π-electron bridge joining D and A. The presence of D and A no doubt enhances the nonlinear absorption, but the co-planarity of the molecule plays a key role in enhancing the extent of conjugation, which in turn improves the polarizability of the molecule [19].

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* Corresponding author.
E-mail address: gnageswararao@sssihl.edu.in (G.N. Rao).

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Various design strategies have been established in the past to tailor the molecules with large hyperpolarizabilities. They are asymmetric D-π-A; symmetric D-π-D; A-π-A; D-π-A-π-D; A-π-D-π-A; and branched $(A)_n$-D and $(D)_n$-A motifs where n is greater than 2 [19]. Most of the D-π-A-π-D type, extended π-conjugated molecules may have the band gap occurring in either the visible region or in the UV region. This feature enables them to have high two-photon absorption (2PA) cross-section (non-resonant nonlinearity) in the near infrared region or at visible region respectively, where they are transparent.

Of all the motifs aforementioned, D-π-A-π-D has very captivating features as well as applications. Diarylideneacetones with D-π-A-π-D molecular configuration are closely related to the class of organic chromophores known as 'chalcones'. In recent years, this class of molecules have been extensively used in numerous applications ranging from anti-cancer [20,21], radio-protective and anti-viral activities [22], synthons for heterocycles [23], chemoprotective agents, phase 2 enzyme inducers, radical scavengers [24], catalysis [25,26] and nonlinear optics [27]. Dibenzylideneacetone derivatives are known for their anti-cancer activity [28–34]. Some of these compounds showed considerable anti-bacterial [35] and anti-malarial activity [36]. Photo-physical properties of some of these compounds have also been investigated [37]. Though chalcone derivatives have been extensively investigated for their SHG NLO activity [1,7,27], similar studies on bis-chalcones viz., dibenzylideneacetone derivatives are sparse.

In this article, we report the synthesis, characterization and nonlinear optical properties of these new class of bis-chalcones derived from DBA, namely, (1E, 4E)-1,5-bis (3-bromophenyl)-1,4-pentadiene-3-one (3-DBDBA), (1E, 4E)-1,5-bis(4-bromophenyl)-1,4-pentadiene-3-one (4-DBDBA), (1E,4E)-1,5-bis(4-methylphenyl)-1,4-pentadiene-3-one (4-DTDBA), (1E,4E)-1,5-Bis(4-N,N-dimethylaminophenyl)-1,4-pentadiene-3-one (4-DNMDBA), (1E,4E)-1,5-Bis(4-isopropylphenyl)-1,4-pentadiene-3-one (4-DIDBA), (1E,4E)-1,5-bis(3-chlorophenyl)-1,4-pentadiene-3-one (3-DCDBA), (1E,4E)-1,5-Bis(2-chlorophenyl)-1,4-pentadiene-3-one (2-DCDBA), (1E,4E)-1,5-bis(4-chlorophenyl)-1,4-pentadiene-3-one (4-DCDBA). The nonlinear optical properties, viz., Second Harmonic Generation (SHG) and Multiphoton absorption of these compounds have been investigated. Finally, we have attempted to correlate the observed NLO enhancement to different electron pumping and withdrawing groups substituted at different positions in the aromatic ring. Some of these compounds namely 4-DTDBA and 4-DBDBA showed very high SHG compared to related compounds [1,38–41]. These two compounds also have superior third order NLO properties exhibiting higher two photon absorption than reported DBAs [42].

2. Experimental

2.1. Synthesis of various substituted dibenzylideneacetones

The substituted dibenzylideneacetones (DBAs) were synthesized by Claisen–Schmidt reaction [43]. A solution of ethanol (50 ml) and 10% sodium hydroxide (50 ml) were taken in a round bottomed flask (rbf). One-half of previously prepared mixture of substituted benzaldehyde (0.05 mol) and acetone (0.025 mol) was added to the NaOH-EtOH solution with stirring at room temperature. A yellow flocculent solid precipitated within 2–3 min of addition. After 15 min, the remaining half of the substituted benzaldehyde–acetone mixture was added into the rbf. The mixture was stirred for further 45 min. The contents of the rbf were filtered and washed repeatedly with ice-cold water to eliminate the residual alkali. The solid thus obtained was dried overnight at room temperature in a desiccator. The compounds were purified by recrystallization. Melting points of all the samples were determined by open capillary method and are uncorrected.

Table 1
Yield and melting points of DBA derivatives.

Sample label	Melting point°C	Recrystallizing solvent	Yield %
3-DBDBA	128–130	MeOH	66
4-DBDBA	220–222	MeOH-$CHCl_3$	74
4-DTDBA	177–179	MeOH	85
4-DNMDBA	198–201	Pet.ether-CH_2Cl_2	61
4-DIDBA	88–90	MeOH	78
3-DCDBA	118–120	MeOH	80
2-DCDBA	116–117	MeOH	77
4-DCDBA	192–194	MeOH-$CHCl_3$	76

2.2. Instrumentation

Powder X-ray diffraction patterns of all the samples were recorded with PANalytical X'Pert Pro MPD diffractometer using Cu K_α radiation ($\lambda = 1.54$ Å) as the source with the following settings: voltage 45 kV, current 40 mA and scan step size 0.05^0. The FTIR spectra were recorded between 400 and 4000 cm^{-1} using KBr pellets employing Thermo-Nicolet Avatar 370 spectrophotometer. The UV–vis spectra in chloroform were recorded in the wavelength range 200–600 nm using a Shimadzu 2450 spectrophotometer. ^1H NMR spectra were obtained on VARIAN 400 MHz, ^{13}C NMR on VARIAN 100 MHz using TMS as the internal standard and $CDCl_3$ as solvent. For mass spectra AGILENT 6430 Triple Quad LC/MS was employed.

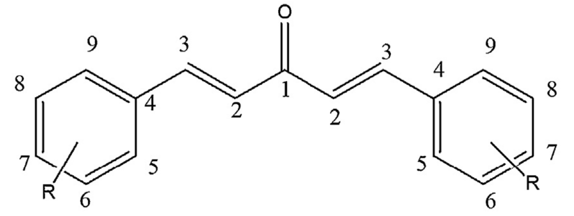
2.3. Nonlinear optical measurements

2.3.1. Powder SHG measurement

The SHG efficiency measurement was carried out using the conventional Powder (Kurtz and Perry) SHG technique [44] with Nd:YAG laser excitation wavelength at 1064 nm. The pulse energy of 6 mJ/pulse was used as an excitation source with a pulse width of 8 ns at a repetition rate of 10 Hz. It was optically steered to be incident on to the microcrystalline powder samples which were tightly packed in a glass capillary. Second harmonic separator was used to remove the fundamental harmonic from the output obtained. The second harmonic wavelength (532 nm) generated from the sample was detected by a sensitive photomultiplier tube and the SHG signal was converted into an electrical signal. The converted electrical signals were displayed on an oscilloscope. Finely ground urea crystals with uniform particle size were used as the reference in the SHG experiment. The SHG efficiency of the samples with reference to urea is listed in Table 2.

2.3.2. Third order NLO measurement

Z-scan technique [45] was employed for the investigation of the third order nonlinearity in all the DBA derivatives. A Q-switched frequency-doubled (532 nm) Nd:YAG laser (Surelite III, Continuum) with a 10 ns pulse width was used as the excitation source. The input pulse was divided into two parts using a beam splitter. The reflected part from the beam splitter was taken as the reference for the incident light energy; and the transmitted part was focused on to the sample using a converging lens (with focal length 20 cm) that yields a gradual variation in the incident intensity as the sample was translated across the focal plane. The reference beam and the transmitted beam were monitored using calibrated silicon photodiode (UDT sensors). The sample was mounted on a computer controlled automated translation stage which varies the sample's position along the z-axis with respect to the focal point ($z = 0$). By keeping constant incident laser energy, the light transmission through the



R= 6-Br (3-DBDBA)
= 7-Br (4-DBDBA)
= 7-Me (4-DTDBA)
= 7-NMe2 (4-DNMDBA)

R = 7-CHMe2 (4-DIDBA)
= 6-Cl (3-DCDBA)
= 5-Cl (2-DCDBA)
= 7-Cl (4-DCDBA)

Figure 1. Molecular structure of various DBA derivatives synthesized.

sample was measured as a function of the sample position. In order to preclude the influence of accumulative thermal effects, the laser was operated in a single-shot mode. The data collections from both photodetectors were done using the digital oscilloscope (YOKOGAWA DL1700) and retrieved to a PC for analysis using LabVIEW®. Throughout our nonlinear optical measurements, the concentration of all the DBA derivatives was fixed at 3 mg/ml in chloroform. The linear transmittance of all the samples was adjusted to be ~82% at 532 nm.

3. Results and discussion

3.1. Compounds characterization

The DBA derivatives were characterized using UV–visible absorption spectroscopy, FTIR, ^{1}H NMR, ^{13}C NMR, mass spectroscopic technique and powder XRD. In the supplementary material, ^{1}H NMR, ^{13}C NMR and mass spectroscopy data have been provided.

3.1.1. Physical data

All the compounds have been purified by recrystallization and the solvents for recrystallization, melting points and significant yields have been listed in Table 1. In general crystals with higher melting point are preferred for making devices. Figure 1 shows the molecular structure of each DBA derivative that has been synthesized.

3.1.2. UV–visible absorption spectroscopy

UV–visible absorption spectra of all the DBA derivatives have been shown in Figure 2. Typically all these compounds showed two absorption maxima. The absorption maximum (λ_{max}) in these α,β-unsaturated carbonyl compounds in the UV–visible region can be assigned to the $n \rightarrow \pi^*$ transition of carbonyl. The UV–vis spectra can be explained taking terminal substitution of various electron donating groups into consideration. The lone pair on chlorine of 2-DCDBA was found to be more in conjugation with the carbonyl compared to 3-DCDBA and thus has a larger λ_{max} value. Bromo compounds also have similar values as their chloro analogues. Because of the strong electron-pumping nature of N,N-dimethylamino group, 4-DNMDBA has the largest λ_{max} of all the DBAs. The isopropyl group in 4-DIDBA is more electron pumping compared to the methyl group of 4-DTDBA and hence was found to have a larger λ_{max} value.

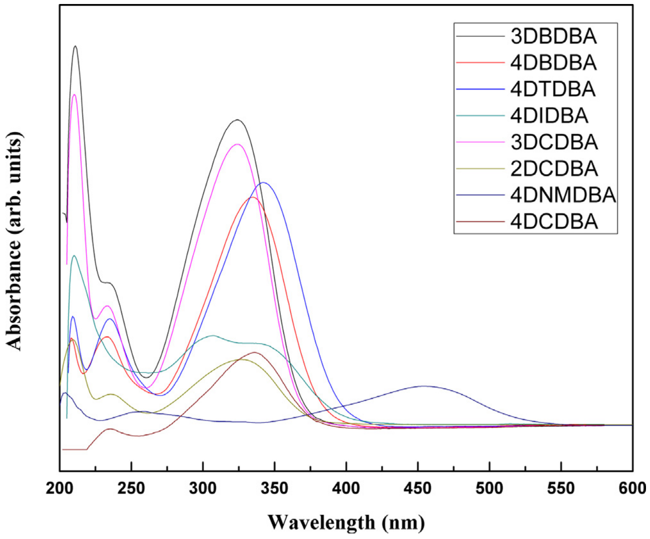


Figure 2. UV–visible absorption spectra of all DBA derivatives.

3.1.3. Energy band gap determination

The UV–visible absorption spectroscopy is frequently used to determine the energy band gap. In the present case, optical transmission spectra of DBA derivatives dispersed in chloroform were recorded between 200 nm and 600 nm. The absorption coefficient (α) was calculated from the transmission values and a tauc plot was generated [46]. The tauc equation used for the analysis is given by,

$$(\alpha h\nu)^2 = const \cdot (h\nu - E_g) \qquad (1)$$

where E_g is the energy band gap. The linear portion of the graph was extrapolated to the energy axis and the energy band gap values were determined (Table 2).

3.1.4. FT-IR vibrational spectroscopy

The recorded FTIR spectra revealed the presence of characteristic peaks (shown in Table 3) corresponding to different functional groups present in different DBA derivatives.

3.1.5. Powder XRD studies

It was inferred from the diffraction patterns in Figure 3 that all the samples are crystalline in nature. The d-spacing in Å of various

Table 2
UV–visible absorption maxima, SHG efficiency, energy band gap and two-photon absorption coefficient values of all DBA derivatives.

S. no.	Sample	UV–vis absorbance maxima nm	SHG signal comparison with urea × times	Energy band gap eV	Two-photon absorption coefficient m/W
1	3-DBDBA	324, 242	0.01	3.49	1.8e−11
2	4-DBDBA	335, 236	0.35	3.38	7e−11
3	4-DTDBA	343, 237	6.84	3.26	7.4e−11
4	4-DIDBA	341, 311	0.01	3.28	3.6e−11
5	3-DCDBA	325, 237	0.01	3.51	3.5e−11
6	2-DCDBA	330, 239	0.25	3.44	3.2e−11
7	4-DCDBA	335, 237	5.03	3.36	0.98e−11[a]
8	4-DNMDBA	458, 254	0.45	2.46	5.98e−11[a]

[a] Reference [42].

Table 3
Assignment of functional groups in DBA derivatives from FTIR spectra.

Sample label	$\nu_{c=o}$ cm^{-1}	$\nu_{c=c}$ cm^{-1}	$\nu_{c=c}$ (Ar) cm^{-1}	ArC-H (oop) cm^{-1}	ν_{misc} cm^{-1}
3-DBDBA	1653	1627	1557, 1469	658, 791, 874	$\nu_{C\text{-}Br}$: 993
4-DBDBA	1649	1592	1560, 1486	823	$\nu_{C\text{-}Br}$: 1008
4-DTDBA	1667	1644	1566, 1509	822	ν_{sp3} C-H: 2916
4-DNMDBA	1634	1602	1560, 1510	817	$\nu_{C\text{-}N}$: 1344,sp^{3}C-H: 2894, 2802
4-DIDBA	1648	1623	1564, 1511	830	ν_{sp3} C-H: 2958,2869
3-DCDBA	1655	1629	1561, 1479	684, 794, 875	$\nu_{C\text{-}Cl}$: 1076
2-DCDBA	1668	1615	1560, 1467	763	$\nu_{C\text{-}Cl}$: 1039
4-DCDBA	1667	1626	1564, 1489	822	$\nu_{C\text{-}Cl}$: 1091

DBA derivatives have been reported in the supplementary information (Table S1).

3.2. SHG measurement

For compounds to show good SHG there should be an extensive conjugation within the system. Both electron donating and withdrawing groups play a major role in enhancing this type of conjugation. In the present systems the benzene π electrons are in cross conjugation with the carbonyl group. All the compounds under study were symmetrical about the central carbonyl group. The chlorine and bromine atoms are amphiprotic, i.e., can act as both electron donor and acceptor. Thus the molecules with Cl and Br also fall into the category of D-π-A-π-D. According to Zhao et al. [47], the ability of electron donation of the Cl depends on the acceptors strength. The SHG efficiency of the samples with reference to urea has been listed in Table 2. Among all the compounds that were studied, 4-DTDBA was found to have the highest SHG efficiency and was found to be 6.84 times that of urea, because the methyl group in para position is a strong electron donating group by inductive effect and hyperconjugation. The SHG efficiency of 4-DTDBA was higher than the dibenzylidenecyclopentanones reported [38] and also highest when compared to its many counterparts of recent times [1,39–41]. However the SHG efficiency of 4-DTDBA was less than that of p-methoxydibenzylideneacetone [48]. 4-DIDBA showed lesser SHG efficiency than that of 4-DTDBA, although the isopropyl group is inductively better donor group than methyl. This was attributed to the better hyperconjugation effect of methyl group than isopropyl. 4-DNMDBA showed next highest SHG efficiency of 2.46 times that of urea because of strong resonance effect of N,N-dimethyl amino group in the para position. N,N-dimethyl amino is a stronger electron donating group than methyl but has lesser SHG efficiency because 4-DNMDBA absorbs in visible region. 4-DCDBA had higher SHG value than 4-DBDBA due to greater resonance effect of Cl than Br. This is because the energy difference involving 3p orbital of chlorine and 2p orbital of benzene carbon is less compared to energy difference of bromine 4p orbital and 2p orbital of benzene carbon. Meta substituted analogues showed lesser SHG efficiency than the p-substituted derivatives because the substituents at meta position are not in direct conjugation with carbonyl group (Figure 4).

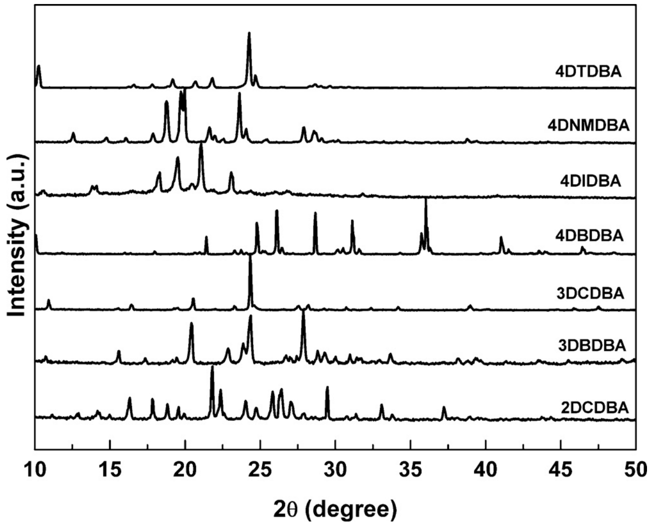


Figure 3. Powder XRD graphs of substituted DBA derivatives.

3.3. Third order NLO measurement

Z-scan method was used to investigate the third order NLO property of these compounds. It is a highly sensitive measurement with its entire simple experimental configuration. It has been extensively used to determine the magnitude and sign of the optical nonlinearity and a wide variety of samples have been investigated. Conventionally, it is used in two major configurations namely, 'closed aperture' and 'open aperture' that estimates nonlinear refraction and nonlinear absorption parameters respectively. We have adopted the 'open aperture' configuration to measure the intensity dependent nonlinear absorption. Typically, in an open aperture z-scan, the nonlinear optical transmittance of the sample is measured as a function of sample position, which is translated across the focal plane of a converging lens focusing the intense laser beam.

In general, organic molecules and chromophores express various kinds of nonlinear optical absorption through various mechanisms like free-carrier absorption, saturable absorption, multiphoton absorption and excited state absorption. Open aperture z-scan configuration is sensitive to the presence of NLA but will not be able to infer the kind of NLA. In general, numerical modelling is adopted to fit the experimental for determining the type of NLA. We have fitted the data using the following nonlinear transmission equation which could incorporate different types of nonlinear absorption based on Multiphoton absorption [49].

$$T(z) = \frac{(1-R)^2 \exp(-\alpha_0 L)}{\sqrt{\pi} p_0} \times \int_{-\infty}^{+\infty} \ln\left[\sqrt{1 + p_0^2 \exp(-2x^2)} + p_0 \exp(-x^2)\right] dx \qquad (2)$$

Here z is the sample position with respect to the focal point, α_0 is the linear absorption coefficient, R is the Fresnel reflection at the interface of the sample material with air, L (= l) is the sample length, and $p_0^n = n\gamma^{(n+1)}((1-\exp(-n\alpha_0 l))/n\alpha_0)(1-R)^n I_0^n$, I_0 being the intensity at the focal point, $p_0^n = q_0$ for a two-photon absorption

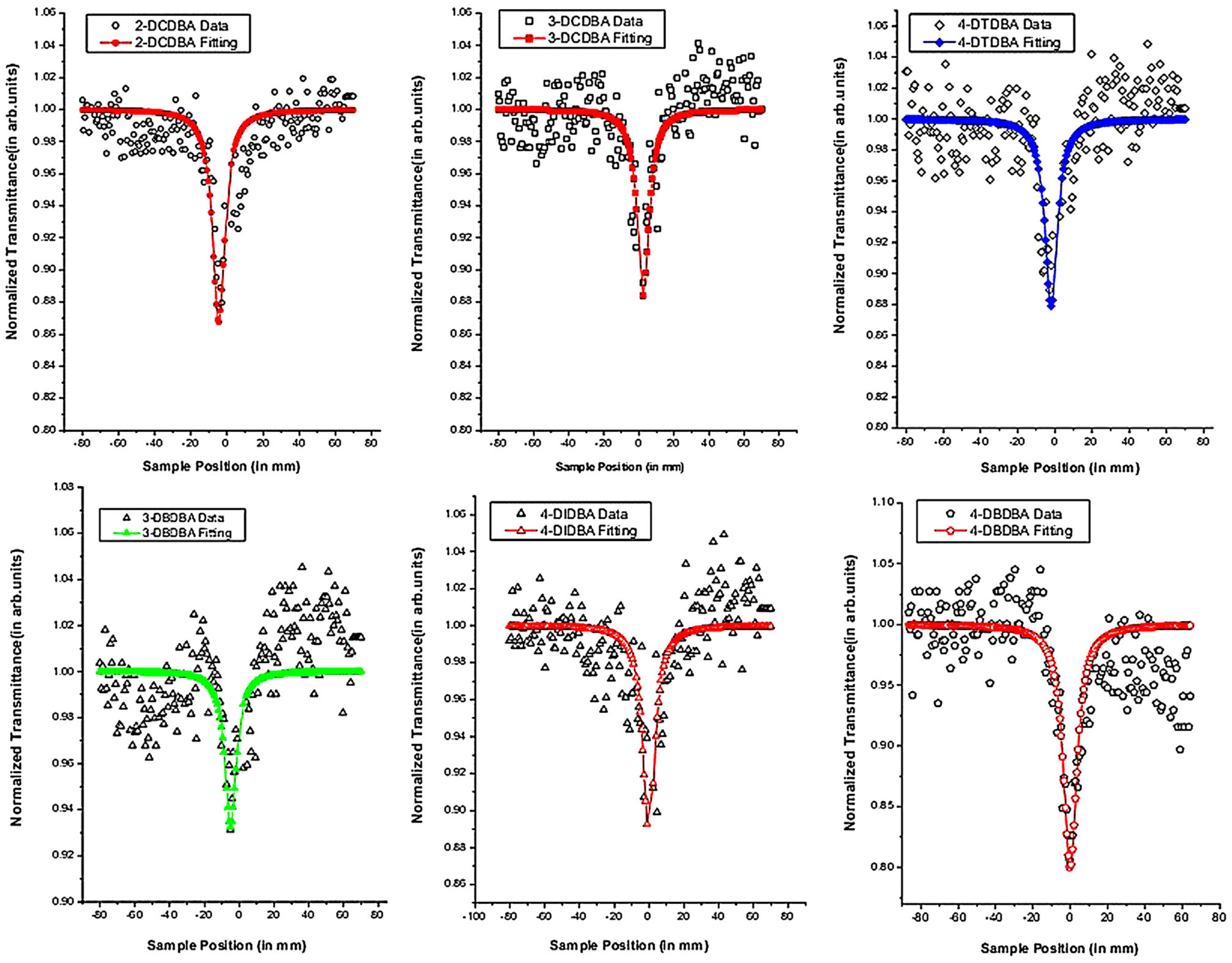


Figure 4. Open aperture z-scan curve for DBA derivatives fitted with 2PA equation in the ns excitation regime.

process with $n = 1$ and $q_0(z) = (\beta I_0 L_{eff}/(1 + (Z^2/Z_0^2))$ and $\gamma^{(n+1)}$ is the nonlinear absorption co-efficient.

In case of all the DBA derivatives, the mechanism of NLA has been deduced to be an effective two-photon absorption (2PA) process. Particularly, 4-DTDBA has shown highest nonlinear absorption with two photon absorption coefficient (β) of 7.4×10^{-11} m/W followed by 4-DBDBA (7×10^{-11} m/W), 4-DIDBA (3.6×10^{-11} m/W) and 3-DCDBA (3.5×10^{-11} m/W) (Table 2) that were found to be higher than that of 4-DCDBA (0.98×10^{-11} m/W) reported earlier [42].

The 2PA property of these molecules can be attributed to their peculiar D-π-A-π-D type molecular structure. The coefficient of 2PA can be varied by the variation of π-electron donor and acceptor. The donor and the acceptor groups variation alter the extent of π-electron delocalization. The introduction of strong π-electron donor or acceptor increases the extent of π-electron delocalization in the ground state. Consequently this leads to a large hyperpolarizability that results in the improvement of NLO response to the incident electric field [50]. Auxochrome is a strong π-electron donating substituent that induces bathochromic shift to the absorption maxima of the parent chromophore. The presence of auxochrome increases the extent of π-electron conjugation which is an outcome of the reduction of the electronic energy levels in the chromophore. This can be easily understood by comparing the absorption maxima of the chromophores. The larger the absorption maxima, the greater the extent of conjugation. Another important criteria is the position of the auxochrome on the benzene ring. If the auxochrome is para substituted, then the extent of conjugation is greater than when it is at the meta position. This can be easily understood by drawing the canonical forms of the molecules. So, the nature of auxochrome and its position are important criteria for increasing the extent of π-conjugation of the chromophore. Among the various auxochromes we have employed, the molecule with $-CH_3$ as a substituent at the 4th position was found to be having the highest 2PA coefficient. This is because of the aforementioned reasons (hyperconjugation and inductive effect of CH_3). This molecule has shown better NLA than all the molecules of the DBA family reported earlier [42].

4. Conclusion

Eight substituted dibenzylideneacetone derivatives have been synthesized and were purified by recrystallization. These bis-chalcones have also been well characterized by various spectroscopic techniques (UV–vis, FTIR, NMR and MS) and their crystalline nature has been validated by powder XRD. Kurtz Powder method and z-scan technique have been employed to investigate the second and third order NLO properties respectively. By substituting different groups – electron withdrawing and electron donating – at the 'para' and 'meta' positions of the aromatic ring, we observed an enhancement in the second harmonic generation with substitution only at the 'para' position for chromophores like 4-DTDBA and 4-DCDBA. Further, extensive conjugation in certain bis-chalcones (4-DTDBA and 4-DBDBA) resulted in enhancement of third order

NLO effects. Open aperture z-scan measurement revealed stronger two photon absorption in these organic chromophores. Thus, these bis-chalcones with D-π-A-π-D type structure exhibiting both second and third order NLO effects are plausible candidate materials in photonic devices like wavelength convertors and optical limiting devices.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2014.10.043.

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