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$\chi^{(3)}$ measurements and optical limiting in dibenzylideneacetone and its derivatives

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Abstract

We investigated the third order nonlinear optical properties of dibenzylidene acetone (1,5-diphenyl-1, 4-pentadeine-3-one) and its derivatives. The nonlinear measurements were performed by using single beam Z-scan technique with Q-switched Nd:YAG nanosecond laser pulses at 532 nm. Open aperture data for dibenzylidene and its derivatives demonstrate the presence of two-photon absorption at this wavelength. The dependence of $\chi^{(3)}$ on donor/acceptor type substituents to the basic compound clearly shows the electronic origin of nonlinearity and hence demonstrates that the mechanism by which the third order nonlinear response enhanced is not by the thermal effects, but instead due to the strong nonlinear absorption and nonlinear refraction of the compounds. The derivatives of the basic compound show very good optical limiting behavior.
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1. Introduction

The highly promising development in optoelectronics has greatly increased the demand for new nonlinear optical materials in recent years. In this regard, organic materials are most attractive owing to the known rich variety organic compounds and the inherent flexibility in synthesizing such compounds with desired properties [1–4]. The conjugated organic materials exhibiting nonlinear absorption are currently of interest because of their large third order nonlinearities, instantaneous response times, high damage thresholds, ease of processing and structural modifications and due to their optical power limiting behavior [5–8]. The strong delocalization of π-electrons in these conjugated systems determines a very high molecular polarizability and their remarkable third order nonlinearities [9]. Although

great efforts have been expended on the investigation of the relationships that exist between the molecular structure of an organic material and the resulting third order nonlinearities, the complete understanding of these dependences is still incomplete. The study of the linear and nonlinear optical coefficients is fundamental for increasing the ability to tune nonlinear optical properties by appropriate design of organic systems at the molecular level.

In this paper, we report on our experimental investigation of the third order nonlinear optical susceptibility $\chi^{(3)}$ in dibenzylideneacetone (DBA), which is a very good precursor for the preparation of many types of heterocyclic compounds of medical and biological importance, and its derivatives, namely, p-chlorodibenzylideneacetone, o-chlorodibenzylideneacetone, p-methoxydibenzylideneacetone and p-(N,N-dimethyl)dibenzylideneacetone with the single beam Z-scan technique at 532 nm. The measurements on sample o-chlorodibenzylideneacetone are not reported because nonlinearity is too small to be detected. As increasing π delocalized electrons in the compound can enhance

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the third order optical nonlinearity, we were interested in the strong electron donating substituents [10]. We also report on the two-photon absorption and optical limiting behavior of these compounds and the influence of acceptor/donor type of substituents on the third order nonlinearity.

2. Experiment

The compounds were synthesized by using the procedure given in [11]. To prepare dibenzylideneacetone a solution of alcohol (200 ml) and sodium hydroxide (25 g in 250 ml of water) was taken in a round-bottomed flask fitted with a mechanical stirrer. The flask was cooled in cold water so as to maintain the temperature between 20 and 25 °C. The solution was vigorously stirred and one half of the previously prepared mixture of benzaldehyde (25.5 ml, 0.25 mole) and acetone (9.3 ml, 0.126 mole) was added. After 15 min, the remaining of the benzaldehyde–acetone mixture was added. The reacting mixture was stirred for 30 min more. The separated product was filtered, washed with water and dried. It was crystallized from ethyl alcohol. The remaining derivatives were also prepared through the same procedure.

The single beam Z-scan technique [12] was used to measure the nonlinear susceptibility of the samples. This method allows the simultaneous measurement of both nonlinear refractive index and nonlinear absorption coefficient. Basically, the method consists of translating a sample through the focus of a Gaussian beam and monitoring the changes in the far field intensity pattern. When the intensity of the incident laser beam is sufficient enough to induce nonlinearity in the sample, it either converges the beam (self-focusing) or diverges (self-defocusing) depending on the nature of that nonlinearity. By moving the sample through the focus, the intensity dependent absorption is measured as a change of the transmittance through the sample (open aperture). The nonlinear refraction is determined by the spot size variation at the plane of a finite aperture detector combination (closed aperture), because the sample itself acts as a thin lens with varying focal length as it moves through the focal plane.

The Q-switched Nd:YAG laser with a pulse width of 8 ns at 532 nm was used as a source of light in the Z-scan experiment. The Z-scan experiment was performed using Gaussian beam. A lens of focal length 26 cm was used to focus the laser pulses into a 1 mm quartz cuvette, which contained the sample solution. The resulting beam waist radius at the focused spot was 19.6 μm. This corresponds to the Rayleigh length of 2.274 mm. Thus the sample thickness of 1 mm was less than the Rayleigh length and thus it could be treated as a thin medium. The scan was obtained with a 50% ($S = 0.5$) aperture and at pulse energy of 0.2 mJ, which corresponds to a peak irradiance of 3.8 GW/cm^2. In order to avoid cumulative thermal effects, data were collected in single shot mode [13]. In optical limiting experiment, the laser beam was focused at the center

of a 1 mm path-length quartz cell by a 26 cm convex lens giving a spot radius of 19.6 μm. Optical limiting was obtained by varying the input energy and by monitoring input and output energy with two 13PEM001 series Melles Griot Power/Energy meters (detectors).

3. Results and discussion

The linear absorption spectra of three compounds are shown in Fig. 1. The UV–VIS absorption spectra of samples were recorded at room temperature in dilute solutions [1×10^{-2} g/l] using the fiber optic spectrometer model SD2000, supplied by Ocean Optics Inc. The linear refractive indices of samples obtained by using Abbe refractometer are shown in Table 1. The structures of compounds are shown in Fig. 2.

The nonlinear transmission of compounds with and without aperture was measured in the far field as the sample moved through the focal point. This allows us to separate the nonlinear refraction from the nonlinear absorption. The closed aperture curves, open aperture curves and pure nonlinear refraction curves of samples are shown in Figs. 3–5, respectively. Fig. 3 shows the normalized transmission without an aperture at 532 nm. Here, the transmission is symmetric with respect to focus ($z = 0$), where it has a minimum transmission, showing an intensity dependent absorption effect. The shape of the open aperture curves suggests that all three compounds exhibit two-photon absorption [14–17]. The model described in [12] was used to determine the magnitude of nonlinear absorption coefficient (β) of the samples.

The normalized transmittance for the open aperture Z-scan is given by

$$T(z) = \frac{\ln[1 + q_0(z)]}{q_0(z)} \quad \text{for} \quad |q_0(z)| < 1, \tag{1}$$

where $q_0(z) = \frac{\beta I_0 (1 - e^{-\alpha L})}{(1 + z^2/z_0^2)\alpha}$, α is the linear absorption coefficient, L is the thickness of the sample, I_0 is the on axis peak irradiance at the focus, and z_0 is the Rayleigh length given by the formula $z_0 = kw_0^2/2$, where k is the wave vector. Eq. (1) is used to fit the open aperture experimental data.
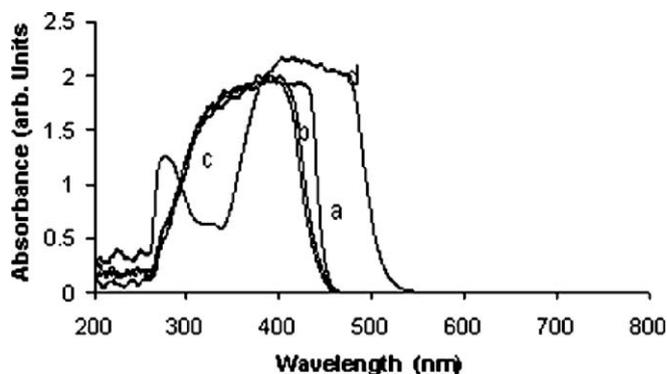

Fig. 1. Linear absorption spectra of compounds dissolved in DMF in 1 cm quartz cell: (a) p-methoxyDBA, (b) DBA, (c) p-chloroDBA, (d) p-(N,N-dimethyl)DBA.

Table 1
Values of n_2, β and $\chi^{(3)}$ determined experimentally for different compounds

Name of the sample	n_0	n_2 (esu)	β (cm/GW)	Re $\chi^{(3)}$ (esu)	Im $\chi^{(3)}$ (esu)
DBA	1.425	-1.032×10^{-12}	0.72	-0.38×10^{-13}	0.10×10^{-13}
p-chloroDBA	1.412	-3.18×10^{-12}	0.98	-0.33×10^{-13}	0.11×10^{-13}
p-methoxyDBA	1.417	-5.745×10^{-12}	0.77	-0.613×10^{-13}	0.12×10^{-13}
p-(N,N-dimethyl)DBA	1.423	-1.964×10^{-11}	5.986	-2.11×10^{-13}	0.93×10^{-13}
o-chloroDBA	1.413	No detectable response			

Fig. 2. Structure of compounds.

Fig. 4 shows the normalized transmission of compounds through a closed aperture. In order to obtain a pure non-linear refraction curve the division method [12] was used. The curves thus obtained by dividing closed aperture curve by open aperture curve for samples are shown in Fig. 5. A prominent peak in the Z-scan curve shows a strong refractive nonlinearity. The nonlinear refractive index γ is given by the formula

$$\gamma = \frac{\Delta\phi_0 \lambda}{2\pi L_{\text{eff}} I_0}, \tag{2}$$

where $L_{\text{eff}} = \frac{(1-e^{-\alpha L})}{\alpha}$ and $\Delta\phi_0$ is the on axis nonlinear phase shift.

For a Gaussian spatial and temporal distribution,

$$I_0 = \frac{4\sqrt{\ln 2} E_{\text{total}}}{\sqrt{\pi^3} w_0^2 \tau}, \tag{3}$$

where E_{total} is the incident energy on the sample after the reflection from the front surface of the cuvette is taken into account, w_0 is the beam waist radius at the focus,
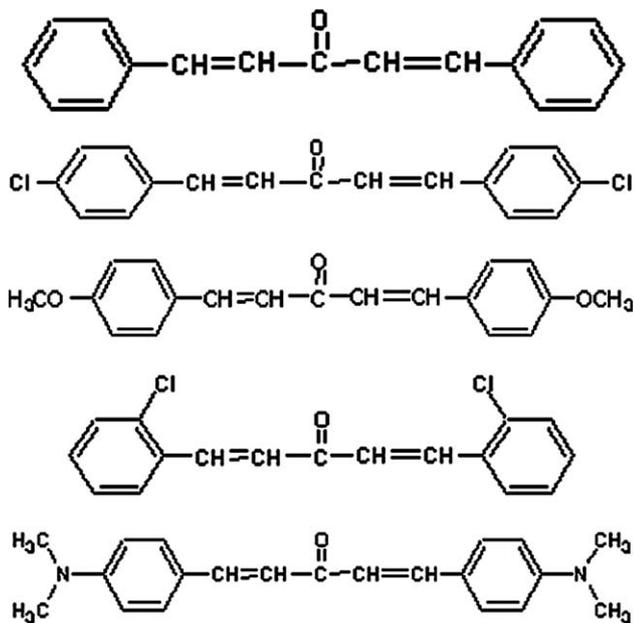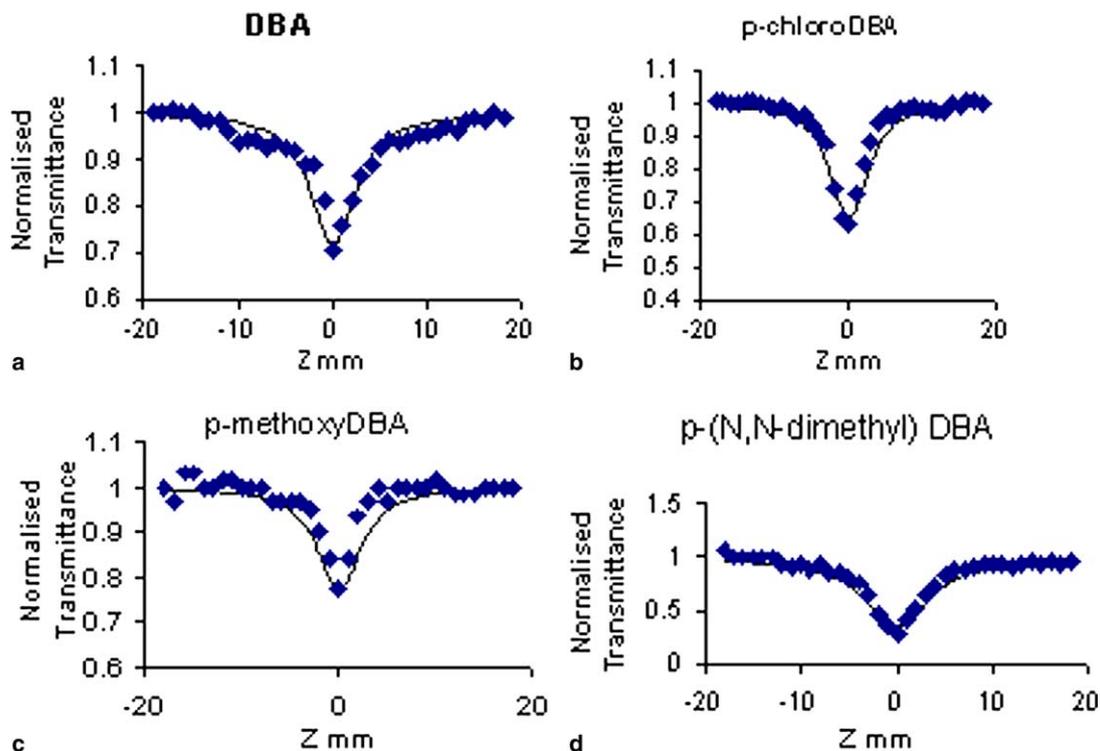

Fig. 3. Open aperture curves for (a) DBA, (b) p-chloroDBA and (c) p-methoxyDBA (d) p-(N,N-dimethyl)DBA. The solid line is fitted with (a) $\beta = 0.72$ cm/GW, (b) $\beta = 0.98$ cm/GW, (c) $\beta = 0.77$ cm/GW and (d) $\beta = 12.5$ cm/GW.
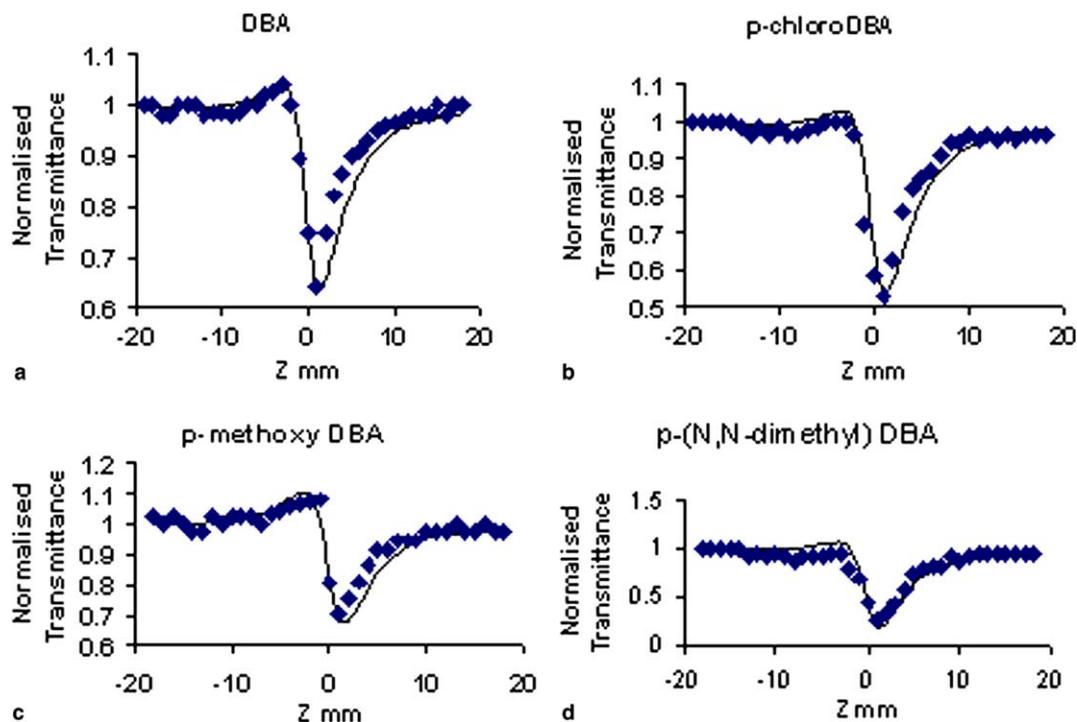
Fig. 4. Closed aperture curves for (a) DBA, (b) *p*-chloroDBA, (c) *p*-methoxyDBA and (d) *p*-(*N*,*N*-dimethyl)DBA. The solid lines are fitted by using Eq. (5) with $\Delta\phi_0 = 0.97$, 1.1, 1.35 and 1.9, respectively.
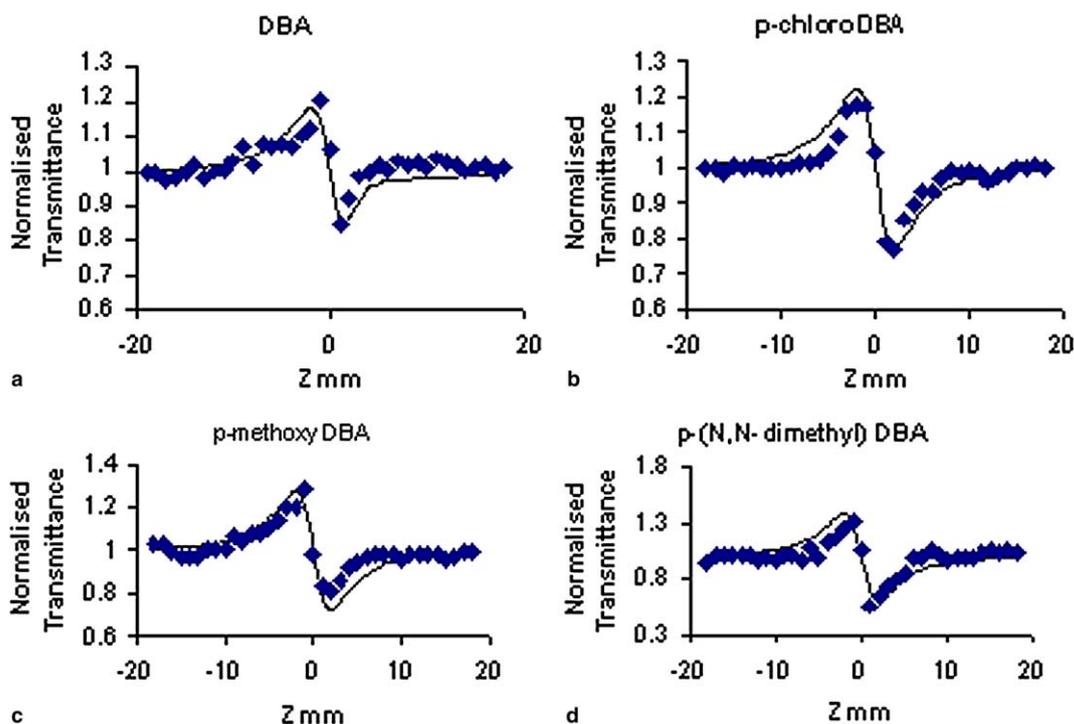

Fig. 5. The curves are obtained by dividing the closed aperture data by respective open aperture data. Solid lines are theoretical fit to the experimental data.

and τ is the pulse width of laser (full width at half maximum). The sign of $\Delta\phi_0$ and hence n_2 is determined from the relative position of the peak and valley with z.

$\Delta\phi_0$ is calculated from the relationn

$$\Delta\phi_0 = \frac{\Delta T_{\text{p-v}}}{0.34(1-S)^{0.25}} \quad \text{for} \quad |\Delta\phi_0| \leqslant \pi, \tag{4}$$

where $\Delta T_{p\text{-}v}$ is the peak valley transmittance difference and S is the linear aperture transmittance.

The normalized transmittance for the closed aperture Z-scan is given by [18,19]

$$T(x) = 1 + \frac{4x\Delta\phi_0}{[(x^2+9)(x^2+1)]} - \frac{2\Delta\psi_0(x^2+3)}{[(x^2+9)(x^2+1)]}, \qquad (5)$$

where $\Delta\psi_0$ is the on axis phase shift due to nonlinear absorption, given by $\Delta\psi_0 = \frac{1}{2}\beta I_0 L_{\text{eff}}$.

Now, the real part of the third order nonlinear susceptibility is related to γ through $\text{Re}\ \chi^{(3)} = 2n_0^2\varepsilon_0 c\gamma$ and the imaginary part is related to the nonlinear absorption through $\text{Im}\ \chi^{(3)} = n_0^2\varepsilon_0 c\lambda\beta/2\pi$, where n_0 is the linear refractive index, ε_0 is the permittivity of free space, and c is the velocity of light in vacuum.

The experimentally determined values of n_2, β, $\text{Re}\ \chi^{(3)}$ and $\text{Im}\ \chi^{(3)}$ are shown in Table 1. The nonlinear refractive index n_2 (esu) was calculated by using the conversion formula n_2 (esu) $= cn_0\gamma/40\pi$.

The peak-valley configuration of the pure nonlinear refraction curves for different compounds shown in Fig. 5 clearly demonstrates that the index change is negative, and the response is electronic in origin and thus shows that thermal effect is not the dominant effect for the third order nonlinear response of the solution [20]. Further, to determine the contributions of the solvent to n_2 we conducted z-scan experiment on the pure DMF, and found that neither nonlinear refraction nor nonlinear absorption was observed at the input energy used. Hence, any contribution form the solvent to the nonlinearity of the samples is negligible.

The values of n_2, $\text{Re}\ \chi^{(3)}$ and $\text{Im}\ \chi^{(3)}$ reported in Table 1 were obtained by repeating the Z-scan on each sample, and the values were found to be consistent in all trials. The determined value of $\text{Re}\ \chi^{(3)}$ for p-(N,N-dimethyl)dibenzylideneacetone is 2.11×10^{-13} esu, which is large compared to that of other samples [Table 1]. The increased nonlinear response in the case of p-methoxydibenzylideneacetone and p-(N,N-dimethyl)dibenzylideneacetone is mainly due to the enhanced π-electron density in the molecules [2,10,21]. The results show that the increase in $\chi^{(3)}$ of p-methoxyDBA is nearly double compared to the $\chi^{(3)}$ value of DBA and the increase is much more in the case of p-(N,N-dimethyl)dibenzylideneacetone. Comparing to Chlorine, which is an electron-withdrawing group due to high electronegativity, methoxy and N,N-dimethyl groups are an electron releasing by resonance. So, among the five compounds the order of electron density is p-(N,N-dimethyl)DBA $> p$-methoxyDBA $>$ DBA $> p$-chloroDBA $> o$-chloroDBA. Among p-chloroDBA and o-chloroDBA although both are having chlorine substituents, in the case of o-chloroDBA, chlorine is very close vicinity of double bond, so it withdraws electrons more powerfully than chlorine present in the *para*-position. Consequently, o-chlorodibenzylideneacetone showed least nonlinear response among all other compounds studied. It showed no detectable nonlinear response at the input energy used during our experiment.

Figs. 6–9 show the optical limiting behavior of compounds. The derivatives, excluding o-chloroDBA, showed good optical limiting compared to DBA at 532 nm. These derivatives exhibited strong two-photon absorption at that wavelength. The nonlinear absorption is more in the case of p-(N,N-dimethyl)dibenzylideneacetone. In the case of DBA for input energies less than 500 μJ/pulse, the output energy increases linearly with incident energy. But for energies more than 500 μJ/pulse, the output energy is almost constant assuming the value of 350 μJ/pulse. In the case of p-(N,N-dimethyl)dibenzylideneacetone (Fig. 9), for input energies less than 200 μJ/pulse the output varies linearly with the input, but for energies more than 200 μJ/pulse the output energy is almost a constant at 60 μJ/pulse.
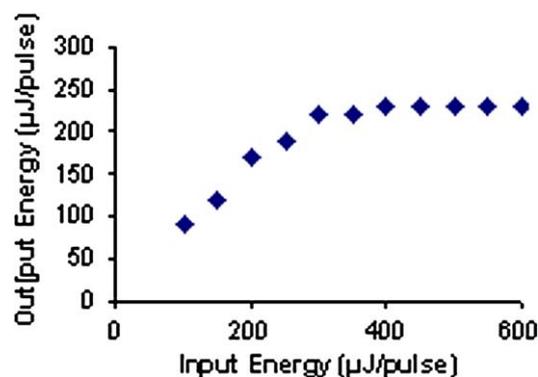

Fig. 6. Optical limiting of laser pulses in p-methoxyDBA.

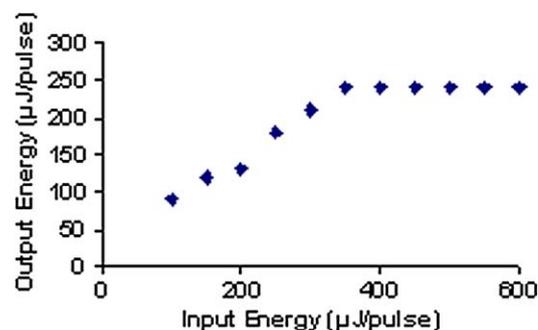Fig. 7. Optical limiting of laser pulses in p-chloroDBA.

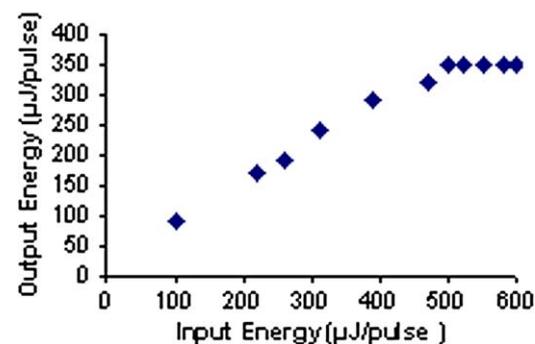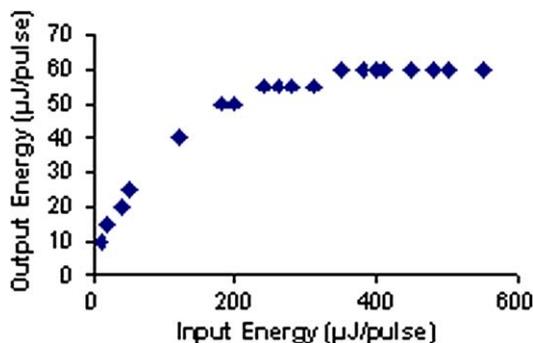Fig. 8. Optical limiting of laser pulses in DBA.

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Fig. 9. Limiting action of *p*-(*N*,*N*-dimethyl)DBA.

For input energies less than 350 μJ/pulse, in the case of *p*-chloroDBA, and 300 μJ/pulse, in the case of *p*-methoxyDBA, the output energy increases linearly with incident energy. However, in excess of 300 μJ/pulse (for *p*-methoxyDBA) and 350 μJ/pulse (for *p*-chloroDBA), the output energy is nearly a constant value of 230 μJ/pulse and 240 μJ/pulse, respectively. *p*-(*N*,*N*-dimethyl)dibenzylideneacetone shows limiting action at low energy compared to other compounds. It is seen that the limiting threshold is decreased from 500 to 60 μJ/pulse and 350 μJ/pulse, respectively, in donor and acceptor type substituted compounds. This can be attributed to the variation in delocalized electron density among these compounds. Based on these observations we believe that the mechanism of the effect arises from nonlinear two-photon absorption [22]. This fact demonstrates that these compounds possess interesting optical limiting properties. In summary, this knowledge of variation of nonlinear response with substituents could be employed to design such organic materials at the molecular level and hence to finely tune $\chi^{(3)}$ for future specific applications in photonic and other optoelectronics fields.

4. Conclusion

The third order nonlinear optical properties of dibenzylideneacetone and its derivatives were investigated at 532 nm using the nanosecond single-beam Z-scan technique. The dependence of nonlinear response of these samples on donor/acceptor type substituents was investigated. We conclude that the variation in π-electron density in these conjugated materials is responsible for the variation in their third order nonlinear response. These compounds exhibit strong two-photon absorption at 532 nm. The compounds *p*-chlorodibenzylideneacetone, *p*-methoxydibenzylideneacetone and *p*-(*N*,*N*-dimethyl)dibenzylideneacetone show very strong optical limiting properties. Hence, these compounds can be used for designing devices such as optical limiters, optical switches and optical modulators.

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