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Third order nonlinear optical properties and optical limiting in donor/acceptor substituted 4′-methoxy chalcone derivatives

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ABSTRACT The third order nonlinear optical properties of 4′-methoxy chalcone and its derivatives have been investigated using a single-beam Z-scan technique with nanosecond laser pulses at 532 nm. The 4′-methoxy chalcone and its derivatives are donor–acceptor–acceptor (D–A–A) and donor–acceptor–donor (D–A–D) type intramolecular charge transfer molecules. The nonlinear response in these molecules was found to increase with increase in (a) the electron acceptor strength in D–A–A type and (b) the donor strength of the substituted group in D–A–D type molecules. The $\chi^{(3)}$ value in these molecules is found to be of the order of 10^{-13} esu. The observed increase in the third order nonlinearity in these molecules clearly indicates the electronic origin. The compounds exhibit good optical limiting at 532 nm. The best optical limiting behavior was observed with the molecule substituted by a strong electron donor.

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1 Introduction

Nonlinear optical (NLO) materials with large and fast NLO responses are needed for numerous optical device applications like optical switching, optical rectification and optical limiting [1–4]. A variety of materials have been investigated for NLO properties, in which organic materials are attractive due to their large variety, high nonlinearity, ultra-fast response and the flexibility they offer to tune the optical properties through structural modification [5]. To increase the nonlinear optical response in this class of materials, researchers have established various design strategies, such as donor–acceptor–donor (D–A–D), acceptor–donor–acceptor (A–D–A) and donor–π–donor (D–π–D) types of molecules [6]. Chalcones are intramolecular charge transfer molecules, which allow one to design them based on the above design criteria. Chalcones are well known for their excellent blue-light transmittance and high second harmonic generation (SHG) conversion efficiency [7, 8]. These chalcones crystallize in a non-centrosymmetric crystal structure [7] and provide a necessary configuration for NLO activity with two

planar benzene rings connected through a conjugated double bond [9]. Most of the work reported on these chalcones is about SHG [9, 10]. Recently, John Kiran et al. [11] have explored dibenzylideneacetone and its derivatives for third order nonlinear optical properties. The nonlinear susceptibility in these molecules was found to be of the order of 10^{-13} esu. The nonlinear response was found to increase as the donor strength of the molecules increased.

In this article we report our studies on 4′-methoxy chalcone {(compound 1) (1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one)} and its derivatives {(1,3-bis(4-methoxyphenyl)prop-2-en-1-one (compound 2), 1-(4-methoxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (compound 3), 3-(4-chlorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (compound 4) and 1-(4-methoxyphenyl)-3-(3-nitrophenyl)prop-2-en-1-one (compound 5)} dissolved in dimethylformamide (DMF) using a single-beam Z-scan technique with nanosecond laser pulses at 532 nm. We discuss the influence of substituted donor/acceptor strength on the third order nonlinear optical properties of these molecules. We demonstrate good optical limiting behavior based on strong nonlinear absorption in these compounds.

2 Experiment

The compounds were synthesized using a standard procedure [12]. Solutions of ethanol and 10% sodium hydroxide were taken in a conical flask. A previously prepared small portion of aldehyde (0.001 mol) and *p*-methoxy acetophenone (0.001 mol) dissolved in ethanol was added to the conical flask with stirring and the temperature of the solution was maintained at 20–25 °C. A precipitate was obtained after stirring the solution for about 5 min. The remaining portion of the aldehyde and ketone mixture was added and the solution was stirred for about 60 min. The separated product was filtered, washed with excess of water to remove as much alkali as possible and dried. The chalcones were then purified by a recrystallization process using acetone as solvent.

The single-beam Z-scan technique [13] was employed to study the nonlinear optical properties of these compounds. This technique is particularly useful when the nonlinear refraction is accompanied by nonlinear absorption and allows one to measure both sign and magnitude of the nonlinear re-

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fractive index. The transmittance of the nonlinear medium through a finite aperture in the far field as a function of the sample position is measured with respect to the focal plane of the focused Gaussian laser beam. Here the sample itself acts as a thin lens with varying focal length as it moves through the focus. When the intensity of the laser beam is sufficient to induce the nonlinearity in the sample, the laser beam either focuses or defocuses depending on the nature of the nonlinearity of the material. By monitoring the transmittance change through a small aperture placed at the far-field position, one is able to determine the nonlinear refractive index (closed aperture Z-scan). An open aperture Z-scan gives information on the nonlinear absorption coefficient.

A *Q*-switched Nd:YAG nanosecond laser pulse at 532 nm was used as a source of light in our experiment. A lens of focal length 26 cm was used to focus the laser beam into a 1-mm quartz cuvette that contained sample solution. The resulting beam waist radius at the focus was 19.6 μm that corresponds to the Rayleigh length of 2.274 mm. The sample thickness of 1 mm was less than the Rayleigh length and, hence, it could be treated as a 'thin medium'. The Z-scan was performed at a laser pulse energy of 80 μJ, which resulted in an on-axis peak irradiance of 1.557 GW/cm^2. All the sample measurements were done at room temperature. In order to avoid the cumulative thermal effect the data were collected in a single-shot mode [14]. The optical limiting measurements were carried out when the sample was at the focal point by varying the input energy and recording the output energy without placing an aperture in front of the detector. Two pyroelectric detectors with a Laser Probe Rj-7620 energy ratio meter were used to record the incident and the transmitted energies simultaneously.

The linear refractive index of these samples dissolved in DMF was measured using an Abbe refractometer. The linear absorption spectra of these compounds (2×10^{-2} mol/L) were collected using a fiber optic spectrometer model SD2000, supplied by Ocean Optics Inc., and are shown in Fig. 1.
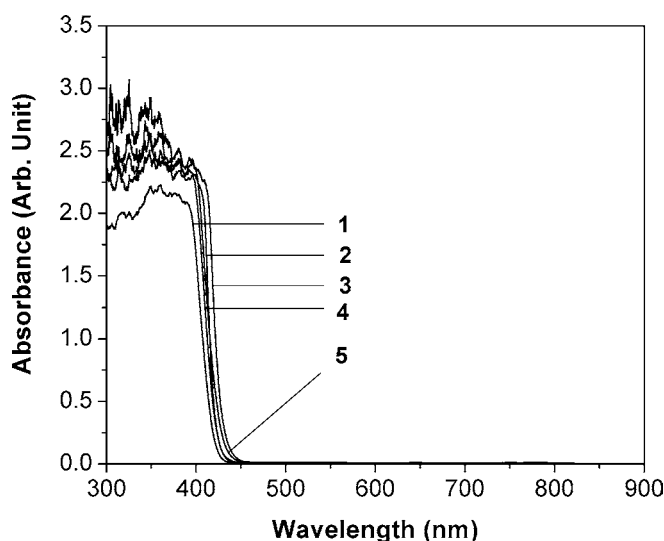

FIGURE 1 Linear absorption spectra of 4′-methoxy chalcone and its derivatives

3 Result and discussion

The molecular structures of all the five compounds are shown in Fig. 2. The synthesized molecules possess D–A–A and D–A–D type structures. In D–A–A type chalcone, the methoxy group attached at one end acts as a donor and the oxygen of the carbonyl group in the center and the chloro or nitro group attached at the other end of the molecules act as electron acceptors, whereas in D–A–D type molecules, one methoxy group is fixed at one end and at the other end the donor group is varied to increase the donating ability. The oxygen of the carbonyl group at the center acts as an electron acceptor. Compounds 1, 2 and 3 possess D–A–D type structure and compounds 4 and 5 are D–A–A type.

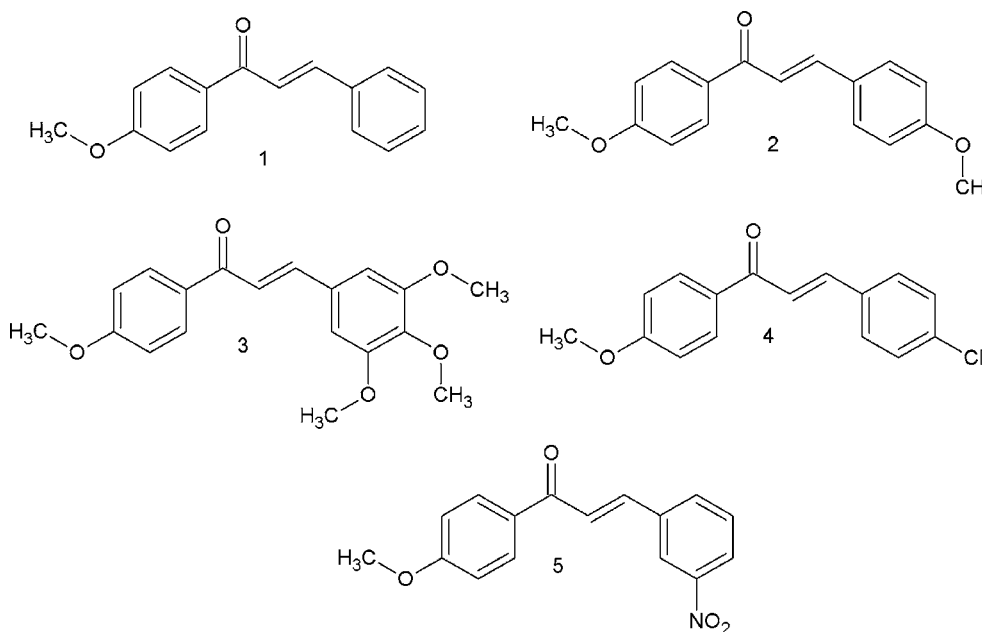The open aperture Z-scan curves for compounds 3 and 4 are shown in Figs. 3 and 4, respectively. The open aperture

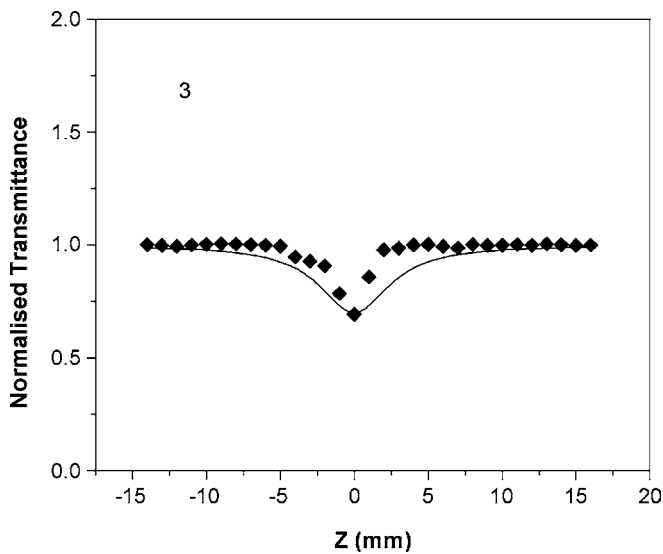**FIGURE 2** Molecular structures of 4′-methoxy chalcone and its derivatives

FIGURE 3 Open aperture Z-scan curve of compound 3 at $I_0 = 1.557\,\mathrm{GW/cm}^2$. The *solid line* is fitted with $\beta_{\mathrm{eff}} = 6.27\,\mathrm{cm/GW}$ to (1)
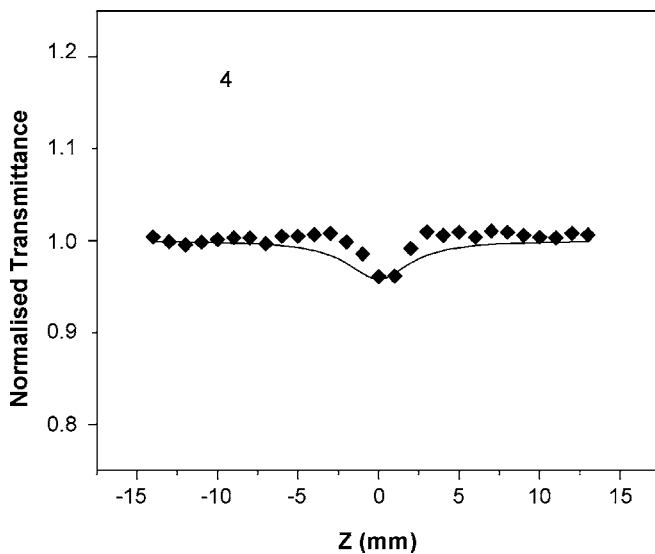

FIGURE 4 Open aperture Z-scan curve of compound 4 at $I_0 = 1.557\,\mathrm{GW/cm}^2$. The *solid line* is fitted with $\beta_{\mathrm{eff}} = 0.58\,\mathrm{cm/GW}$ to (1)

transmittance curve is symmetric with respect to the focus and has minimum transmittance at the focus, indicating the intensity-dependent absorption effect.

The normalized transmittance for the open aperture Z-scan is given by [13]

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

where $q_0(z) = I_0 \beta_{\mathrm{eff}} L_{\mathrm{eff}}/(1 + z^2/z_0^2)$, I_0 is the on-axis peak irradiance at the focus, L_{eff} is the effective thickness of the sample, β_{eff} is an effective value of the two-photon absorption coefficient and z_0 is the Rayleigh length. The open aperture data of all the compounds were fitted with (1).

In order to extract the information on nonlinear refraction, the sample is moved through the focal point and the nonlinear transmission was measured as a function of sample position with an aperture placed at the far field. In almost all mate-

rials the nonlinear refraction (NLR) is accompanied by the nonlinear absorption (NLA); thus, in the case of negative refractive nonlinearity, the transmittance curve for the closed aperture Z-scan has a suppressed peak and an enhanced valley. To obtain a pure nonlinear refraction curve we used the division method described in [13]. The difference between the peak and valley ($\Delta T_{\mathrm{p-v}}$) transmittance in the pure NLR curve is used to calculate the nonlinear refractive index of the compounds using the relation

$$\gamma = \frac{\Delta\varphi_0 \lambda}{2\pi L_{\mathrm{eff}} I_0} \,, \tag{2}$$

where λ is the wavelength of the laser light and $\Delta\varphi_0$ is the nonlinear phase shift given by the relation

$$\Delta\varphi_0 = \frac{\Delta T_{\mathrm{p-v}}}{0.406(1 - S)^{0.25}}$$

for $|\Delta\varphi_0| \leq \pi$, where S (50%) is the aperture linear transmittance.

The normalized transmittance for a closed aperture Z-scan is given by [13]

$$T(x) = 1 - \frac{4x\Delta\varphi_0}{[(x^2 + 9)(x^2 + 1)]} \,, \tag{3}$$

where $x = z/z_0$ and z_0 is the Rayleigh length.

The real and imaginary parts of the third order nonlinear susceptibility can be calculated using the relations $\mathrm{Re}\,\chi^{(3)} = 2n_0^2 \varepsilon_0 c\gamma$ and $\mathrm{Im}\,\chi^{(3)} = n_0^2 \varepsilon_0 c\lambda\beta/2\pi$, 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 nonlinear refractive index n_2 (in esu) can be obtained by the conversion formula $n_2\,(\mathrm{esu}) = (cn_0/40\pi)\gamma\,(\mathrm{m}^2/\mathrm{W})$.

The pure NLR curves of compounds 3 and 4 are shown in Figs. 5 and 6, respectively. The peak and valley configuration of the pure NLR curves clearly indicates the negative sign of the nonlinear refractive index. In order to know the contribution from the solvent to the observed nonlinear response,
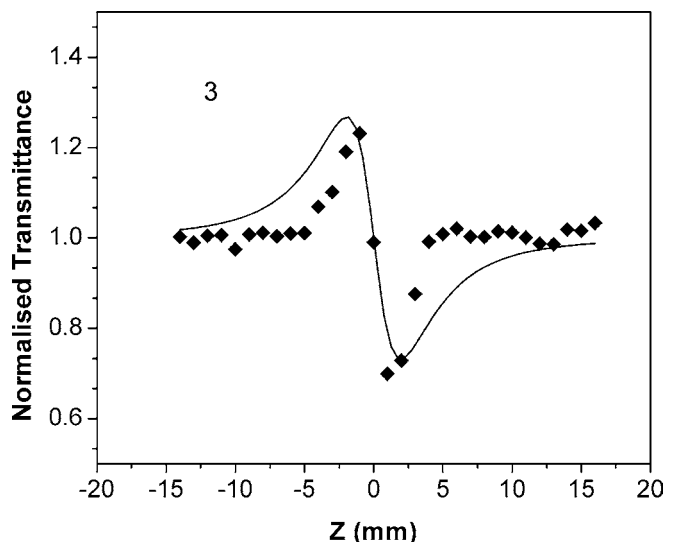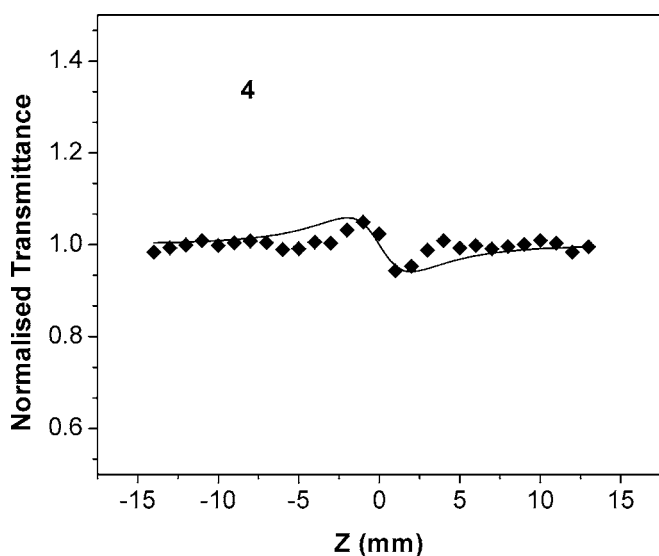

FIGURE 5 The pure NLR curve of compound 3 at $I_0 = 1.557\,\mathrm{GW/cm}^2$. The *solid line* is a theoretical fit of experimental data

FIGURE 6 The pure NLR curve of compound 4 at $I_0 = 1.557$ GW/cm^2. The *solid line* is a theoretical fit of experimental data

the Z-scan was performed on pure solvent. Neither nonlinear absorption nor nonlinear refraction was observed at the pulse energy used. The experimental data was fitted with a theoretical formula assuming only the two-photon absorption. The slight discrepancy among the fitted line and the experimental data could be due to contributions like higher-order effects, nonlinear scattering and a thermal contribution to the nonlinearity. The experimentally determined values of β_{eff}, n_2, Re $\chi^{(3)}$ and Im $\chi^{(3)}$ are given in Table 1.

Among the five compounds studied, the compound 3 substituted with three methoxy groups showed the highest nonlinear response and $\chi^{(3)}$ was found to be -2.633×10^{-13} esu. In compounds 1, 2 and 3, at one end a single methoxy group was fixed at the *para* position and at the other end donor groups with increasing donor strength (3,4,5-trimethoxy > *p*-methoxy > hydrogen) were substituted. Hence, the observed enhancement in the nonlinear response is due to the presence of a high donor trimethoxy group in compound 3. The compounds 4 and 5 are D–A–A type molecules. The nonlinear optical susceptibility was found to increase from compound 4 to compound 5. If one assumes that the charge transfer is from end to end of the molecule, the observed increase in the nonlinear response can be explained based on the electron accepting ability of the groups present in the molecule. The nitro group in compound 5 is a strong electron acceptor compared to chlorine in compound 4. Thus, the charge transfer is more effective in compound 5 and hence shows a higher nonlinear response compared to compound 4. Further, compound 3 has more absorption at 532 nm compared to compounds 1, 2 and 4. The enhancement in the nonlinear response may also be partly due to a resonant contribution. The linear absorption at 532 nm in compound 5 is more compared to compound 4 and hence there could be a contribution from the resonant part of the nonlinearity to the observed nonlinear response. The nonlinear susceptibility of the molecules increased in the order compounds $3 > 2 > 5 > 1 > 4$. The dependence of $\chi^{(3)}$ on donor/acceptor type substituents to the basic compound clearly shows the electronic origin of the nonlinearity and hence demonstrates that the thermal effects do not play a dominant role in the third order nonlinear response of the compounds.

The second order hyperpolarizability, γ_h, of a molecule in an isotropic medium is related to the macroscopic third order susceptibility $\chi^{(3)}$ as below [15, 16]:

$$\gamma_h = \chi^{(3)}/L^4 N, \qquad (4)$$

where N is the density of molecules in the unit of number of molecules per cm^3 and L is the local field factor given by $L = (n^2 + 2)/3$; here n is the linear refractive index of the medium. The calculated values of the microscopic second order hyperpolarizability for compounds 1–5 are 0.183×10^{-32}, 0.619×10^{-32}, 0.919×10^{-32}, 0.170×10^{-32} and 0.526×10^{-32} esu, respectively.

The molecular hyperpolarizability of these molecules was compared with the organic molecules and polymers reported in the literature. The molecular hyperpolarizability of $4'$-methoxy chalcone and its derivatives was found to be less than that of copolymers reported by John Kiran et al. [16] and greater than that of thiophene (dimer, trimer, tetra and pentamers) and comparable with that of thiophene (hexamer) [15].

The β, n_2 and $\chi^{(3)}$ values of dibenzylideneacetone and its derivatives were reported by John Kiran et al. [11]. Among the molecules, the one substituted with a N, N-dimethyl amino group showed high β, n_2 and $\chi^{(3)}$ values of 5.986 cm/GW, -1.964×10^{-11} esu and -2.11×10^{-13} esu, respectively. The β_{eff}, n_2, and $\chi^{(3)}$ values of 6.27 cm/GW, -2.442×10^{-11} esu and -2.633×10^{-13} esu were obtained for the molecule substituted with three methoxy groups (compound 3) in the $4'$-methoxy chalcone derivatives. It is found that the β_{eff}, n_2 and $\chi^{(3)}$ values of compound 3 are higher compared to those of dibenzylideneacetone substituted with a strong donor N, N-dimethyl amino group.

The knowledge of the on-axis irradiance dependence of the nonlinear absorption (NLA) coefficient gives the information about the mechanism of the nonlinear absorption. The NLA can be generally caused by free-carrier absorption, sat-

Sample number	α (cm^{-1})	β_{eff} (cm/GW)	n_2 (esu)	Re $\chi^{(3)}$ (esu)	Im $\chi^{(3)}$ (esu)
1	0.003	0.81	-0.555×10^{-11}	-0.598×10^{-13}	1.26×10^{-14}
2	0.003	3.25	-1.784×10^{-11}	-1.923×10^{-13}	5.04×10^{-14}
3	0.008	6.27	-2.442×10^{-11}	-2.633×10^{-13}	9.73×10^{-14}
4	0.003	0.58	-0.536×10^{-11}	-0.579×10^{-13}	0.89×10^{-14}
5	0.011	2.65	-1.502×10^{-11}	-1.619×10^{-13}	4.11×10^{-14}

TABLE 1 Experimentally determined values of β_{eff}, n_2, Re $\chi^{(3)}$ and Im $\chi^{(3)}$

urated absorption, direct multiphoton absorption or excited-state absorption. If the mechanism belongs to the simple two-photon absorption, then β should be a constant that is independent of the on-axis peak irradiance I_0. If the mechanism is due to direct three-photon absorption then β should be a linearly increasing function of I_0 and the intercept on the vertical axis must be zero [17]. But, in compounds 1 and 4 (substituted with chlorine), we find that β_{eff} increases with increase in I_0 despite the excited-state absorption being greater than that of the ground state and the intercept on the vertical axis is non-zero. This suggests that a higher-order effect, such as excited-state absorption (ESA) accessed via two-photon absorption, is contributing to the NLA [18]. However, in all other investigated compounds β_{eff} was found to decrease with increasing I_0. The excited state absorption cross section, σ_{ex}, for all the compounds was determined by the procedure described in the literature [16]. The σ_{ex} of compounds 2, 3 and 5 was found to be $2.9 \times 10^{-19}\,\mathrm{cm}^2$, $6.1 \times 10^{-19}\,\mathrm{cm}^2$ and $2.3 \times 10^{-19}\,\mathrm{cm}^2$, respectively. The ground state absorption cross section of compounds 2, 3 and 5 (σ_{g}) calculated from $\alpha = \sigma_{\mathrm{g}} N_A C$, where N_A is Avogadro's number and C is the concentration in $\mathrm{mol\,cm}^{-3}$, was $0.249 \times 10^{-21}\,\mathrm{cm}^2$, $0.664 \times 10^{-21}\,\mathrm{cm}^2$ and $0.913 \times 10^{-21}\,\mathrm{cm}^2$. The value of σ_{ex} was found to be larger than the value of σ_{g} for compounds 2, 3 and 5, which is in agreement with the condition for observing reverse saturable absorption [16, 19]. We note that John Kiran et al. [16] have reported a similar fall-off of β with increasing I_0 for reverse saturable absorption in copolymers. However, we also note that a decrease of β with increasing I_0 has also been reported for the optical limiting action of thiophene oligomers by Hein et al. [20], where it was attributed to saturation of instantaneous two-photon absorption.

By following the analysis described in [21] we found from the pure nonlinear refraction curves of these compounds that $\Delta Z_{\mathrm{vp}} \approx 1.2 Z_0$, which is the case of fifth order nonlinearity. If we define the phase distortion induced by fifth order nonlinearity as [22]

$$\Delta\varphi_0 = k\eta I_0^2 [1 - \exp(-2\alpha L)]/2\alpha \qquad (5)$$

and the difference between the normalized peak and valley transmittance as $\Delta T_{\mathrm{p-v}} = 0.21|\Delta\varphi_0|$ [13], then the nonlinear refractive index of these compounds responsible for fifth order nonlinearity, η, can be calculated to be of the order of $\approx 10^{-23}\,\mathrm{cm}^4\,\mathrm{W}^{-2}$. Here L is the nonlinear medium length, $k = 2\pi/\lambda$ and α is the absorption coefficient of the samples.

Optical limiting behavior of all the compounds is shown in Figs. 7–9. Based on the reverse saturable absorption, a good optical limiting property can be expected for compounds 2, 3 and 5. Compound 3 (three methoxy groups) showed better optical limiting compared to all other molecules and compound 4 showed the least. The optical limiting behavior was found to be in the order of compounds 3 > 2 > 5 > 1 > 4. Optical limiting was found to vary according to the extent of donor/acceptor strength. Hence, 4′-methoxy chalcone and its derivatives may be used for optical limiting applications.

4 Conclusion

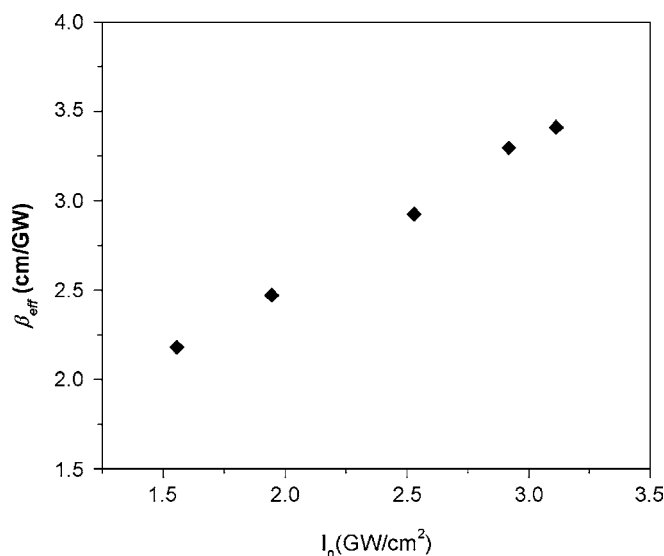The third order nonlinear optical properties of 4′-methoxy chalcone and its derivatives have been investi-

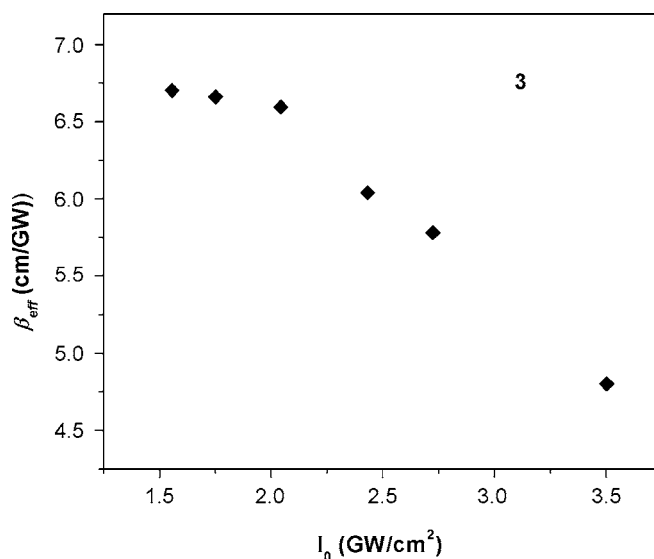**FIGURE 7** A plot of β_{eff} vs. I_0 for compound 4

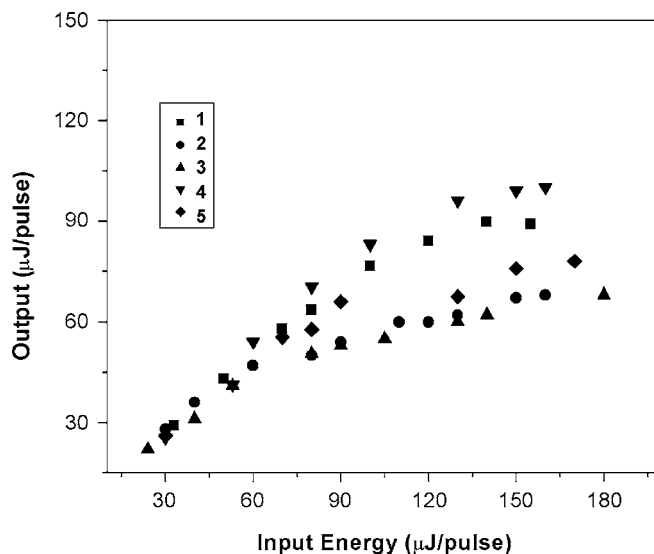**FIGURE 8** A plot of β_{eff} vs. I_0 for compound 3

FIGURE 9 Optical limiting in 4′-methoxy chalcone and its derivatives

gated using a single-beam Z-scan technique with nanosecond laser pulses at 532 nm. The 4′-methoxy chalcone and its derivatives show a good third order nonlinear response. The nonlinear refractive index, n_2, of the investigated 4′-methoxy chalcone and its derivatives is found to be negative and the magnitude is as high as 10^{-11} esu. The nonlinear response is found to increase with increase in donor/acceptor strength in D–A–D and D–A–A type molecules. The compounds 2, 3 and 5 show strong reverse saturable absorption. All compounds show good optical limiting behavior at 532 nm. Compound 3 showed the best optical limiting behavior among the compounds studied. These compounds may be used for optical limiting applications. The present study reveals that by increasing the donor/acceptor strength in chalcone molecules, one can increase the third order nonlinear response and hence it is possible to tailor the nonlinear optical property through structure modification in this class of materials.

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