ELSEVIER

Nonlinear optical studies of 1-3-diaryl-propenones containing 4-methylthiophenyl moieties

A. John Kiran [a], Ashok Mithun [b], B. Shivarama Holla [b], H.D. Shashikala [a], G. Umesh [a], K. Chandrasekharan [c,*]

[a] *Department of Physics, National Institute of Technology, Surathkal, Karnataka 575 025, India*
[b] *Department of Chemistry, Mangalore University, Karnataka 574 199, India*
[c] *Lasers and Nonlinear Optics Lab, Department of Science and Humanities, National Institute of Technology Calicut 673 601, India*

Abstract

The third-order nonlinear optical properties of chalcone derivatives have been studied using the single beam Z-scan technique. The dependence of $\chi^{(3)}$ on different donor and acceptor type substituents demonstrates the electronic nonlinearity of compounds. The largest value of nonlinear refractive index, n_2, measured for a high electron donor substituted molecule is -2.033×10^{-11} esu. These molecules exhibit a strong two-photon absorption and interesting optical limiting of nanosecond laser pulses at 532 nm.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Nonlinear optical properties; Z-scan; Two-photon absorption; Optical limiting; Nonlinear refractive index

1. Introduction

Molecules with large third-order optical nonlinearities are required for photonic applications including all-optical switching, data processing, and eye and sensor protection [1–4]. Molecules those exhibit strong two-photon absorption are currently of considerable interest for a variety of applications including optical limiting because of their fast response and the advantage of high transmission at low intensity for fundamental optical frequencies well below the band gap frequency [5]. Recently, we have studied chalcone derivatives (dibenzylideneacetone and its derivatives) for their large third-order nonlinear response [6]. Many researchers have been reporting large two-photon absorptivities for several organic materials [7,8]. High values of the nonlinear refractive index n_2 (which is proportional to the real part of $\chi^{(3)}$) are essential for electro-optical and all-optical switching, where as high nonlinear absorption

coefficients, β (which is proportional to the imaginary part of $\chi^{(3)}$) are important for optical limiting [9]. The third-order nonlinearity of these conjugated organic compounds can be enhanced by (i) increasing the conjugation length, to increase the distance over which charge can be transferred; (ii) creating a donor–acceptor–donor motif by substitution to increase the extent of charge transfer from the ends of the molecule to the center and (iii) reversing the sense of symmetric charge transfer by substituting electron acceptors and donors, and there by creating acceptor–donor–acceptor compounds [10].

In this paper, we report on our efforts to enhance the third-order nonlinearity of a series of π-conjugated organic compounds by using the above strategy. We have examined a series of chalcone derivatives substituted with donor and acceptor groups. We were interested in high electron donating groups since the increased delocalized electron density can enhance the third-order nonlinearity. We report that, among all investigated compounds, the molecule with strongest electron donor group exhibits large two-photon absorption at 532 nm as measured with

nanosecond laser pulses and shows high value of n_2 and $\chi^{(3)}$. We demonstrate the strong optical limiting of visible, nanosecond pulses with these compounds.

2. Experiment

The chalcone compounds we investigated are: 1-(4-methylphenyl)-3-(4-methylthiophenyl)-2-propen-1-one (labeled mc-4), 1-(4-methoxyphenyl)-3-(4-methylthiophenyl)-2-propen-1-one (labeled mc-6), 1-(4-chlorophenyl)-3-(4-methylthiophenyl)-2-propen-1-one (labeled mc-3), 1-(4-methylthiophenyl)-3-(4-tertiarybutylphenyl)-2-propen-1-one (labeled mc-10), 2-bromo-1-(4-methylphenyl)-3-(4-methylthiophenyl)-2-propen-1-one (labeled mc-6m), 2-bromo-1-(4-methoxyphenyl)-3-(4-methylthiophenyl)-2-propen-1-one (labeled mc-4m) and 2-bromo-1-(4-chlorophenyl)-3-(4-methylthiophenyl)-2-propen-1-one (labeled mc-3m). The compounds were synthesized according to the standard literature procedure [11]. The *p*-methylthio benzaldehyde (0.01 mol) and substituted acetophenones (0.01 mol) were stirred for 2–3 h in presence of sodium hydroxide solution (0.01 mol). After stirring, it was kept aside for about an hour. Then the precipitated solid was filtered and dried. It was then recrystallised from ethanol.

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. Because of the light-induced lens like effect, the sample has the tendency to recollimating or defocusing the incident beam, depending on its *z* position with respect to the focal plane. By properly monitoring the transmittance change through a small aperture placed at the far-field position (closed aperture), one is able to determine the amplitude of the phase shift. By moving the sample through the focus and without placing an aperture at the detector (open aperture), one can measure the intensity dependent absorption as a change of transmittance through the sample.

The Q-switched Nd:YAG laser with a pulse width of 7 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. 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 0.16 mJ, which corresponds to a peak irradiance of 2.91 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 Laser Probe Rj-7620 Energy Ratiometer with two pyroelectric detectors.

3. Results and discussion

The linear absorption spectra of compounds mc-3–mc-10 and mc-3m–mc-6m are shown in Fig. 1a and 1b, respectively. The UV–VIS absorption spectra of samples were recorded at room temperature in dilute dimethylformamide (DMF) solutions $[1 \times 10^{-2}\ \text{mol/L}]$ using the fiber optic spectrometer model SD2000, supplied by Ocean Optics Inc. The absorption spectra show that all compounds are transparent at 532 nm and hence we measure nonresonant nonlinearity. The linear refractive indices of samples obtained by using an Abbe refractometer are shown in Table 1.

The general structure of compounds coded mc-3, mc-4, mc-6 and mc-10 is shown in Fig. 2a. The group H$_3$CS is common on right hand side to all the compounds where as, D2 is different for different compounds. The compounds mc-4, mc-6 and mc-10 have donor–π–acceptor–π–donor structure in which there is a symmetric charge transfer from ends to the center, while the compound mc-3 has donor–π–acceptor–π–acceptor structure. In order to study the variation in nonlinear response we synthesized another type of derivatives of these compounds. The general structure of these compounds coded mc-3m, mc-4m and mc-6m is shown in Fig. 2b. In mc-3m, mc-4m and
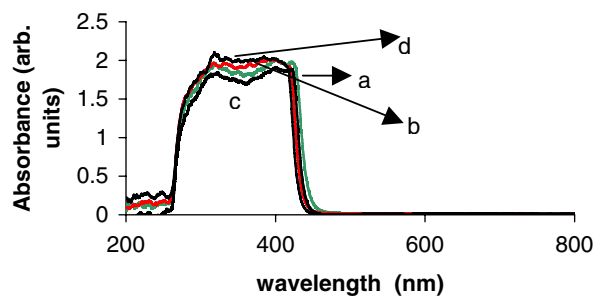

Fig. 1a. Linear absorption spectra of samples. (a) mc-3, (b) mc-6, (c) mc-10 and (d) mc-4.
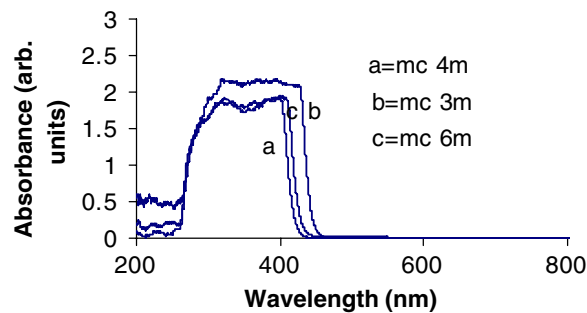

Fig. 1b. Linear absorption spectra of samples coded mc-3m, mc-4m and mc-6m.

Table 1
Values of n_0, n_2, β, $\mathrm{Re}\,\chi^{(3)}$ and $\mathrm{Im}\,\chi^{(3)}$ determined experimentally for different compounds

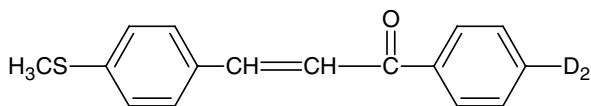| Name of the samples	n_0	n_2 (10^{-11} esu)	β (cm/GW)	$\mathrm{Re}\,\chi^{(3)}$ (10^{-13} esu)	$\mathrm{Im}\,\chi^{(3)}$ (10^{-13} esu)
mc-3	1.423	−1.098	1.472	−1.181	0.23
mc-4	1.421	−1.21	2.046	−1.296	0.26
mc-6	1.421	−1.23	2.690	−1.320	0.42
mc-10	1.420	−2.023	3.035	−2.170	0.47
mc-3m	1.423	−0.719	1.440	−0.770	0.22
mc-4m	1.421	−0.251	0.330	−0.269	0.05
mc-6m	1.423	−0.33	0.321	−0.356	0.049

Fig. 2a. The structure of compounds coded mc-3, mc-4, mc-6 and mc-10. D_2 is Cl, CH_3, OCH_3 and $C(CH_3)_3$, respectively for mc-3, mc-4, mc-6 and mc-10.
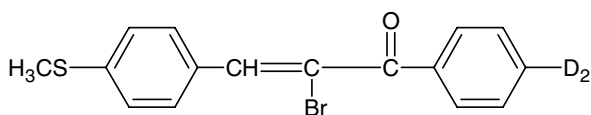

Fig. 2b. The structure of compounds coded mc-3m, mc-4m and mc-6m. D_2 is Cl, CH_3 and OCH_3, respectively for mc-3m, mc-4m and mc-6m.

mc-6m one more acceptor atom, bromine, is attached at the center.

Z-scan measurements were performed on the sample solutions of concentration 1×10^{-2} mol/L. 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 open aperture curves, closed aperture curves, and pure nonlinear refraction curves of mc-10 and mc-6 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 these compounds exhibit two-photon
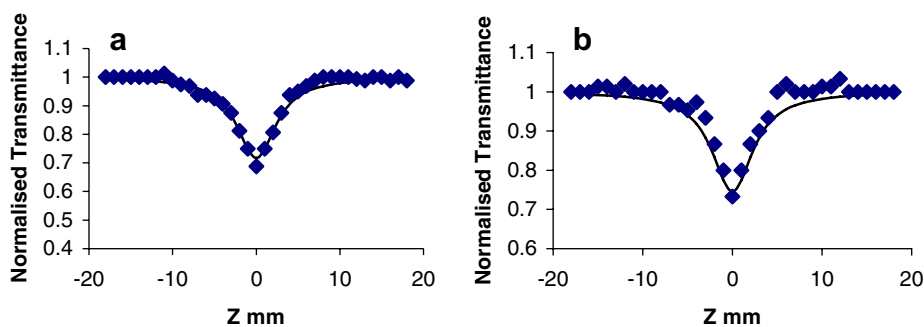

Fig. 3. Normalized open aperture curves for (a) mc-10 and (b) mc-6. Solid lines are fit of data to Eq. (1), fitted with $\beta = 3.035$ cm/GW and 2.046 cm/GW, respectively.
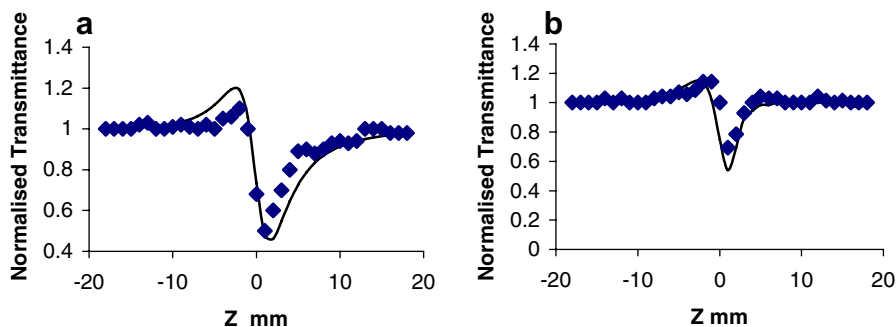

Fig. 4. Normalized closed aperture Z-scan curves for (a) mc-10 and (b) mc-6. Solid lines are fit of data to Eq. (5) with $\Delta\phi_0 = 1.8$ and 1.32, respectively.
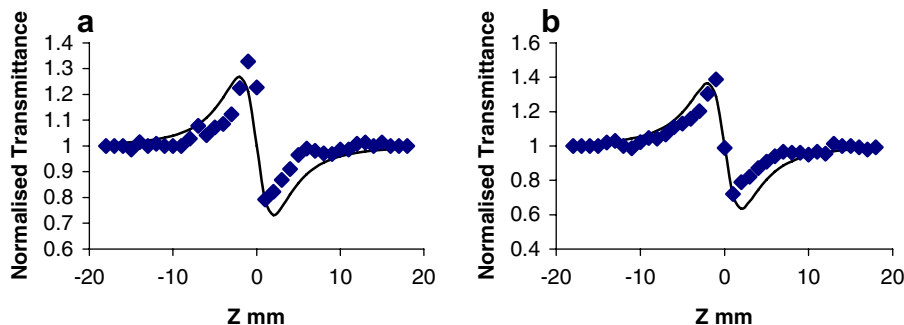
Fig. 5. Normalized pure nonlinear refraction curves obtained by division method for (a) mc-10 and (b) mc-6. Solid lines are fit to the experimental data.

absorption [14–16]. 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 [12]:

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

where

$$q_0(z) = \frac{\beta I_0(1 - \exp -\alpha L)}{(1 + z^2/z_0^2)\alpha},$$

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 and w_0 is the beam waist radius at the focus. Eq. (1) is used to fit the open aperture experimental data. In Fig. 3(a) and (b), the solid lines are fitted with $\beta = 3.035$ cm/GW and 2.046 cm/GW, respectively.

Fig. 4 shows the normalized transmission of compounds through a closed aperture. In order to obtain a pure nonlinear refraction curve the division method described in [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 [12]:

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

where

$$L_{\text{eff}} = \frac{(1 - \exp^{-\alpha L})}{\alpha}$$

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, and τ is the pulse width of laser (full width at half maximum) [17]. 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 relation:

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

where $\Delta T_{p\text{-}v}$ is the peak-valley transmittance difference and S is the linear aperture transmittance [12].

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

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

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 [12]. 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 [12]. The experimentally determined values of n_2, β, $\text{Re}\,\chi^{(3)}$ and $\text{Im}\,\chi^{(3)}$ for all the compounds are shown in Table 1. The results were consistent in all trials with a maximum error in measurements less than 8.5%. The nonlinear response was found to increase on going from mc-3 to mc-10. The electron donating ability of $C(CH_3)_3 > OCH_3 > CH_3 > Cl$. Among the investigated compounds, the nonlinear response is highest in the case of mc-10. In mc-10 there is a S–CH_3 group on the left hand side of the molecule and a $C(CH_3)_3$ on the right hand side. The S–CH_3 group is known to be a good electron donor and it gives away electrons easily to form a stable π-electron distributed system. This donates more electrons into the molecule and on the other side $C(CH_3)_3$ also releases electrons in to the molecule. The acceptor, $C{=}O$, at the center accepts electrons and hence there is a strong delocalization of electrons in

the molecule. There is a symmetric charge transfer from the ends to the center and hence the extent of π-electron transfer is increased in the molecule. Consequently, a highest nonlinear response was observed with mc-10. In mc-3, mc-4 and mc-6 the response was observed to vary according to the density of delocalized electrons in the molecule. Therefore, the enhanced nonlinear response of mc-10 is mainly due to the increased π-electron density in the molecule [9,19]. In mc-3, due to the inductive effect of chlorine, the π-electron density and the charge transfer in the system is reduced considerably. Therefore the response is minimum compared to that of other three samples.

In compounds mc-3m, mc-4m and mc-6m there is a bromine atom at the center of molecule. Br is a good electron acceptor due to its high electronegativity. Bromine, being a heavy atom, affects the planarity of the molecule, which in turn reduces the delocalization of electrons through out the molecule. In conjugated systems, like those of chalcones, co-planarity is required for the transfer of electrons from donor to acceptor. In α-Bromo chalcones, the bulky bromine atom sterically interferes with adjacent *cis*-phenyl ring and pushes this phenyl ring out of plane. Hence there is no co-planar arrangement of two phenyl rings with the double bond and the π-conjugation is thus not effective in the transfer of electrons from one end to the other in the system [20]. As a result, nonlinear response of these samples was found to decrease upon substitution of Br atom at position −2 of the propenones. These results indicate that the nonlinearity varies among these molecules upon substitution of different electron donating and electron withdrawing groups and thus show that the response is electronic in origin and that the thermal effect is not the dominant effect for the third order nonlinear response of the samples.

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 from the solvent to the nonlinearity of the samples is negligible.

Compounds mc-3, mc-4, mc-6 and mc-10 show very strong two-photon absorption. Hence, optical limiting based on the two-photon absorption is expected for the nanosecond laser pulses. The linear transmittance of all samples (in the region far from the focus) was in the range 90% to 92%. In Fig. 6a optical limiting behavior of these compounds is shown for nanosecond pulses. An interesting limiting was observed in the case of mc-4, mc-6 and mc-10, which have donor–acceptor–donor structure. The nonlinear absorption was observed to increase on going from mc-3 to mc-10. In the case of mc-10, for input energies less than 220 μJ/pulse, the output energy increased linearly with the incident energy. But for energies more than 220 μJ/pulse, the output energy was almost constant assuming the value of 140 μJ/pulse. The limiting threshold increased from 220 μJ/pulse to 250 μJ/pulse in the case of mc-4 and the output was clamped at around 153 μJ/pulse.
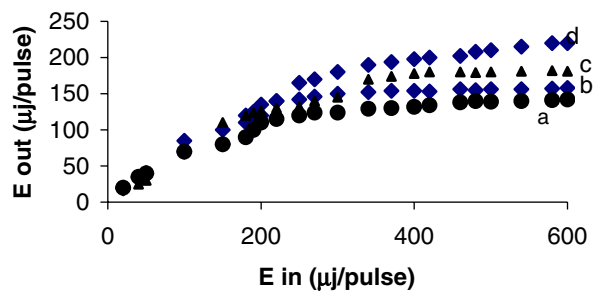

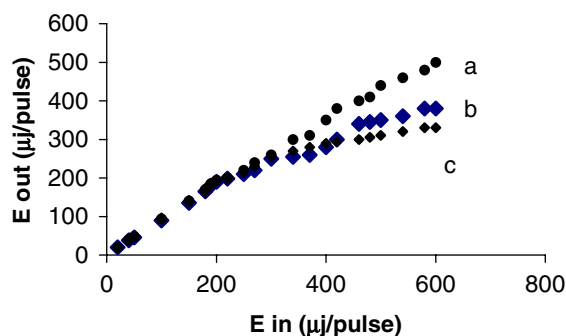Fig. 6a. Optical limiting of nanosecond pulses in samples a = mc-10, b = mc-4, c = mc-6 and d = mc-3.

Fig. 6b. Optical limiting action of samples a = mc-6m, b = mc-4m, c = mc-3m.

Further, this threshold increased to 370 μJ/pulse in the case of mc-3 and there the output became almost constant at 220 μJ/pulse. The limiting behavior diminished in compounds mc-3m, mc-4m and mc-6m, as shown in Fig. 6b. As discussed above, the substitution of Br atom affects the planarity and electron delocalization in molecule. Hence, these compounds show low two-photon absorption and very low nonlinear refraction at 532 nm. Therefore, the output energy is almost linear with the input energy showing the reduced optical limiting in these three samples.

4. Conclusions

The third order nonlinear optical properties of 1-3-diaryl-propenones containing 4-methylthiophenyl moieties 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. The variation in π-electron density in these conjugated materials was found to be responsible for the variation in their third order nonlinear response. The compounds with strong electron donor groups exhibit strong two-photon absorption at 532 nm. This makes them promising nonlinear optical absorbers and optical limiters. The compounds coded mc-4, mc-6 and mc-10 show very good optical limiting properties. The present results may help us in designing organic materials suitable for device applications such as optical limiters, optical switches and optical modulators.

Acknowledgements

References

[1] Seth R. Marder, William E. Torruellas, Mirelle Blanchard-Desce, Vincent Ricci, George I. Stegeman, Sharon Gilmour, Jean-Luc Bredas, Jun Li, Greg U. Bublitz, Steve G. Boxer, Science 276 (1997) 1233.

[2] J.W. Perry, K. Mansour, I.-Y.S. Lee, X. –L. Wu, P.V. Bedworth, C.-T. Chen, D. Ng, S.R. Marder, P. Miles, T. Wada, M. Tian, H. Sasabe, Science 273 (1996) 1533.

[3] R.W. Munn, C.N. Ironside (Eds.), Principles and Applications of Nonlinear Optical Materials, Chapman and Hall, 1993.

[4] Chunfei Li, Lei Zhang, Miao Yang, Hui Wang, Yuxiao Wang, Phys. Rev. A 49 (1994) 1149.

[5] J.E. Ehrlich, X.L. Wu, I.-Y.S. Lee, Z.-Y. Hu, H. Rockel, S.R. Marder, J.W. Perry, Opt. Lett. 22 (1997) 1843.

[6] A. John Kiran, K. Chandrasekharan, Satheesh Rai Nooji, H.D. Shashikala, G. Umesh, Balakrishna Kalluraya, Chem. Phys. 324 (2006) 699.

[7] Guang S. He, Raz Gvishi, Paras N. Prasad, Bruce A. Reinhardt, Opt. Commun. 117 (1995) 133.

[8] Sergey S. Sarkisov, Burl H. Peterson, Michael J. Curley, V.N. Nesterov, T. Timofeeva, M. Antipin, E.I. Radovanova, Alex Leyderman, P.A. Fleitz, J. Nonlinear Opt. Phys. Mater. 14 (2005) 21.

[9] P. Prem Kiran, D. Raghunath Reddy, Bhaskar G. Maiya, Aditya K. Dharmadikari, G. Ravindra Kumar, D. Narayana Rao, Opt. Commun. 252 (2005) 150.

[10] Marius Albota, David Beljonne, Jean-Luc Brebas, Jaffrey E. Ehrlich, Jia-Ying Fu, Ahmed A. Heikal, Samuel E. Hess, Thierry Kogej, Michael D. Levin, Seth R. Marder, D. McCord-Maughon, Joseph W. Perry, Harald Rockel, M. Rumi, G. Subramaniam, Watt.W. Webb, Xiang L. Wu, Chris Xu, Science 281 (1998) 1653.

[11] V.K. Ahluwalia, Renu Agarwal, Comprehensive Practical Organic Chemistry Preparation and Quantitative Analysis, Universities Press (India) Ltd, Hyderabad, 2000.

[12] Sheik-Bahae Mansoor, Ali A. Said, Tai-Huei Wei, David J. Hagan, E.W. Van Stryland, IEEE J. Quantum Electron. 26 (1990) 760.

[13] Pingxiong Yang, J. Xu, J. Ballato, R.W. Schwartz, D.L. Carroll, Appl. Phys. Lett. 80 (2002) 3394.

[14] R.A. Ganeev, A.I. Ryasnyanskii, M.K. Kodirov, Sh.R. Kamalov, T. Usmanov, Opt. Spectrosc. 93 (2002) 789.

[15] Rik R. Tykwinski, K. Kamada, D. Bykowski, F.A. Hegmann, R.J. Hinkle, J. Opt. A: Pure Appl. Opt. 4 (2002) S202.

[16] M. Yin, H.P. Li, S.H. Tang, W. Ji, Appl. Phys. B 70 (2000) 587.

[17] Wenfang Sun, C.M. Lawson, G.M. Gray, Opt. Commun. 180 (2000) 361.

[18] Xiaodong Liu, S. Guo, Huitian Wang, L. Hou, Opt. Commun. 197 (2001) 431.

[19] T. Cassano, R. Tommasi, F. Babudri, A. Cardone, G.M. Farinola, F. Naso, Opt. Lett. 27 (2002) 2176.

[20] P.S. Kalsi, Stereochemistry – Conformation and Mechanism, Wiley Eastern Ltd, 1990.