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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.
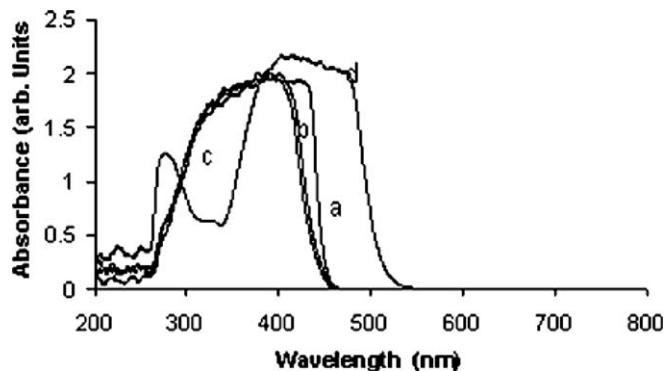

Fig. 1. Linear absorption spectra of compounds dissolved in DMF in 1 cm quartz cell: (a) *p*-methoxyDBA, (b) DBA, (c) *p*-chloroDBA, (d) *p*-(*N,N*-dimethyl)DBA.