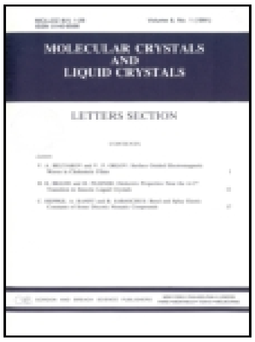

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Xiangke Wang, Yongsheng Mi, Dong Wang, Wanli He, Hui Cao & Huai Yang (2016) Third-order nonlinear optical properties of a novel series of azobenzene liquid crystal derivatives, Molecular Crystals and Liquid Crystals, 630:1, 1-5, DOI: 10.1080/15421406.2015.1044698

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1044698

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 630, 1–5
http://dx.doi.org/10.1080/15421406.2015.1044698

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Third-order nonlinear optical properties of a novel series of azobenzene liquid crystal derivatives

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ABSTRACT
A novel series of D-π-A bi-alkyne liquid crystal derivatives were designed and synthesized, which had typical D-π-A structures. The third-order nonlinearities of the compounds were studied by “open aperture” and “closed aperture” Z-scan techniques. Both compounds showed typical nonlinear absorptions and refractions, and the third-order nonlinear susceptibilities have been found to be very high in all cases. The significant nonlinear optical response, combined with the possibility to further modify it, by changing the π-linking groups and the electron donors or acceptors, suggests that these systems can prove to be important candidates for a variety of photonic/optoelectronic applications.

KEYWORDS
Azobenzene liquid crystal; third-order nonlinear; Z-scan

1. Introduction

Nonlinear optical (NLO) effects generally occur when high-intensity electric fields, such as intense laser beams, interact with matter to modify its optical properties, generating new components (i.e., amplitude, phase, and polarization) [1]. NLO effects are of technological importance because these are considered promising elements for optical devices related to a plethora of applications, such as optical data storage, telecommunications, biophotonics, and nanophotonics [2–6]. In the direction of synthesizing novel materials exhibiting high NLO response, compounds comprising electron donating and accepting groups connected with a π-conjugated chain are of great interest. In many cases the presence of electron donating and accepting groups has been reported to result in a significant increase of nonlinearities [7–11].

Although there are several classes of materials that exhibit intrinsic large NLO responses, molecular organic materials containing typical D-π-A structures are generally considered to be the most promising candidates for optoelectronic and photonic applications [12]. This trend is further supported by the great synthetic versatility exhibited by molecular organic materials, which ultimately allows fine tuning of their linear optical properties, and consequently their optical nonlinearities. Typically, the preparation of π-conjugated organic backbones with electron donating moieties is of particular interest because upon extension of the conjugation length and increasing the electron density of molecular system, the second

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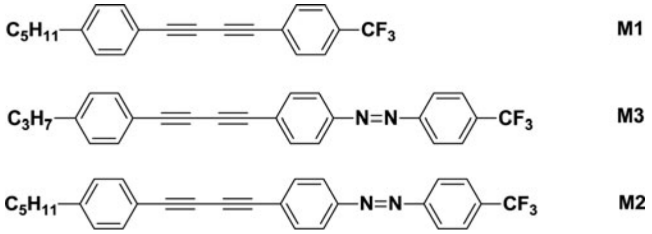

Figure 1. Molecular structures of **M1**, **M2**, and **M3**.

hyperpolarizability (γ), which expresses the strength of the third-order nonlinearity per molecule, increases considerably [13].

The azobenzenes are a category of materials with very interesting chemical/optical and, in particular, NLO properties, which can satisfy the prerequisites for a variety of optoelectronic applications. One of their most important features is that they can exist in two isomeric forms (trans and cis), while the ratio of the two isomers can be modified by proper irradiation and can be detected by the modification of their absorption spectra [14]. Moreover, photo-induced birefringence and dichroism are well known to take place in such systems [15]. It has also been demonstrated that two-photon absorption processes can be employed in order to photo-orient azobenzene molecules [16]. Because of their interesting properties the azobenzenes can be useful in a variety of applications, including optical data storage, surface relief gratings, all optical switching, etc. [17]. For the aforementioned reasons, the second- (after introducing necessary non-centrosymmetry to the systems) and third-order nonlinearities of azobenzenes are widely investigated [18].

Herein, we report new results obtained from the Z-scan investigation of the NLO properties of three electronically rich derivatives, namely, molecules **M1**, **M2**, and **M3**, the structures of which are depicted in Fig. 1. Specifically, our solution studies have probed the structure–property relationships that govern the nonlinearity of these compounds, and ultimately reveal the influence of the containing azobenzene and non-azobenzene composition of π-linking on their third-order NLO response.

2. Experimental

2.1. General procedure for the synthesis of compounds M1–M3

Molecules **M1–M3** were synthesized according to the reported procedures [19]. The solvents used for the preparation of the solutions and materials were purchased from Sigma Aldrich and used without further purification.

2.2. Nonlinear optical measurements

The NLO response of the compounds was measured by means of Z-scan technique, employing 20-ps laser pulses at 532 nm delivered by a mode-locked Nd:YAG laser (EKSPLA PL2143B). The linearly polarized laser beam was focused with a 200-mm focal length lens and the sample was moved across the focus by means of a computer-controlled micrometric translation stage. The beam waist at the focus was typically 20 ± 5 μm and the pulse energy, after suitable attenuation, was in the range 0.2–0.5 μJ. Z-scan is a relatively simple experimental technique allowing for the simultaneous determination of real and imaginary parts of the third-order susceptibility, $\chi^{(3)}$ [20]. All the samples were measured in 10^{-6} M solution of tetrahydrofuran (THF) solvent (spectra). The solvent itself does not show any third-order nonlinearity under our experimental conditions.

The details of the experimental techniques, as well as the procedure to analyze the experimental data, are briefly described here, and extended information can be found in literature. Here a laser beam is focused using a lens and passed through the sample. The beam's propagation direction is taken as the z-axis, and the focal point is taken as Z = 0. The beam will have maximum energy density at the focus, which will symmetrically reduce toward either side for the positive and negative values of Z. In our experiment, THF solutions of the samples were taken in 1-mm cuvettes, and the measurement was done by placing the samples in beam at different positions with respect to the focus (different values of Z) and measuring the corresponding light transmission. The graph plotted between the samples T_{norm} (transmission normalized to the linear transmission of the sample) was known as the Z-scan curve. From the "open aperture" Z-scan curves the nonlinear absorption coefficient (β) has been determined using the following equation:

$$\int \beta\left(\mathrm{m}\cdot\mathrm{w}^{-1}\right) = \frac{2\sqrt{2}[1 - T(Z=0)]}{I_0 L_{\text{eff}}}, \tag{1}$$

where T is the normalized transmittance, $L_{\text{eff}} = (1 - \exp(-\alpha_0 L))/\alpha_0$ is the effective thickness of the sample, α_0 is the linear absorption coefficient of the sample at the laser excitation wavelength, L is the sample thickness, and I_0 is the on-axis irradiance at the focus. From the nonlinear absorption coefficient, the imaginary part of the third-order nonlinear susceptibility has been determined using the following equation

$$\mathrm{Im}\chi^{(3)}\,(\mathrm{esu}) = \frac{c^2\eta_0^2\beta}{240\pi^2\omega}, \tag{2}$$

where c is the speed of light in $\mathrm{m}\cdot\mathrm{s}^{-1}$, η_0 is the linear refractive index, and $\omega = \frac{2\pi c}{\lambda}$ is the fundamental frequency in cycles per second.

From the "closed aperture" Z-scan curves, the nonlinear refraction coefficient (η_2) has been determined using the following equation:

$$\eta_2\left(\mathrm{m}\cdot\mathrm{w}^{-1}\right) = \frac{\Delta T_{\text{pv}}}{0.406\,(1-s)^{0.25}\,kI_0L_{\text{eff}}}, \tag{3}$$

where $\Delta T_{\text{pv}} = T_{\text{peak}} - T_{\text{valley}}$, and $k = \frac{2\pi}{\lambda}$ is the wave vector. The real part of the third-order nonlinear susceptibility has been determined using Equation (4):

$$\mathrm{Re}\chi^{(3)}\,(\mathrm{esu}) = \frac{\eta_0^2 c\eta_2}{120\pi^2}. \tag{4}$$

$\chi^{(3)}$ can be calculated by Equation (5),

$$\left|\chi^{(3)}\right| = \sqrt{\left|\mathrm{Im}\chi^{(3)}\right|^2 + \left|\mathrm{Re}\chi^{(3)}\right|^2}. \tag{5}$$

3. Third-order nonlinear properties

In investigating the third-order NLO properties, the third-order susceptibility values $\chi^{(3)}$ of **M1–M3** were measured by means of the Z-scan technique. Figure 2 gave the open Z-scan

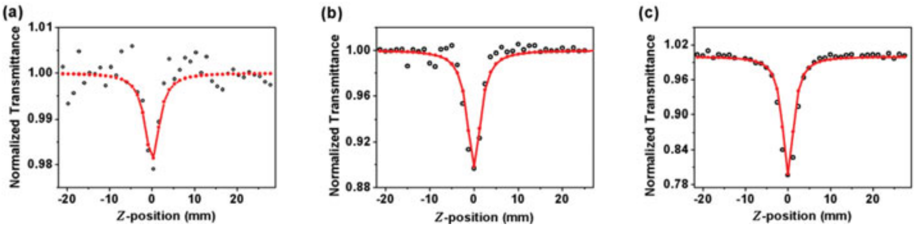

Figure 2. Open-aperture Z-scans measured in the THF solution of **M1–M3**. As seen in figures, optical transmission is a function of sample option ($Z = 0$ is the beam focus). T_{norm} is the measured transmission normalized by the linear transmission of sample. Solid curves correspond to numerical fits to the data.

curves of **M1–M3**, which exhibited saturable absorption (SA) behaviors, while the closed-aperture Z-scan curves are shown in Fig. 3. All the nonlinear optical response parameters were summarized in Table 1. All the compounds had both nonlinear absorption and nonlinear refraction, and all exhibited saturable absorption behavior and positive nonlinear refractive index. A plausible explanation to this effect could be attributed to the existence of charge transfer (CT) interactions between the donor (alkyl chains) and the introduced acceptor (trifluoromethyl group). Compared with **M1**, the containing azo group molecules **M2** and **M3** showed larger nonlinear absorption susceptibilities but lower nonlinear refraction susceptibilities, which could be attributed to the insertion of azo groups into π-linking regions leading to the increment of π-conjugation. This could help to further investigate the functions of azo group in some D-π-A structures except the trans-cis photoisomerization. In addition, it was worth noticing that the compounds **M1**, **M2**, and **M3** showed $\chi^{(3)}$ values of the order of 2.21 $\times 10^{-12}$, 1.61 $\times 10^{-12}$, and 1.36 $\times 10^{-12}$ esu, which were much larger than the third-order susceptibility of fused silica (1.9 $\times 10^{-21}$ m^2 V^{-2}) and were comparable with other potent NLO chromophores [21–23]. Another conclusion could be drawn by comparing **M2** and **M3** with the increments of alkyl chains in the donor groups of the molecules, the third-order nonlinear susceptibilities decreased and this might be due to the change of CT in molecule structures.

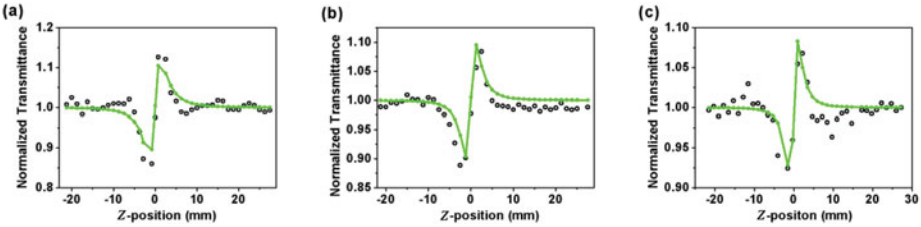

Figure 3. Closed-aperture Z-scans measured in the THF solution of **M1–M3**. As seen in figures, optical transmission is a function of sample option ($Z = 0$ is the beam focus). T_{norm} is the measured transmission normalized by the linear transmission of sample. Solid curves correspond to numerical fits to the data.

Table 1. Third-order nonlinear optical parameters of compounds **M1-M3**.

Samples	$\beta(\mathrm{m} \times \mathrm{w}^{-1})$	$\mathrm{Im}\chi^{(3)}$ (esu)	n_2 ($\mathrm{m} \times \mathrm{w}^{-1}$)	$\mathrm{Re}\chi^{(3)}$ (esu)	$\chi^{(3)}$ (esu)
M1	4.57×10^{-12}	9.67×10^{-14}	4.43×10^{-18}	2.21×10^{-12}	2.21×10^{-12}
M2	2.23×10^{-11}	4.72×10^{-13}	3.08×10^{-18}	1.54×10^{-12}	1.61×10^{-12}
M3	3.85×10^{-11}	8.15×10^{-13}	2.18×10^{-18}	1.09×10^{-12}	1.36×10^{-12}

4. Conclusions

A novel series of π-conjugated azo-based molecules were synthesized and investigated by the Z-scan technique with 20-ps laser excitation in 532-nm visible region. All three D-π-A structure compounds exhibited very large optical nonlinearities in THF solution. The third-order nonlinear susceptibility values of the samples were 2.21×10^{-12}, 1.61×10^{-12}, and 1.36×10^{-12} esu under 20-ps laser excitation at 532 nm. Large optical nonlinearities of molecules make them potential candidates of several optoelectronic and photonic applications, and in particular, by the introduction of azobenzene, these compounds could also be used in ultra-fast switching applications.

Funding

This work was supported by the Major Project of International Cooperation of the Ministry of Science and Technology (Grant No. 2013DFB50340), the National Natural Science Foundation of China (Grant Nos. 51173017, 51203011, 51103010, and 61370048), the Major Project of Beijing Science and Technology Program (Grant No. Z121100006512002), the Beijing Higher Education Young Elite Teacher Project, And the National Key Basic Research Program of China (2014CB931804).

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