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A study of third-order nonlinear optical properties for anthraquinone derivatives

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Abstract

The ground-state geometry, second hyperpolarizabilities of the anthraquinone derivatives have been studied using finite field (FF) The molecular configurations and calculated γ_{zzzz} values are considerably affected by substituents. The third-order nonlinear optical property of 1,4-diamino-2,3-diphenoxy-anthraquinone has been measured using picosecond degenerate four-wave mixing. The third-order nonlinear optical susceptibility $\chi^{(3)}$ of the dye is as high as 1.16×10^{-12} esu. The second hyperpolarizability (γ) value is 5.71×10^{-31} esu.

Keywords: 1,4-Diamino-2,3-diphenoxy-anthraquinone; Finite field; Molecular configuration; Second hyperpolarizability; Degenerate four-wave mixing

1. Introduction

In the past decade, design and fabrication of nonlinear optical devices continued to be an exciting area in applied science, such as optical switching and optical limiting [1,2]. As an important class of dyes with large delocalized two-dimensional π-electron system [3] and exceptionally high thermal stability [4], anthraquinone derivatives have attracted researchers' interests in nonlinear optical applications [3,5]. The proposed anthraquinone structures typically contain an electron-withdrawing central ring and some electron-donating groups at the side-rings in form of donor–acceptor–donor (D-A-D). Such anthraquinone derivatives could be conveniently prepared from halogenated anthraquinones [6] or leucoquinizarin [4]. The structural flexibility provides the possibility to use molecular engineering to maximize the optical nonlinearity. MO calculation of molecular hyperpolarizabilities is of importance in establishing the structure–property relationship and designing molecules with large NLO responses.

In this contribution, the substitution effects on the ground-state geometry and hyperpolarizability tensor components of the anthraquinone derivatives are studied using finite field (FF) approaches. And then, the third-order nonlinear optical susceptibility of 1,4-diamino-2,3-diphenoxy-anthraquinone is measured using three-dimensional degenerate four-wave mixing (3D-DFMW) measurement.

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2. Experimental

2.1. Calculation of the second-order hyperpolarizabilities

Nine anthraquinone derivatives containing different substituents (Table 1) were designed. The molecule geometry was fully optimized on the basis of the semiempirical AM1 Hamiltonian in the MOPAC package. The PRESICE option was used as a convergence criterion for geometry calculation. The second-order hyperpolarizabilities were theoretically evaluated by finite-field method (FF) implemented in GAMESS package.

2.2. Experimental evaluation of the nonlinearity

The chemical structure of 1,4-diamino-2,3-diphenoxy-anthraquinone (An9) is given in Fig. 1. It was synthesized by the procedure of Mori [7]. After repeated crystallization from ethanol, the pure product was obtained as dark red needles. M.p. 193 °C (Lit. m.p. 189–91 °C [7]); ^{1}H-NMR ($CDCl_3/\delta$, ppm): 8.39–8.36 (m, 2H), 7.78–7.75 (m, 2H), 7.27–7.22 (m, 4H), 7.09–7.04 (m, 2H), 6.74–6.71 (m, 4H), 5.60–5.10 (br, 4H).

The purified dye was dissolved in *N,N*-dimethylformamide at a concentration of 1.027×10^{-3} mol/l for measurements. Its absorption spectrum in *N,N*-dimethylformamide solution is displayed in Fig. 2. As an anthraquinone dye with two amino groups in 1- and 4-positions, the main band of the absorption typically has a double head at 545 and 584 nm. The laser wavelength (532 nm) used in the experiment of 3D-DFWM is in the resonant absorption region of the dye. Thus strong electronic resonance enhancement of the optical nonlinearity should be expected.

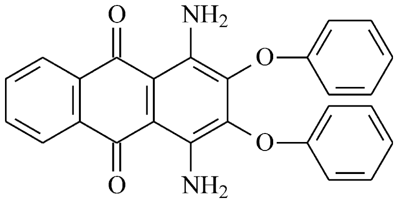

Fig. 1. The chemical structure of 1,4-diamino-2,3-diphenoxy-anthraquinone (An9).

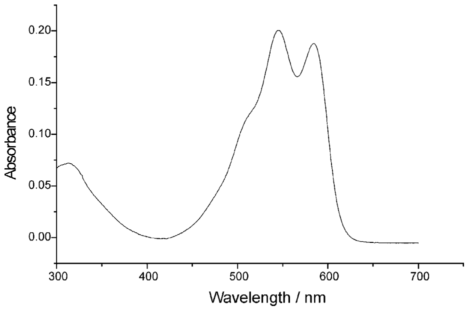

Fig. 2. The absorption spectrum of An9 in *N*,*N*-dimethylformamide solution.

The third-order optical nonlinearity of An9 in *N*,*N*-dimethylformamide solution was measured by the 3D-DFWM technique. The experimental setup was shown in Fig. 3(a). The pump source was a mode-locked and frequency-doubled Nd:YAG laser with 35 ps pulse-width, 532 nm wavelength, and 10 Hz pulse repetition rate. The low repetition rate was used to avoid thermal effects. The input beam was split into three beams

Table 1
The second-order hyperpolarizabilities of anthraquinone derivatives

	Substituents	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{xxzz}	γ_{yyzz}	$\langle\gamma\rangle$ (a.u.)	$\langle\gamma\rangle$ (esu)$\times10^{-36}$
An1	1,4-NH_2	175 399	23 853	3	16 093	1404	1648	47 509	24.00
An2	1,4-NHC_2H_4OH	67 787	262 528	−45	30 829	2669	1638	80 108	40.46
An3	1,5-NHC_2H_4OH	195 676	68 195	162	66 975	3718	17 866	88 230	44.57
An4	1-NHC_2H_4OH	139 356	34 834	12	24 745	2149	1354	46 140	23.31
An5	1,5-$NHC_2H_4NH_2$	211 390	34 539	−66	56 681	3378	1496	73 795	37.27
An6	1,4-OH	120 099	12 512	14	18 894	1725	1229	35 265	17.81
An7	1,5-OC_2H_4OH	102 402	37 066	96	28 764	2339	1725	41 044	20.73
An8	1,4-$NHCH_2CH(CH_3)OH$	107 878	186 881	1718	25 672	6303	4806	74 008	37.38
An9	1,4-NH_2-2,3-OAr	290 476	23003	6538	44 071	14 869	5396	89 738	45.33

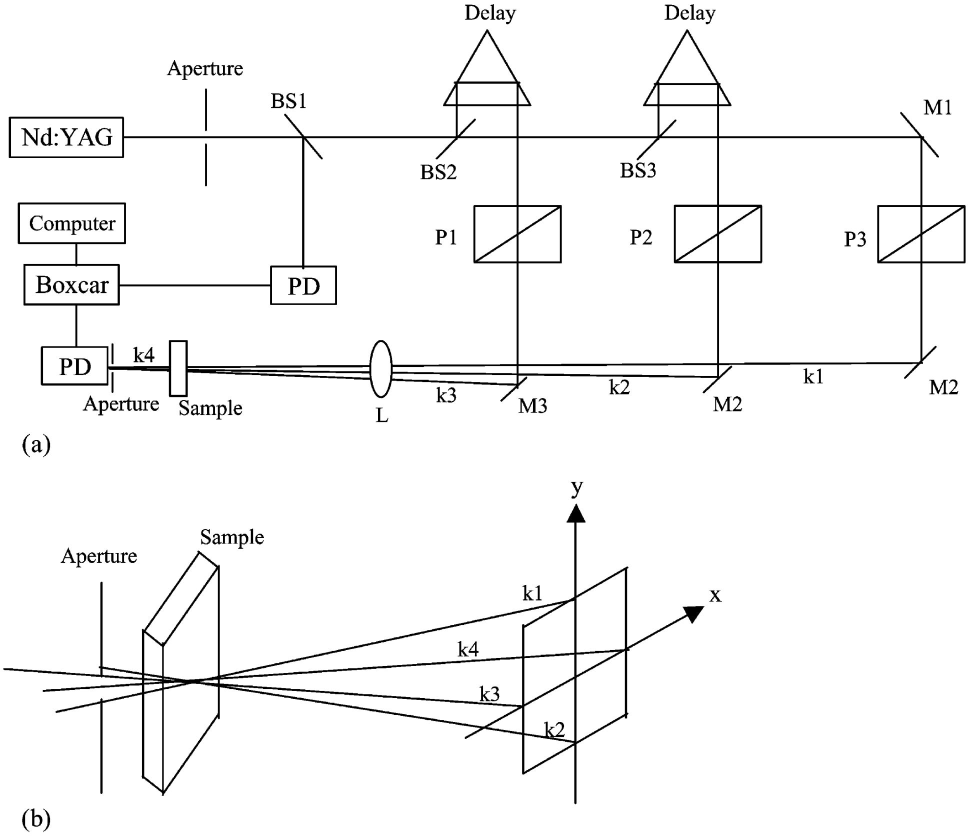

Fig. 3. (a) Experimentl setup of 3D-DFWM; (b) wave vector diagram of the three-dimensional configuration.

k1, k2, and k3 with nearly equal energy by use of reflecting beam splitters (BS1, BS2, and BS3), then focused on a plot of the sample by a lens (L) with 20 cm focal length. The beam geometry was shown in Fig. 3(b), where k4 was signal beam generated by input beams through the sample. The angles between the beams k1, k2, and k3 were about 2°. The k2 and k3 could be controlled by stepping motors so that the arrival time at the sample could be varied. When k1, k2, and k3 were overlapped spatially and temporally in the sample, the generated signal beam k4 was detected to slits, recorded by a photodiode, and then analyzed by a boxcar and computer.

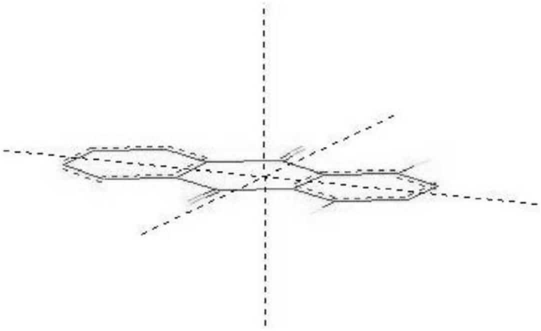

Fig. 4. The molecular configuration of 1,4-diaminoanthraquinone (An1).

3. Results and discussion

3.1. Geometric structures

From the result of geometric optimization, it is observed that the anthraquinone ring always remains its planarity (in *x*–*y* plane). Simple anthraquinone derivatives as An1 (Fig. 4) have good coplanar configurations, and the molecules could be stacked in compact layers. Although effective three-dimensional molecular stacking is helpful to produce large third order nonlinear optical susceptibility [8], this staking behavior would also lead to higher melting point and less solubility [4], which should be taken for consideration during application.

However, the configurations of substituents are not always kept in the same plane of the anthraquinone ring. 1,4-diamino-2,3-diphenoxy-anthraquinone (An9) is in such a case that there are two large substituents (phenoxy groups) in the 2- and 3-positions of anthraquinone ring. Both substituents have bulky volumes and repel each other outside from the anthraquinone plane (Fig. 5). Then the π–π intermolecular interactions between the anthraquinone rings are decreased and the affinities to solvents are improved.

3.2. Calculation of nonlinearity parameters

For each molecular geometry, the hyperpolarizability tensor components were theoretically evaluated and listed in Table 1. The isotropic average (γ) is defined as:

$$\langle\gamma\rangle=(\gamma_{xxxx}+\gamma_{yyyy}+\gamma_{zzzz}+2\gamma_{xxyy}+2\gamma_{xxzz}+2\gamma_{yyzz})/5$$

As x–y plane is defined by the anthraquinone ring, the γ_{zzzz} components are mainly contributed by the substituents. Obviously, the γ_{zzzz} values of An1-7 are quite small because of their small volumes of substitutes and coplanar configurations. For An9, the γ_{zzzz} value is significantly improved for the reason of molecular configuration and the additional delocalized π-electron system in substituents.

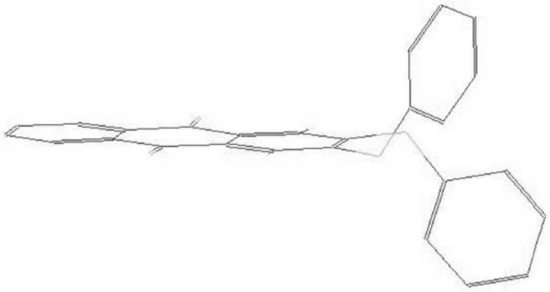

Fig. 5. The molecular configuration of 1,4-diamino-2,3-diphenoxy-anthraquinone (An9).

3.3. Experimental evolution of the nonlinearity

With a large second-order hyperpolarizability and better processability, An9 is then subjected to three-dimensional degenerate four-wave mixing (3D-DFMW) measurements for experimental evolution of its nonlinearity. The temporal response of the phase conjugate signal as a function of the delay time of the input beam is shown in Fig. 6. The phase conjugate signal is asymmetrical with respect to the zero time delay, that formation of a response persists for time longer than the exciting pulse. As the working wavelength (532 nm) lay in the region of absorption, the observed effects should involve resonant processes.

The third-order nonlinear optical susceptibilities $\chi^{(3)}$ is obtained by comparing the measured signals for the sample with that for carbon disulfide as reference under the same experimental condition according to the following formula [9]:

$$\chi^{(3)}=\left(\frac{I_4}{I}\right)^{1/2}\frac{L_r}{L}\left(\frac{n}{n_r}\right)\frac{\alpha L\exp(\alpha L/2)}{1-\exp(-\alpha L)}\chi_r^{(3)}$$

where I_4 is the intensity of the phase conjugate beam k4, L is the sample path length, n is the linear refractive index, and α is linear absorption coefficient of the sample at 532 nm. The subscript

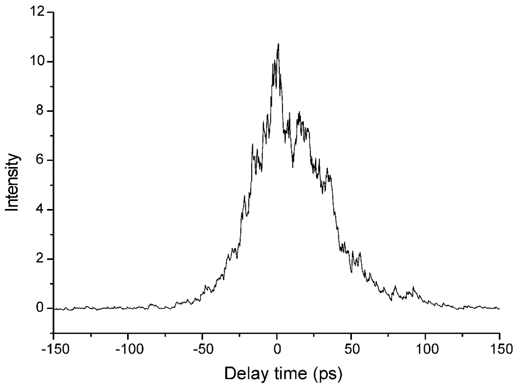

Fig. 6. 3D-DFWM signal versus delay time for An9 in *N*,*N*-dimethylformamide solution.

"r" refers to carbon disulfide (CS_2) and the $\chi^{(3)}$ value of CS_2 is 6.8×10^{-13} esu [10]. The $\chi^{(3)}$ value of An9 in *N*,*N*-dimethylformamide (1.027×10^{-3} mol/l) is then obtained as 1.16×10^{-12} esu.

The second hyperpolarizability (γ) of a molecule in isotropic media is related to the solution $\chi^{(3)}$ by:

$$\langle\gamma\rangle = \frac{\chi^{(3)}}{L^4 N}$$

assuming that the solvent makes a negligible contribution to the signal. L^4 is the local field correction factor, which is $[(n^2+2)/3]^4$ under the Lorentz–Lorenz approximation, and N is the number density of the solute per ml. The second hyperpolarizability (γ) value is then calculated to be 5.71×10^{-31} esu. The values of $\chi^{(3)}$ and (γ) of An9 are higher than those of the anthraquinone derivatives with alkylamino substituents, which are only 1.86–3.44×10^{-13} esu and 1.91–3.49×10^{-31} esu respectively [11].

An9 possesses highly delocalized p-conjugate electron systems not only in its nucleus, but also in the substituents. The operating wavelength of the measurement is in the resonant absorption region and thus a strong electronic resonance enhancement of the optical nonlinearity is present. The result suggests that An9 is a promising third-order nonlinear optical material.

4. Conclusion

The ground-state geometry, second hyperpolarizabilities of the anthraquinone derivatives have been theoretically evaluated. The results show that both the configurations and second hyperpolarizability (γ) values could be controlled by the attached substituents at the anthraquinone rings. The third-order nonlinear optical property of 1,4-diamino-2,3-diphenoxy-anthraquinone has been measured using picosecond degenerate four-wave mixing. The third-order nonlinear optical susceptibility $\chi^{(3)}$ and the second hyperpolarizability (γ) of the dye are as high as 1.16×10^{-12} and 5.71×10^{-31} esu, respectively. The results show that this dye has a high potential for nonlinear optical application.

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