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Hydrogen Bond Effect in Nonlinear Optical Properties of Azobenzene Derivatives

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Three kinds of 4-hydroxyl azobenzene compounds with different substituents varied as $-\text{NO}_2$, $-\text{H}$, $-\text{OCH}_3$ in the para-position were synthesized and characterized. Their nonlinear optical properties in tetrahydrofuran (THF) and chloroform (CHCl_3) solution were determined using Z-scan technique. The results revealed that the nonlinear absorption (β) and nonlinear refraction (γ) values of three azobenzene compounds in THF solution were larger than those in CHCl_3 solution. It was mainly due to the regular arrangement and effective π -conjugation of azobenzene molecules caused by the formation of hydrogen bonds between the hydroxyl groups of azobenzene molecules and the oxygen atom of the THF molecules. Among three kinds of azobenzene compounds, the 4-nitro-4'-hydroxyazobenzene (NAzoOH) had the largest coefficients of β and γ values in both THF and CHCl_3 solution. It was mainly because that a push-pull (D- π -A) electron system was formed by the electron withdrawing nitro-substituent with electron donating hydroxyl-group in both extremities of azobenzene, resulting in a higher electron delocalization.

Key words: Azobenzene, Nonlinear property, Hydrogen bond, Substituent, Z-scan

I. INTRODUCTION

Conjugated organic nonlinear optical (NLO) materials have received much attention owing to their potential application in optical data storage [1, 2], NLO materials [3–7], optical switching [8] and surface-relief gratings [9]. In recent years, azobenzene systems are widely investigated because of the properties of NLO with photoresponsive behaviour [10–13].

The origin of nonlinear optical effects lies in the nonlinear response of a material to an electric field. To maximize the nonlinearities in materials, a collective effort has been made by scientists of fields including physics, chemistry and materials. It has been found there are mainly two approaches to enhance the nonlinearities of materials. One way is to synthetically design molecules with large dipole moment and nonlinear coefficients, and the other is to maximize the applied poling field strength or change the environment [3]. The molecular parameters that can be tuned are different donor (D) and acceptor (A) groups in the dipole and conjugation length. Li *et al.* found that the nonlinear optical coefficients of azo polymers with

different substituents exhibited different nonlinear absorption [14]. The nitro-substituted polymer film has the largest coefficients of the nonlinear absorption and nonlinear refraction values because a push-pull (D- π -A) electron system was formed by the electron withdrawing nitro-substituent with dimethylamino-group in the azobenzene side chain, which enhances the delocalization effect and is favorable to increase the NLO effect. The environment can be changed by the introduction of hydrogen bond. Many chemists and material scientists have utilized the hydrogen bond to obtain the bigger nonlinear optical materials [15–23]. Liakatas *et al.* discovered that intermolecular interactions had a large influence on the optical nonlinearity of the molecules both in solution and in guest-host polymers [22]. An enhancement effect of intramolecular hydrogen bond on the third-order nonlinear optical properties of azobenzene compounds were found by Yin *et al.* [23]. However, how the hydrogen bond affects the NLO properties of azobenzene compounds with different substituents are still unknown.

In this work, three kinds of hydroxyl-azobenzene compounds were synthesized by differing the substituted group in the para-position as $-\text{NO}_2$, $-\text{H}$ and $-\text{OCH}_3$, respectively. The effects of hydrogen bond on the NLO properties of hydroxyl-azobenzene compounds were investigated systematically to understand the cor-

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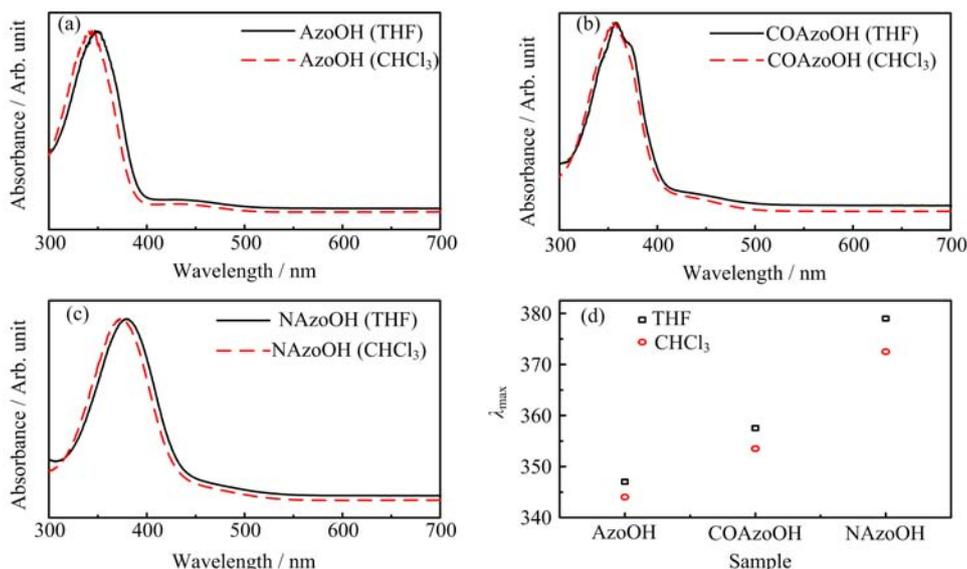


FIG. 1 UV-Vis absorption spectra of (a) AzoOH, (b) COAzoOH, (c) NAzoOH. And (d) λ_{\max} of AzoOH, COAzoOH, and NAzoOH in THF and CHCl₃ solution.

relation between their structure and NLO properties.

II. EXPERIMENTS

A. Materials Preparation

4-hydroxyazobenzene (AzoOH), 4-nitro-4'-hydroxyazobenzene (NAzoOH) and 4-methoxy-4'-hydroxyazobenzene (COAzoOH) was synthesized according to Ref.[24]. Analytical grade tetrahydrofuran (THF) and chloroform (CHCl₃) was used as received.

B. Measurements

Fourier-transform infrared spectra (FT-IR) were recorded on a spectrometer Nicolet 8700. UV-Vis absorption spectra were obtained using a spectrophotometer SHIMADZU UV-2550 PC.

The third-order nonlinear optical properties were investigated using the Z-scan technique [25]. In our experiment, azobenzene compounds were dissolved in freshly distilled THF and CHCl₃ to give 1 mmol/L solution, respectively. The solution was then placed in a 2-mm quartz cell. The optical response of the sample was measured with a Q-switched ns/ps Nd:YAG laser system continuum ($\lambda=532$ nm, repetition frequency $\nu=10$ Hz, pulse width $\tau=16$ ns). The relation between the normalized transmittance $T(z)$ and z position was obtained by moving the samples along the axis of the incident beam (z direction) with respect to the focal point. The incident and transmitted energies were detected simultaneously by a dual-channel joule meter (Moletron, EPM2000).

III. RESULTS AND DISCUSSION

A. Materials characterization

AzoOH ¹H NMR (400 MHz, DMSO): δ (ppm)=6.75 (d, $J=4.00$ Hz, 2H), 7.80 (d, $J=4.12$ Hz, 2H), 7.90 (d, $J=4.24$ Hz, 2H), 8.40 (d, $J=4.44$ Hz, 2H). NAzoOH ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.00 (d, $J=4.00$ Hz, 2H), 7.85 (d, $J=4.04$ Hz, 2H), 7.95 (d, $J=4.04$ Hz, 2H), 8.40 (d, $J=4.80$ Hz, 2H). COAzoOH ¹H NMR (400 MHz, DMSO): δ (ppm)=3.85 (s, 3H, CH₃O), 6.85 (d, $J=4.00$ Hz, 2H), 7.15 (d, $J=4.04$ Hz, 2H), 7.75 (d, $J=3.98$ Hz, 2H), 7.85 (d, $J=3.98$ Hz, 2H), 10.30 (s, 1H, -OH).

The UV-Vis absorption spectra of AzoOH, COAzoOH and NAzoOH in THF and CHCl₃ solution are shown in Fig.1. Each azobenzene compound exhibits two major absorption peaks located at around 350 and 420 nm, respectively. The absorption peak at 350 nm is attributed to the strong $\pi-\pi^*$ transitions of *trans* azobenzene groups and 420 nm is due to weak $n-\pi^*$ transitions of *cis* azobenzene groups, respectively. The molecules used in the present study have a similar structure, in general, consisting basically of an azobenzene conjugated bridge substituted with 4-hydroxyl donor group and different moieties in the para-position.

It can be seen from Fig.1(a) that the absorption peaks of AzoOH show a red shift in THF solution compared to that in CHCl₃ solution. Similar phenomena have been observed for COAzoOH and NAzoOH. One possible reason is the solvent polarity effect, and the other is the formation of hydrogen bond between -OH group of azobenzene compounds and oxygen atom of THF molecules [23]. As shown in Fig.1(d), the absorption maxima of AzoOH and COAzoOH in THF solution only

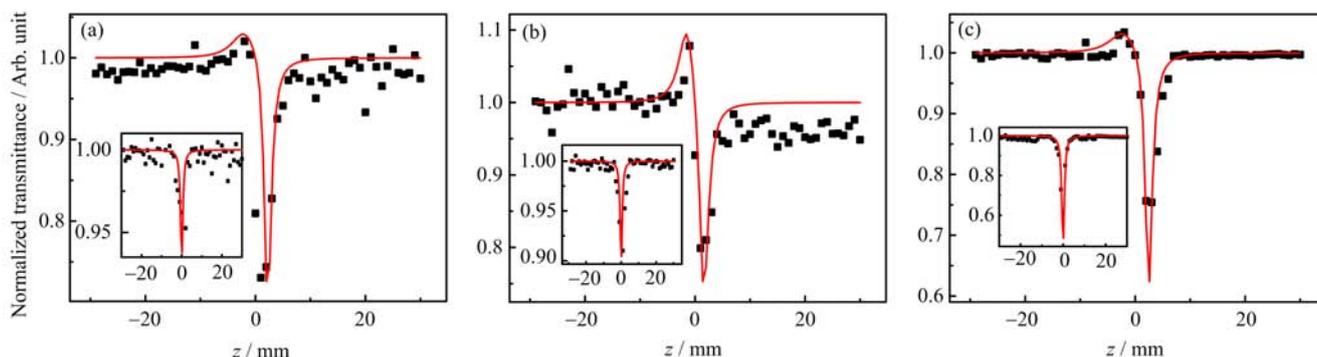


FIG. 2 Closed aperture Z-scan experimental curves under 532 nm laser for (a) AzoOH, (b) COAzoOH, (c) NAzoOH in CHCl_3 solution. Insert are the open aperture Z-scan experimental curves for the corresponding azobenzene compounds.

red shift about 3.0–3.8 nm compared to those in CHCl_3 solution, which are smaller than those for NAzoOH. The absorption maxima of NAzoOH in THF solution show a red shift of 8 nm compared to that in CHCl_3 solution. It may be attributed to a decreased π - π^* transition energy caused by the formation of hydrogen bond, resulting in an efficient charge transfer between the electron-donating group in one benzene ring and the electron-withdrawing group in the other.

B. Nonlinear optical properties

The nonlinear absorption coefficients of these compounds are measured by Z-scan technique. In our experiment, the samples are moved along the direction of laser beam around the focus ($z=0$) forward or backward. The transmittance is simultaneously recorded by a joule meter with and without an aperture in the far field of lens as the function of sample position. It can be seen from Fig.2 that AzoOH and COzoOH have hardly linear absorbance at 532 nm, which promises low intensity loss and little temperature change by photon absorption during the NLO measurements. But NAzoOH has a little linear absorbance at 532 nm. In order to avoid the accumulative intensity loss and heating effect by linear absorption of NAzoOH, all the azobenzene compounds are measured with a low pulse width (16 ns) and a repetition rate of 10 Hz.

The results of Z-scan with and without an aperture showed that all the azobenzene compounds have both nonlinear absorption and nonlinear refraction. The nonlinear absorption coefficient β can be determined through the fitting of the experimental data based on Eq.(1) and Eq.(2):

$$T(z, S = 1) \approx 1 - \frac{\beta I_0 L_{\text{eff}}}{2\sqrt{2}(1 + z^2/z_0^2)} \quad (1)$$

$$\beta = 2^{3/2} \frac{1 - T(z = 0, S = 1)}{I_0 L_{\text{eff}}} \quad (2)$$

Here β is the nonlinear absorption coefficient, $I_0(t)$

is the intensity of laser beam at focus ($z=0$), $L_{\text{eff}}=(1-e^{-\alpha L})/\alpha$ is the effective thickness with α_0 being the linear absorption coefficient and L being the sample thickness, z_0 is the diffraction length of the beam, and z is the sample position.

The nonlinear refractive component of the sample is obtained by dividing the normalized Z-scan measured under a closed aperture configuration by the normalized Z-scan data obtained under the open-aperture configuration. Thus, the refractive curves are obtained. The third-order nonlinear refractive index, γ , can be got by fitting the refractive curves using Eq.(3):

$$\gamma I_0 = \frac{\Delta T_{P-V}}{0.406(1-S)^{0.25} k L_{\text{eff}}} \quad (3)$$

where ΔT_{P-V} is the measured peak-valley transmittance difference from a normalized Z-scan curve, I_0 is the on-axis peak intensity at the focus ($z=0$), s is the transmittance of the aperture ahead the detector in absence of a sample.

The open-aperture and closed-aperture experimental Z-scan curves of azobenzene compounds with different substituents in THF solution are shown in Fig.2. The normalized energy transmittance of hydroxyl-azobenzene compounds carrying different substituents decreases at the focus indicating a reverse saturated absorption (RSA) ($\beta > 0$). The peak-valley pattern of the normalized transmittance curves indicate that each of the hydroxyl-azobenzene compounds has a negative sign for the nonlinear refraction ($\gamma < 0$) and exhibits a strong self-defocusing behavior. As shown in Fig.3, the open-aperture and closed-aperture experimental Z-scan curves of azobenzene compounds in CHCl_3 solution exhibit the same characteristics. The third-order NLO coefficients of hydroxyl-azobenzene compounds are calculated by equations and listed in Table I.

By varying the substituents of the azobenzene compounds, the effect of the intermolecular interaction between the chromophores and their matrices could be studied systematically. NAzoOH has the largest coefficients of β and γ values in both THF and

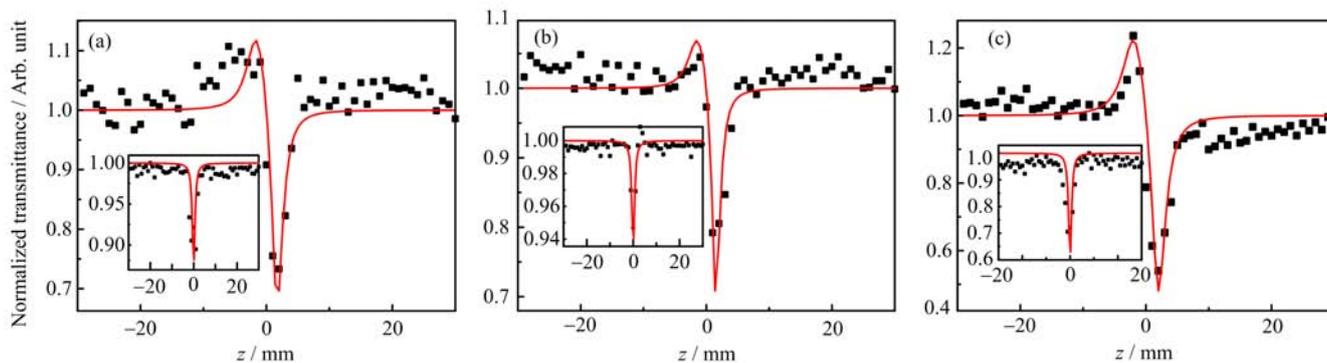


FIG. 3 Closed aperture Z-scan experimental curves under 532 nm laser for (a) AzoOH, (b) COAzoOH, (c) NAzoOH in THF solution. Insert are the open aperture Z-scan experimental curves for the corresponding azobenzene compounds.

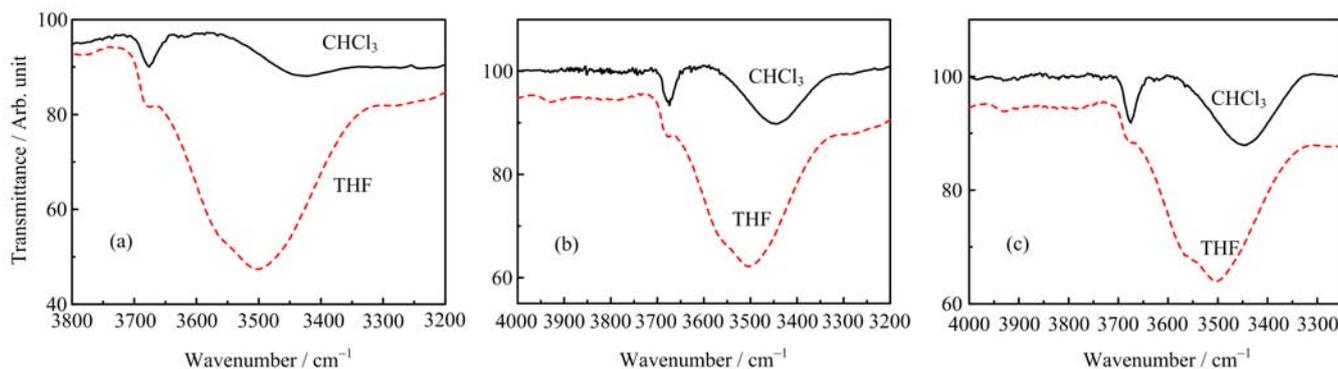


FIG. 4 FTIR spectra of (a) AzoOH, (b) COAzoOH, and (c) NAzoOH in THF and CHCl_3 solution.

CHCl_3 solution compared to AzoOH and COAzoOH. It may be due to a push-pull (D- π -A) electron system formed by the electron withdrawing nitro-substituent with hydroxyl-group in both extremities of azobenzene, which enhances the delocalization effect and is favorable to increase the NLO effect. The β and γ for NAzoOH in THF solution are $20.49 \times 10^{-9} \text{ cm}^2/\text{W}$ and $-15.07 \times 10^{-15} \text{ cm}^2/\text{W}$, respectively, and the corresponding data in CHCl_3 solution is $11.60 \times 10^{-9} \text{ cm}^2/\text{W}$ and $-7.26 \times 10^{-15} \text{ cm}^2/\text{W}$. It is worthy to mention that the nonlinear absorption coefficient β and the nonlinear refractive index γ of NAzoOH in THF solution are higher than those in CHCl_3 solution. Same phenomena are observed for AzoOH and COAzoOH. We attribute this difference to the hydrogen bond formation between the hydroxyl (OH) group of azobenzene chromophore and the oxygen atom of the THF molecule. This bonding reduces the possibility for formation of dimerization of hydroxyl azobenzene through hydrogen bonding interaction ($\text{O}-\text{H} \cdots \text{N}$) which would result in, as in the case of chloroform, an increase of the molecule aggregation and a decrease of the electron donating strength of the hydroxyl group.

It can also be seen from Table I that β and γ of COAzoOH do not increase as much as those of AzoOH and

TABLE I Nonlinear absorption index β and nonlinear refraction index γ of azobenzene compounds in THF solution and CHCl_3 solution.

Sample	$\beta/(10^{-9} \text{ cm}^2/\text{W})$		$\gamma/(10^{-15} \text{ cm}^2/\text{W})$	
	THF	CHCl_3	THF	CHCl_3
AzoOH	7.13	4.02	-7.97	-5.30
COAzoOH	3.75	3.64	-5.55	-5.21
NAzoOH	20.49	11.60	-15.07	-7.26

NAzoOH. It is mainly because that the repulsive interaction between methoxyl group and hydroxyl group strengthen with the increase of donating ability of hydroxyl group caused by the formation of hydrogen bond, which restricts the increase of nonlinear coefficient of COAzoOH.

To confirm the existence of hydrogen bonds, we performed infrared absorption measurements of azobenzene compounds (Fig.4). All azobenzene compounds have strong characteristic absorption band in the spectral region ($3300\text{--}3800 \text{ cm}^{-1}$), attributed to the hydroxyl vibrations. Thus, any change in the FT-IR spectra in this region is attributed to the change in the



FIG. 5 Schematic model for hydrogen bond formation in (a) CHCl₃ and (b) THF.

chemical environments of the hydroxyl groups, especially the formation of hydrogen bonds. For a 1 mmol/L solution in chloroform, the sharp band at 3695 cm⁻¹ is assigned to the free OH groups. The broad band at 3420 cm⁻¹ is a strong indication of hydrogen bonding. It can be due to the formation of dimerization of hydroxyl azobenzene through hydrogen bonding between azobenzene molecules which may cause aggregation (Fig.5). For a 1 mmol/L solution in THF, the 3695 cm⁻¹ peak decreases significantly indicating the decrease of free OH groups. The 3420 cm⁻¹ band shifts to longer wave numbers (3500 cm⁻¹) indicating that the -OH groups now form hydrogen bonds with the oxygen atom of the THF molecules, the donating strength increases and molecule aggregation greatly reduces. Moreover, it induces more effective π -conjugation in the compounds and regular arrangement of molecules leading to the enhancement of NLO effect.

IV. CONCLUSION

Three kinds of 4-hydroxyl azobenzene compounds with different substituent in the para-position were synthesized and characterized. Their third-order nonlinear optical properties were investigated systematically using Z-scan technique with a wavelength of 532 nm. The results showed that the formation of hydrogen bonds between the hydroxyl group of azobenzene compounds and the oxygen atom of the THF molecules strongly reduced the formation of aggregates and induced more effective π -conjugation in the compounds, resulting in larger coefficients of the nonlinear absorption (β) and nonlinear refraction (γ) values.

V. ACKNOWLEDGMENTS

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