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Third Order Nonlinear Optical Properties of Some Organic Nitroxyls

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Abstract. The degenerate four-wave mixing experiments have been performed in the dichloromethane solutions of 2,2,6,6-tetramethyl-pipridine-4-ol-N-oxyl p-hydroxybenzaldehyde oxime benzoic ester (TPOHBOBE and bis-(TPOHBOBE) cobalt (II), respectively. The result is in agreement with the theoretical prediction of γ depending on the molecular chain length l as l^5. A large off-resonant third order hyperpolarizability γ_{xxxx} of 1.3×10^{-30} esu for bis-(TPOHBOBE) cobalt (II) was obtained. The corresponding value of the third order nonlinear optical susceptibility $\chi^{(3)}_{xxxx}$ for its solid state is estimated to be 7.8×10^{-9} esu.

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Recently, organic materials have become the forefront of research in nonlinear optics because of their potential applications in optical signal processing, optical computing, dynamic holography and various electro-optical devices [1, 2]. Polydiacetylenes [3], polyacetylenes [4], azodyes [5], organic charge-transfer complex [6], and other have been reported to possess large and fast nonlinear optical response. Their nonlinearity is associated with the π-electron system. The third order hyperpolarizability γ is theoretically predicted [7] to have a relation with conjugation length l as $\gamma \propto l^5$. In this letter, we will report the nonlinear optical investigation on some nitroxyls with π-electron system through a degenerate four wave mixing (DFWM) experiment. The results show that the off-resonant third order hyperpolarizability γ is large and the relation of $\gamma \propto l^5$ is experimentally demonstrated.

The nitroxyls studied were 2,2,6,6-tetramethyl-pipridine-4-ol-N-oxyl p-hydroxybenzaldehyde oxime benzoic ester (TPOHBOBE) and bis-(TPOHBOBE) cobalt (II). Their molecular structures are shown in Fig. 1. It is evident that the conjugation length of bis-(TPOHBOBE) cobalt (II) is twice that of TPOHBOBE. Both were disolved in dichromethane (DCM). The absorption spectra are given in Fig. 2, which indicate that there is no absorption at 530 nm.

The experimental arrangement was a standard DFWM geometry similar to our previous work [5, 6]. Second harmonic generation of a 10 Hz YAG laser (Datachrom-5000, Quantel, pulse duration is 10 ns) was employed as the light source. Three laser beams: a forward pump beam, a backward pump beam and a probe beam were adjusted to overlap in time and spatially in the nonlinear medium, which was filled in a 1.0 cm cell. The intensities of the three beams were nearly equal. The probe beam and the forward pump beam formed an angle of 1° in the sample. In a DFWM experiment the measured quantity is the intensity of phase conjugate signal (I_4), which is proportional to the square of the third order nonlinear optical susceptibility $\chi^{(3)}$ of the nonlinear medium [8]. Thus $\chi^{(3)}$ can be elucidated. In this experiment, all the optical beams were polarized in the

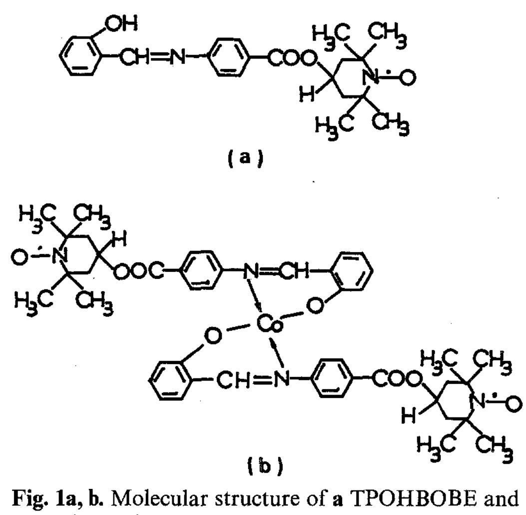

Fig. 1a, b. Molecular structure of **a** TPOHBOBE and **b** bis-(TPOHBOBE) cobalt (II)

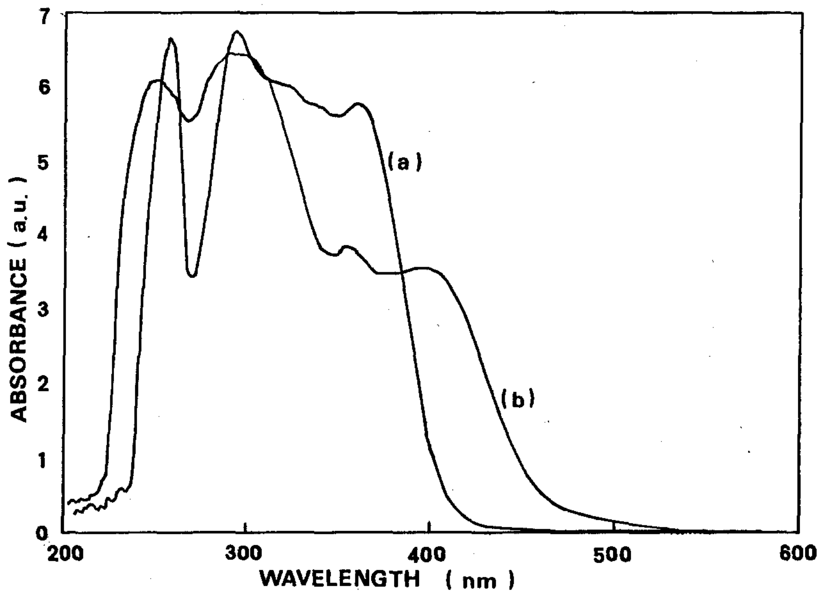

Fig. 2a, b. Absorption spectra of **a** TPOHBOBE and **b** bis-(TPOHBOBE) cobalt (II)

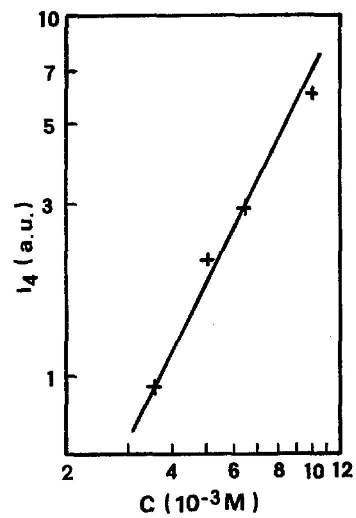

Fig. 3. Solution concentration dependence of I_4 for TPOHBOBE ($I_1 = I_2 = I_3 = 8\,\mathrm{MW/cm^2}$)

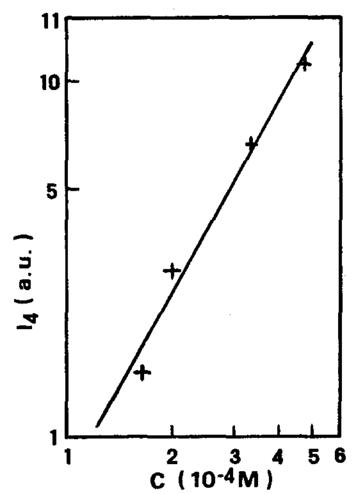

Fig. 4. Solution concentration dependence of I_4 for bis-(TPOHBOBE) cobalt (II) ($I_1 = I_2 = I_3 = 8\,\mathrm{MW/cm^2}$)

x direction. For each sample, $\chi^{(3)}_{xxxx}$ was determined from the measured intensity of the phase conjugate signal for the sample (I_{4S}) relative to that obtained for liquid CS_2 (I_{4R}) under the same excitation conditions. The $\chi^{(3)}_{xxxx}$ of the sample is determined by the expression [5, 6]

$$\chi^{(3)}_{xxxx} = (I_{4S}/I_{4R})^{1/2}(n_S/n_R)^2\chi^{(3)}_{xxxx},$$

where n_S and n_R are the linear refractive index of the sample solution and CS_2, respectively. A value of $\chi^{(3)}_{xxxxR} = 4.0 \times 10^{-13}$ esu for CS_2 at 530 nm is employed [9].

The cubic dependence of the phase conjugate signal (averaged over 1000 pulses) on the laser beam intensity for both two sample solutions is determined to show a third order nonlinear optical process. The concentration dependence of the intensity of the phase conjugate signal is shown in Figs. 3 and 4 for TPOHBOBE and bis-(TPOHBOBE) cobalt (II), respectively. A square dependence is found. Therefore, the tensor $\chi^{(3)}_{xxxx}$ is proportional to the concentration which in turn allows the extraction of the third order hyperpolarizability γ_{xxxx} via [10]

$$\gamma_{xxxx} = \chi^{(3)}_{xxxx}/N_c L_c .$$

Here L_c is the local field correction factor assumed to be the same as that of the pure solvent DCM and equal to $[(n^2+2)/3]^4$, in which $n = 1.4$ is the refractive index of DCM. N_c is the molecular number density of the samples in the solutions.

From the measured $\chi^{(3)}_{xxxx} = 7.1 \times 10^{-13}$ esu for TPOHBOBE at 5×10^{-3} M and $\chi^{(3)}_{xxxx} = 4.8 \times 10^{-13}$ esu for bis-(TPOHBOBE) cobalt (II) at 2×10^{-4} M, γ_{xxxx} can be deduced to be 4.6×10^{-32} esu for TPOHBOBE and 1.3×10^{-30} esu for bis-(TPOHBOBE) cobalt (II). The value of γ_{xxxx} for bis-(TPOHBOBE) cobalt (II) is 2^5 of that for TPOHBOBE, which is in agreement with the theoretical prediction [7] of $\gamma \propto l^5$.

In conclusion, the third order nonlinear optical properties of some nitroxyls were first investigated. Large off-resonant third order hyperpolarizability was obtained. The value of $\chi^{(3)}_{xxxx}$ for the solid samples is estimated to be 5.6×10^{-10} esu for TPOHBOBE and 7.8×10^{-9} esu for bis-(TPOHBOBE) cobalt (II) through an estimated solid density of $1.5\, g/cm^3$ and refractive index of 1.6 for both samples. Besides, the relation between γ and conjugation length l is experimentally demonstrated as $\gamma \propto l^5$.

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