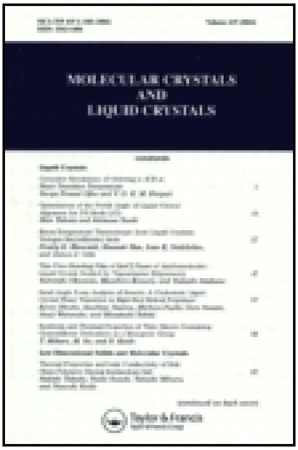

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Determination of Nonlinear Hyperpolarizability of Bent-Shaped Molecules using Hyper-Rayleigh Scattering

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Determination of Nonlinear Hyperpolarizability of Bent-Shaped Molecules using Hyper-Rayleigh Scattering

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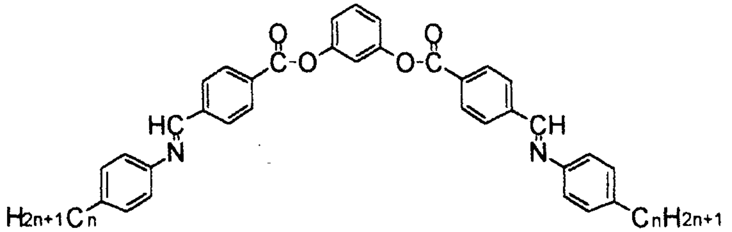
The first-order hyperpolarizability β was determined for bent-shaped molecules P-8-PIMB and P-8-O-PIMB using the Hyper Rayleigh scattering method. βs of these materials were found to be relatively large, about 30×10^{-30} esu. These results are consistent with the second-harmonic generation experiments performed in their liquid crystalline phases.

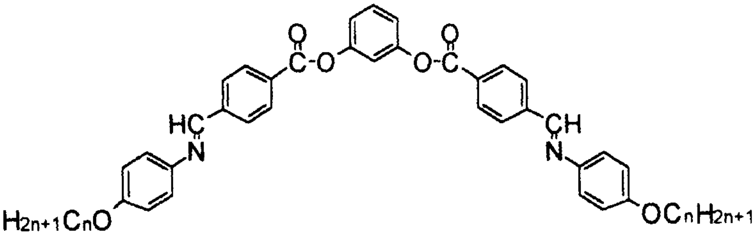
Keywords: bent-shaped molecule; achiral molecule; first-order hyperpolarizability; second harmonic generation; hyper-Rayleigh scattering

INTRODUCTION

Molecular chirality has been regarded as important for ferro- or antiferroelectricity in smectic liquid crystals. But the use of chirality is not necessary to bring about ferro- or antiferroelectricity. Actually it has been proposed that, ferro- or antiferroelectricity can be realized, even in smectic phases, if molecules are packed with C_{2v} symmetry[1-3]. Niori[4] synthesized several types of achiral molecules which have C_{2v} symmetry. Among them, molecules which are bent in the middle of mesogen, are included. There are two types of bent-shaped molecules, one has alkyl chains in its ends (P-*n*-PIMB), and another one has alkoxy chains (P-*n*-O-PIMB), as shown in Fig. 1, where *n* is a carbon number of the end chains. In 1996, ferroelectricity was first observed in smectic layer of the bent-shaped molecules[5].



(a)P-*n*-PIMB



(b)P-*n*-O-PIMB

FIGURE 1 The chemical structures of bent-shaped molecules.

Relatively high nonlinear optical activity was reported in bulk phases consisting of these bent-shape molecules[6]. In spite of the similar structures, P-8-O-PIMB and P-8-PIMB give different second-harmonic generation (SHG) behavior. In this paper, the first-order hyperpolarizability β of these molecules was measured by means of the hyper-Rayleigh scattering (HRS)[7,8] to examine the molecular origin of the different SHG behavior. The HRS technique allows us to determine the hyperpolarizability β in isotropic solution. In this technique, scattered SH light caused by orientational fluctuations of molecules in solution is detected.

The HRS intensity $I_{2\omega}$ is proportional to both a square of the incident light intensity I_ω and a square of the hyperpolarizability β of a molecule. The total intensity of the HRS light $S_{2\omega}$ from a solution is given as a summation of HRS light from molecules in the solution as follows:

$$S_{2\omega} = GB^2 I_\omega^2 = G\Sigma_s N_s \beta_s^2 I_\omega^2 \qquad (1)$$

where G is a proportional constant containing scattering geometrical constants and local field corrections at optical frequencies, B is the macroscopic second-order susceptibilities, and N is a number density of the solution components. For a two-component solution, $S_{2\omega}$ is given as

$$S_{2\omega} = G\,(N_{solvent}\beta^2_{solvent} + N_{solute}\beta^2_{solute})I_\omega^2 \qquad (2)$$

The relation shown in eq.(1) means that there is a linear dependence of the SHG intensity on the concentration of sample solute in sufficient low concentration solution, in which solvent density can be regarded as constant. From the intersection $a = GN_{solvent}\beta^2_{solvent}I_\omega^2$ and the slope $b = G\beta^2_{solute}I_\omega^2$ of the linear relation in the experimental plot of SHG intensity against concentration, the hyperpolarizerbility β is calculated using eq.(2).

$$\beta_{solute} = \beta_{solvent}\sqrt{\frac{bN_{solvent}}{a}} \qquad (3)$$

The hyperpolarizability of solvent $\beta_{solvent}$ value is taken as an internal reference (Internal reference method). For several solvents, the hyperpolarizability βs have been reported previously[7-9].

Experimental

Optical Setup

The optical setup for the HRS measurement is schematically shown in Fig.2. The laser system used in this measurement is a flash lamp pumped 1064 nm Nd:YAG laser (BM Industries, model 501 DNS 4/100). This laser provides pulses with a repetition of 100 Hz. Higher repetition and lower intensity pulses are more convenient for the HRS measurement. Since high intensity beam easily makes samples damaged, sufficiently low intensity laser pulses (less than 17.5 mJ/pulse) were used and signal accumulation was made for a long time. The input beam power was controlled by a polarizer (Pol) and a Fresnel romb (FR). A visible-cut filter was placed just before a lens to prevent any SH light entering the sample cell. The laser beam was focused into the sample cell with a lens (f = 100 mm). A cylindrical cubbette was used as a sample cell. It was about 80 mm height and 30 mm diameter. If the diameter is so small, the cubbette surface is close to the focal point and might be damaged. Conversely, if the size is large, so much sample solution is required. The SH scattered light were collected by a fiber-bundle near the scattering center. The light was led to a monochromator, and the signals were detected by a photomultiplier tube (PMT; Hamamatsu, R955). The signals were amplified by a high speed amplifier (AMP), accumulated by a boxcar integrator and calculated with a computer. The signal from a photodiode (PD) was used for triggering the boxcar.

Samples

The samples used were P-8-PIMB and P-8-O-PIMB shown in Fig. 1. These sample molecules were dessolved in chloroform at concentrations of 20.0×10^{18} number density/ml. The concentrations were chosen so that the signal could be observed in the minimum concentration when the solution was diluted. These values depend on the cell size and nonlinearity of each sample.

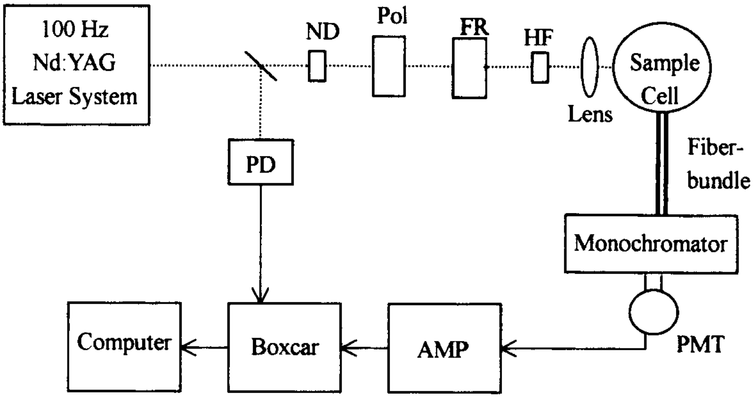
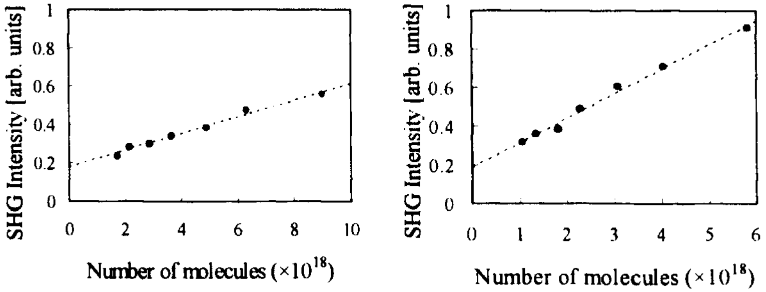


FIGURE 2 Experimental setup for HRS measurement. The components are denoted by; FR: Fresnel rhomb (λ/4); BS: beam splitter; PD: photodiode; ND: neutral density filter; Pol: polarizer; HF: high-pass filter; PMT: photomultiplier tube ; AMP: high speed amplifier

Results and Discussion

SHG intensity is plotted as a function of the number of molecules in Fig.3. Good linear dependence of the intensity on the concentration can be seen in both the compounds. In order to confirm that the SHG signal truly originates from HRS but not from the other sources like fluorescence, a spectrum of the signal was measured. The contribution of fluorescence could cause unrealistic β value[10]. Fortunately, the result shown in Fig. 4 exhibits a sharp Lorentzian peak[11] at 532 nm, clearly indicating that undesirable optical signal is negligible.

Table 1 shows the hyperpolarizability β determined by the experimental results and eq.(2) with a previous data of β (chloroform) = -0.49×10^{-30} esu[12]. The β values of P-8-O-PIMB and P-8-PIMB are about the same.



(a)P-8-PIMB (b) P-8-O-PIMB

FIGURE 3 HRS signal (filled circles) and a linear fitted line in (a) P-8-PIMB and (b) P-8-O-PIMB.

TABLE 1 Hyper polerizability βs determined by HRS measurement

sample	hyperpolarizability β(esu)
P-8-PIMB	22.7×10^{-30}
P-8-O-PIMB	35.3×10^{-30}

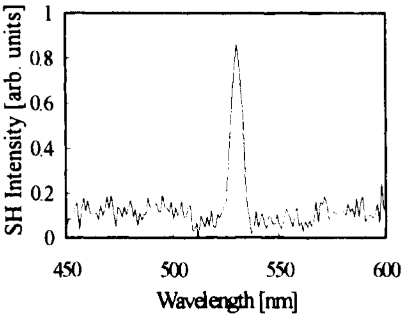


FIGURE 4 HRS spectrum in P-8-O-PIMB.

Conclusion

The HRS measurements have been carried out to determine and compare the β values of the two compounds P-8-PIMB and P-8-O-PIMB. It was found that β values of these materials are almost the same: about 30×10^{-30} esu.

References

[1] T. Sekine, T. Niori, M. Sone, J. Watanabe, S. Choi, Y. Takanishi and H. Takezoe, *Jpn. J. Appl. Phys.*, **36,** 6455 (1997).

[2] T. Sekine, Y. Takanishi, T. Niori, J. Watanabe and H. Takezoe, *Jpn. J. Appl. Phys.*, **36,** L1201 (1997).

[3] J. Watanabe, *EKISHO (in Japanese)*,2, **28** (1998).

[4] T. Niori, PhD Thesis (Tokyo Institute of Technology, 1997).

[5] T. Niori, T. Seine, J. Watanabe, T. Furukawa and H. Takezoe, *J. Mater Chem.*, **6,** 1231 (1996).

[6] S. Choi, Y. Kinoshita, B. Park, H. Takezoe, T. Niori and J. Watanabe, *Jpn. J. Appl. Phys.*, **37,** 3408 (1998).

[7] K. Clays and A. Persoons, *Phys. Rev. Lett.*, **66,** 2980 (1991).

[8] K. Clays and A. Persoons, *Rev. Sci. Instrum.*, **63,** 3285 (1992).

[9] K. Clays, A. Persoons and L. DeMaeyer, *Adv. Chem. Phys.*, **85,** 455 (1992).

[10] M.C. Flipse, R. de Jonge, R.H. Woudenburg, A.W. Marsman, C.A. Walree and L.W. Jenneskens, *Chem. Phys. Lett.*, **245,** 297 (1995).

[11] P.D. Maker, *Phys. Rev.*, **A1,** 923 (1970).

[12] F. Kazjar, I. Ledoux and J. Zyss, *Phys. Rev.*, **A36,** 6766 (1987).

[13] S. Kawauchi, private communication.