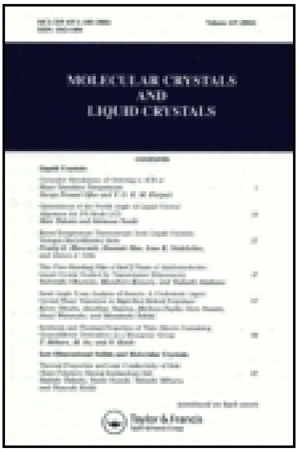

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SECOND-ORDER HYPERPOLARIZABILITIES OF ORGANIC IONIC SPECIES

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Abstract The second-order hyperpolarizabilities (β) of two categories of organic ionic species were evaluated by the hyper Rayleigh scattering method. The |β| of (dimethylamino)stilbazolium analogues in methanol with long cut-off wavelength more than 600 nm, which can be used for electro-optic modulation, were evaluated to be in the order of 10^{-27} esu using 1064 nm light as a fundamental beam. Aromatic sulfonates in the second category were found to have comparatively large |β| values irrespective of short cut-off wavelength: In the case of sodium *p*-toluenesulfonate with cut-off of 280 nm, |β| in methanol was 2.2×10^{-29} esu and was about two thirds of *p*-nitroaniline with cut-off of 445 nm.

INTRODUCTION

Organic ionic crystals, investigated first by Meredith[1] and thereafter by our group[2-6] as well as Marder *et al.*,[7-9] are an interesting class of materials for second-order nonlinear optics, because ionic interaction conquer dipole interaction and numerous derivatives with different crystal structures can be prepared simply by changing the counter ions. Along this line of approach, it has been found that stilbazolium derivatives with *p*-toluenesulfonate as a counter anion tend to crystallize into noncentrosymmetric structures due to a chiral handle character of the anion. When the laser of 1064 nm was used as the fundamental beam, the coefficient for second-harmonic generation d_{11} of about 500 pm/V was achieved with hydroxystilbazolium *p*-toluenesulfonate[4] (HO-1 in FIGURE 1). The electro-optic (EO) coefficient r_{11} of about 400 pm/V was attained with dimethylaminostilbazolium *p*-toluenesulfonate[9] (DMA-1 in FIGURE 1) using 820 nm laser beam. In order to obtain ionic crystals with high efficiencies by molecular and crystal engineering, the second-order hyperpolarizabilities (β) of these ionic species should be first clarified. Thus, in our previous study,[10] the |β| values in methanol of stilbazolium *p*-toluenesulfonates, with cut-off wavelengths shorter than 532 nm, have been figured out using a 1064 nm fundamental beam by the hyper Rayleigh scatting (HRS) method,[11-13] which was recently established as a new technique to determine |β| values.

This paper concerns with |β| values of organic ionic species for the two categories, one of which is for the EO modulation and the other is for SHG. For both applications, diode lasers are supposed to be used as fundamental beams. Thus, for the first category, (dimethylamino)-stilbazolium analogues with long cut-off wavelength more than 600 nm was investigated. The second one includes aromatic sulfonate derivatives without absorption in visible region. The |β| values of those ionic species were elucidated using the HRS methods.

EXPERIMENTAL

Ionic Compounds and Their Solutions

The chemical structures of the two categories of ions are summarized in FIGURE 1. The compounds DMA-1 and -2 were synthesized by the similar procedure described previously.[5] Sodium salts of aromatic sulfonates were purchased or prepared from corresponding aromatic sulfonic acid and sodium methoxide. All these compounds were recrystallized several times from methanol.

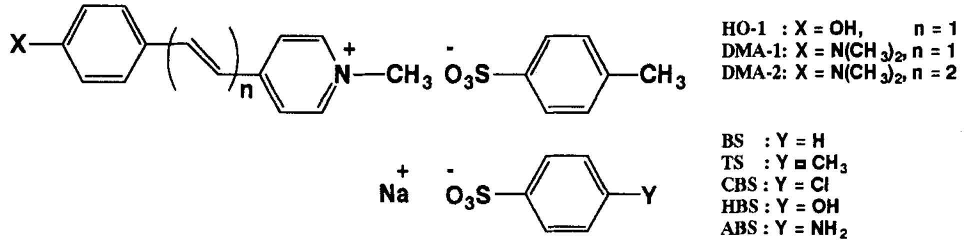

FIGURE 1 Chemical structures of ionic species.

The compounds were dissolved in methanol for the measurement of HRS and absorption spectra. Concentration of the solutions for HRS were 10^{-4} ~ 10^{-7} M for DMA derivatives, and 10^{-2} ~ 10^{-4} M for aromatic sulfonates, respectively. Absorption spectra were measured using about 10^{-5} M solutions, and the cut-off wavelength (λ_{co}) was determined by 99% transmittance of about 10^{-2} M solutions.

Evaluation of |β| Values Using the HRS Method

A Q-switched Nd:YAG laser operated at 1064 nm with 10 ns pulse width and about 10 mJ energy per pulse was used for the fundamental beam of HRS. The intensities of the incident and the second-order scattered light were monitored by the photodiode and photomultiplier, respectively. The scattered light was detected in the direction perpendicular to the incident beam. The relationship between the incident light intensity I_ω and the second-order scattered light intensity $I_{2\omega}$ for a two component system composed of a solute and a solvent can be expressed as

$$I_{2\omega} = GB^2 I_\omega^2 = G\left(N_{solute}\beta_{solute}^2 + N_{solvent}\beta_{solvent}^2\right)I_\omega^2, \tag{1}$$

where G depends upon the scattering geometry and contains the averages of the products of the direction cosines and the local-field corrections. N is the number density of the component. In low solute concentration, GB^2 can be expressed in a linear function of N_{solute}, i.e. $GB^2 = aN_{solute} + b$. From the slope a and the intercept b of the fitted linear function, $|\beta_{solute}|$ is calculated to be $(aN_{solvent} / b)^{1/2}|\beta_{solvent}|$. The $\beta_{solvent}$ value should be known in advance. When there is absorption at 2ω, the detectable scattering intensity $I_{2\omega}'$ is given by

$$I_{2\omega}' = I_{2\omega} e^{-\varepsilon(2\omega) l N_{solute}}, \tag{2}$$

where $\varepsilon(2\omega)$ is the absorption coefficient of solute at 2ω and l is an effective optical path length. Details of the experimental set-up and the calculation procedure of the |β| values have already been described in the previous papers.[10-13]

RESULTS AND DISCUSSION

(Dimethylamino)stilbazolium Derivatives

The absorption spectra of DMA-1 and -2 are shown in FIGURE 2 together with those of HO-1 studied previously. It is clear that DMA derivatives have absorption at the SH wavelength and the absorption coefficient at 532 nm of DMA-2 is larger. When the fundamental laser beam was put into methanol solutions of the DMA derivatives, fluorescence maybe due to two-photon absorption was observed in the transmitted direction of the incident beam. Though the cut-filter for Rayleigh scattering was available, there were no appropriate filters which had high transmittance for 532 nm and high absorption for other wavelengths. Thus, it was impossible to remove only the contribution from fluorescence by filters. Fortunately, however, no signals were detected when the filter with high absorption for wavelengths shorter than 540 nm was attached in front of the detector arranged perpendicular to the incident beam. In this condition, fluorescence light longer than 540 nm was able to pass the filters though the HRS light

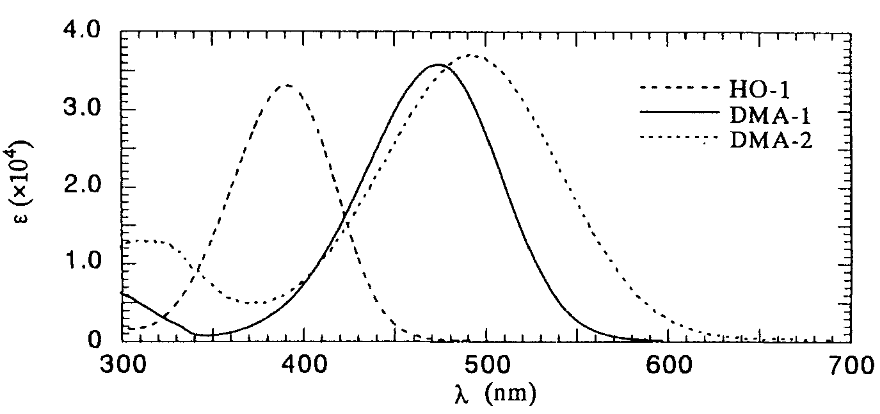

FIGURE 2 Absorption spectra of HO-1 and DMA-1 and -2 in methanol.

TABLE I Absorption data and |β| values of substituted stilbazolium analogues in methanol.

Compound*	λ_{co} (nm)	λ_{max} (nm)	ε_{max}	ε_{532}	|β| (× 10^{-27} esu)
HO-1	480	391	33000	0	0.39±0.08
DMA-1	601	474	35700	8100	2.2±0.5
DMA-2	633	492	37000	26500	5.5±1.0

* See FIGURE 1 for the chemical structures.

could not. This result clearly shows that there is no detectable contribution from fluorescence in the direction perpendicular to the incident beam in our measuring conditions.

Since DMA derivatives have absorption at 532 nm, eq. (2) was applied to evaluate the |β| values. Using the known value of $\beta_{solvent} = (0.69\pm0.07)\times10^{-30}$ esu for methanol,[11] we obtained |β| values in methanol of $(2.2\pm0.5)\times10^{-27}$ and $(5.5\pm1.0)\times10^{-27}$ esu for DMA-1 and -2, respectively. TABLE I summarizes the data of absorption and |β| for HO-1 and DMA-1 and -2. Because of the two-photon resonant effect, |β| of the DMA-1 and -2 are extremely enhanced up to 5.6 and 14 times of that of HO-1, respectively. Large difference in |β| of the DMA derivatives is mainly due to the magnitude of absorption coefficient at 532 nm (ε_{532}), which indicates a degree of two-photon resonance. The ε_{532} values of DMA-2 is about 3.3 times of that of DMA-1, and this roughly corresponds to the ratio $|\beta_{DMA\text{-}1}| / |\beta_{DMA\text{-}2}|$ of 2.5.

Aromatic Sulfonate Derivatives

The UV absorption spectra of aromatic sulfonates used in this study are shown in FIGURE 3. In the spectral region over 210 nm, all of these spectra show a large absorption band and small absorption bands extended to longer wavelength. Those bands can be classified into E_2 and B bands, respectively, according to the Braude's expression.[14] With the increase of electron donating ability of the substituent in the *para* position of benzenesulfonate, the B and E_2 bands of these derivatives shift 5~40 nm to longer wavelength compared with the original benzenesulfonate. The cut-off wavelength (λ_{co}) of these compounds is limited by the small absorption of the B bands. However, there are no electronic absorption over 320 nm even in the case of the longest wavelength.

For the aromatic sulfonate derivatives, the quadratic dependence in eq. (1) was always observed in the HRS measurement. The |β| values of the aromatic sulfonate derivatives are listed in TABLE II together with the data of their absorptions. Although these compounds have no absorption in visible region, they have comparatively large |β| values. For example, TS possesses a |β| value of $(22\pm6)\times10^{-30}$ esu which is about two thirds of that of *p*-nitroaniline with

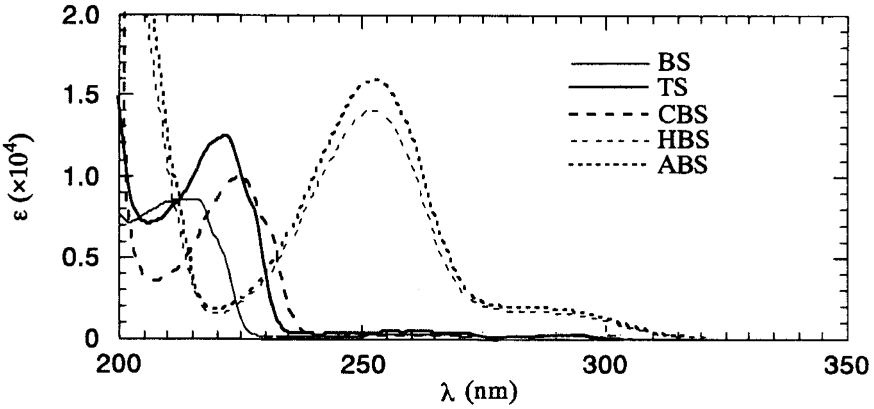

FIGURE 3 Absorption spectra of aromatic sulfonates in methanol.

TABLE II Absorption data and |β| values of aromatic sulfonate derivatives in methanol

Compound*	λ_{co} (nm)	λ_{max} (nm)**	ε_{max}**	|β| ($\times 10^{-30}$ esu)
BS	273	217	8600	15±4
TS	280	222	12300	22±6
CBS	298	226	9900	10±3
HBS	314	252	14100	17±4
ABS	317	253	15900	19±5

* See FIGURE 1 for the chemical structures.

** Data for E_2 band.

the cut-off wavelength of 445 nm. Since methyl *p*-toluenesulfonate, i.e. corresponding neutral methyl ester, shows only about half of the |β| value of TS, ionic structure seems to be advantageous to enhance β values.[15]

The substitution effect on |β| of those benzenesulfonates is complicated. In the case of substituted-stilbazolium derivatives including HO-1 studied previously,[10] a pyridinium ring is the electron withdrawing group. Thus, the absorption cut-off and maximum move to longer wavelengths when stronger electron donating group are attached to the phenyl ring. At the same time, the |β| values also increase except the halogen substituents. In the case of benzenesulfonates in this study, the similar tendency was observed only for absorption, i. e. substitution at the *para* position of benzenesulfonate causes absorption shift to longer wavelength. The |β| values of HBS and ABS with strong electron donor are not larger than those of TS with less electron donating group. Though sulfone and sulfonic acid's ester groups are generally considered as electron acceptors, sulfonate anion group seems to be less electron accepting because of minus charge in the group. Two opposite effects in sulfonate group, i.e. electron withdrawing ability and electrostatic repulsion to minus charge in the anion part, may play an important role to determine β values of this series of derivatives. In order to clarify these facts, further derivation of aromatic sulfonates and quantum chemical calculations are currently in progress.

CONCLUSION

The |β| values of (dimethylamino)stilbazolium analogues and aromatic sulfonates in methanol were evaluated by the HRS method. Because of the absorption at 532 nm, the |β| values of (dimethylamino)stilbazolium analogues become larger than 10^{-27} esu by resonance enhancement. Aromatic sulfonates were found to have comparatively large |β| values of $(1\sim2)\times10^{-29}$ esu irrespective of short cut-off wavelength within UV region. Though a pair of anions and cations are considered as one solute component in this study, main contribution of |β| in DMA and benzenesulfonate derivatives is from stilbazolium cation and sulfonate anion parts, respectively. Aromatic ions seem to be one of the most potential candidates for second-order optical nonlinearity.

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