

Styrylpyrylium Derivatives for Second-Order Nonlinear Optics

Kyoko Tsuji, Shuji Okada, Hidetoshi Oikawa, Hiro Matsuda,[†] and Hachiro Nakanishi
Institute for Chemical Reaction Science, Tohoku University, Sendai 980-8577
[†]*National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba 305-8565*

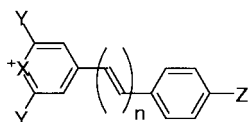
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The first hyperpolarizabilities (β) of styrylpyrylium derivatives were systematically investigated by hyper-Rayleigh scattering experiments and semiempirical calculation in relation to their absorption. They were found to be potential second-order nonlinear optical species covering the longer cutoff-wavelength range compared with the corresponding stilbazolium derivatives.

A variety of organic compounds have been studied to be used as high performance second-order nonlinear optical (NLO) materials.¹ Among them, some of the π -conjugated ionic species such as styrylpyridinium (stilbazolium) cations were found to have larger first hyperpolarizability (β) compared with the corresponding non-ionic species.² Especially, 1-methyl-4-(2-(4-(dimethylamino)phenyl)ethenyl)pyridinium *p*-toluenesulfonate (DAST)³ is considered to be one of the most promising organic crystals for second-order NLO devices because of its very large NLO susceptibility and electro-optic (EO) coefficient.⁴ Preparation of its high quality crystals and their process establishment are being important subjects to be studied.⁵

From the chemistry side, the enhancement of β at molecular level is still worth investigating because it directly connects with usage of lower power laser sources or miniaturization of devices. Thus, we have been studying stilbazolium analogues⁶ and those with extended π -conjugation systems.⁷ In the present study, we focused on styrylpyrylium derivatives, which have similar electronic structure to stilbazolium derivatives. Although a few pyrylium derivatives were recently published for their NLO properties,⁸ systematic study on their β values of styrylpyryliums in connection with absorption has not been reported.

Chemical structures of styrylpyrylium and stilbazolium derivatives studied are shown in Figure 1. Among them, **1a–1f** and **1f(2)** as perchlorate salts were successfully obtained referring the literature⁹ by reacting 2,6-di(*t*-butyl)-4-methylpyrylium perchlorate¹⁰ with 4-substituted benzaldehyde or cinnamaldehyde. Stilbazoliums **2a–2f** and **2f(2)–2f(5)** in iodide form have already been synthesized in the previous studies.⁷



1a–1f : X=O, Y=C(CH₃)₃, n=1

2a–2f : X=NCH₃, Y=H, n=1

(**a** : Z=CN, **b** : Z=Cl, **c** : Z=H,
d : Z=CH₃, **e** : Z=OCH₃, **f** : Z=N(CH₃)₂)

1f(n) : X=O, Y=C(CH₃)₃, Z=N(CH₃)₂

2f(n) : X=NCH₃, Y=H, Z=N(CH₃)₂

Figure 1. Chemical structures of the ionic species studied.

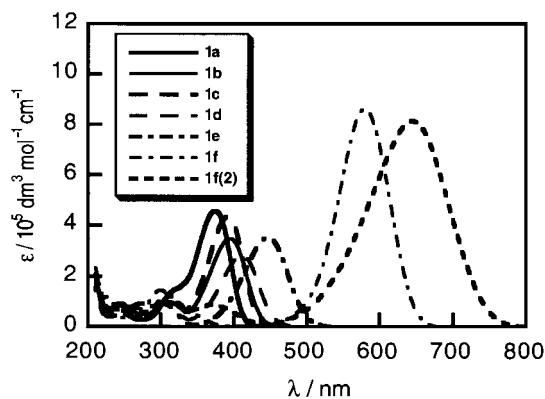


Figure 2. Absorption spectra of styrylpyrylium derivatives in acetonitrile.

Although **1a–1f** and **1f(2)** were stable in the crystalline state, those in methanol were not so stable and their optical properties were evaluated in acetonitrile. Figure 2 shows visible absorption spectra of **1a–1f** and **1f(2)**. For the same substituent Z, the longest absorption maximum wavelength (λ_{max}) of a styrylpyrylium derivative is longer than that of the corresponding stilbazolium derivative. For example, λ_{max} of **1f** is 579 nm, while that of **2f** is 471 nm. Molar extinction coefficient at λ_{max} (ϵ_{max}) of **1f** is quite large, i.e. 86300 dm³ mol⁻¹ cm⁻¹, which is more than twice of that of **2f**. According to the two-level model,¹¹ β value is proportional to $\Delta\mu_{eg}$, f and E_{eg}^{-3} , where $\Delta\mu_{eg}$ is dipole moment difference between the ground and excited states, f is oscillator strength, and E_{eg} is excitation energy. Since f and E_{eg} are roughly proportional to ϵ_{max} and λ_{max}^{-1} , respectively, β values of styrylpyrylium derivatives were expected to be larger than those of the corresponding stilbazolium derivatives.

Among the styrylpyrylium derivatives synthesized, the β values of **1a–1d** were evaluated for their acetonitrile solutions (10^{-4} – 10^{-2} mol dm⁻³) by the hyper-Rayleigh scattering (HRS) method¹² at 1064 nm. Since this series of compounds show fluorescence, reliable β values can be obtained only from these compounds, when an Nd:YAG laser is used.¹³ *p*-Nitroaniline in acetonitrile ($\beta = 29.2 \times 10^{-30}$ esu [1.22×10^{-38} m⁴ V⁻¹] at 1064 nm)¹⁴ was used as an external standard.¹⁵ The obtained β values were corrected into β at zero frequency ($\beta_{0,expt}$) according to the two-level model. For comparison, $\beta_{0,expt}$ values of **2c** and **2d** in acetonitrile were also evaluated. Figure 3 shows the relationship between λ_{max} and $\beta_{0,expt}$ of these compounds. Between the compounds with the same substituent Z, the $\beta_{0,expt}$ values of styrylpyryliums became larger than those of stilbazoliums.

Since the β values of styrylpyryliums with strong donor substituents or those with extended π -conjugation by increasing double-bond number between two aromatic rings were not obtained by the HRS method at 1064 nm, the β values at zero frequency in

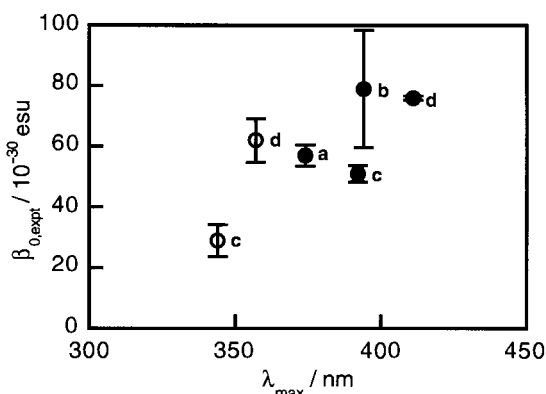


Figure 3. The relationship between λ_{max} and $\beta_{0,expt.}$. Closed and open circles correspond to styrylpyrylium **1** and stilbazolium **2**, respectively. Alphabetical symbols should be referred to Figure 1.

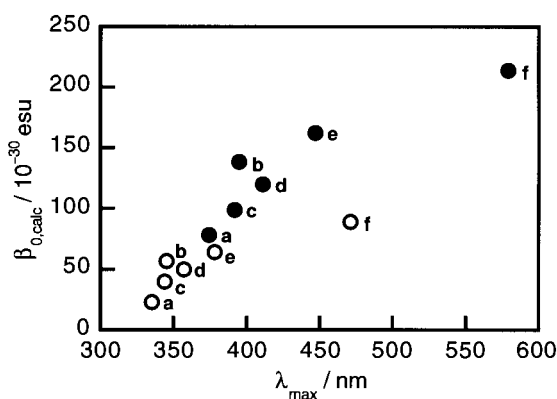


Figure 4. The relationship between λ_{max} and $\beta_{0,calc.}$. Closed and open circles correspond to styrylpyrylium **1** and stilbazolium **2**, respectively. Alphabetical symbols should be referred to Figure 1.

acetonitrile ($\beta_{0,calc.}$) were calculated by the semiempirical method of MOPAC94 PM3/COSMO (CACHe ver. 4.1.1). Figure 4 summarizes the relationship between λ_{max} and $\beta_{0,calc.}$ for **1a–1f** and **2a–2f**. The tendency of $\beta_{0,calc.}$ increasing with λ_{max} is similar between styrylpyrylium and stilbazolium derivatives. Thus, from these series of compounds, we can select a proper NLO species depending on using laser wavelength which should not overlapped with its absorption. Similar to the experimental results, larger β values were obtained for styrylpyrylium derivatives compared with the corresponding stilbazoliums with the same substituent Z.

In the case of stilbazoliums, enhancement of β values was theoretically expected by increasing double-bond number between pyridinium and benzene rings. Accordingly, similar design was considered for styrylpyryliums and $\beta_{0,calc.}$ values were obtained for **1f** and **1f(2)–1f(5)** in comparison with those for **2f** and **2f(2)–2f(5)** as shown in Figure 5. When compared between the compounds possessing same π -conjugation length, styrylpyryliums seem to be more advantageous for enhancement of β . For EO devices, the beam for telecommunication in 1.3 μm or 1.5 μm region could be directly used and absorption cutoff of materials used may extend up to near IR wavelength region. Thus, styrylpyrylium analogues seemed to be more favorable

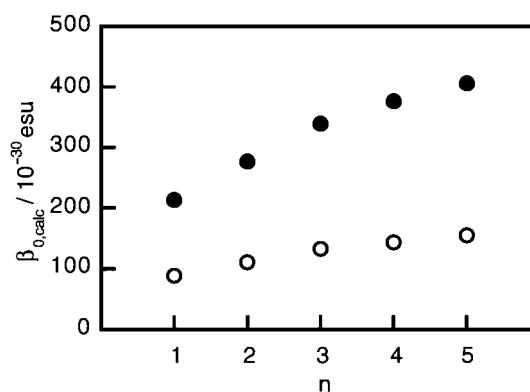


Figure 5. The relationship between the double-bond number n in Figure 1 and $\beta_{0,calc.}$. Closed and open circles correspond to styrylpyrylium **1f(n)** and stilbazolium **2f(n)**, respectively.

than stilbazolium derivatives for EO applications.

In conclusion, styrylpyrylium derivatives were found to be potential NLO species to have larger β than the corresponding stilbazolium analogues and may be good candidates for EO materials. Further studies on β evaluation of the species with absorption cutoff-wavelength longer than 532 nm and counter anion exchange for possessing macroscopic non-centrosymmetric crystal structures are in progress.

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