

# Synthesis and Properties of Novel Stilbazolium Analogues as Second-Order Nonlinear Optical Chromophores

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This study synthesized a series of methoxystilbazolium analogues with  $\pi$ -conjugation extended by attaching a fused aromatic ring, i.e., 6-styrylisoquinolinium and 4-[2-(2-naphthyl)ethenyl]pyridinium derivatives with methoxy substituents. We evaluated their transition energies ( $E_{\text{eg}}$ s) and second-order hyperpolarizabilities ( $\beta$ s) experimentally using their absorption spectra and a hyper-Rayleigh scattering measurement, respectively. Subsequently, we calculated  $\beta$ s using the MOPAC PM3 method. These values were compared with those of 4-[4-(4-methoxyphenyl)-1,3-butadienyl]pyridinium derivative, which is a stilbazolium analogue with  $\pi$ -conjugation that is simply extended by an increase of the double-bond number between two aromatic rings. This study clarified that the fused-ring systems possess large  $\beta$ s, irrespective of their relatively short absorption wavelengths, compared to the double-bond elongation system.

Organic materials have been extensively investigated concerning their large nonlinear optical (NLO) properties and ultrafast response times compared with inorganic materials and semiconductors. Those special characteristics are attributable to their  $\pi$ -electron systems.<sup>1</sup> Their magnitude of second-order optical nonlinearities is indicated by a second-order hyperpolarizability ( $\beta$ ) at the molecular level and a second-order NLO susceptibility ( $\chi^{(2)}$ ) at the molecular aggregate level. To obtain materials with a large  $\chi^{(2)}$ , their component molecules should have a large  $\beta$  value and be aligned in a noncentrosymmetric orientation. The  $\beta$  value of molecules can be estimated using various quantum chemical calculations. The  $\beta$  value can also be evaluated experimentally using the electric-field-induced second-harmonic generation (EFISH) method<sup>2</sup> or the hyper-Rayleigh scattering (HRS) method.<sup>3</sup> The HRS method is especially effective for  $\beta$ -value evaluation of ionic and non-dipolar species. Although some differences exist

between the calculated and experimental  $\beta$  values, the relative order of the values shows good agreement. The microscopic  $\beta$  value of organic molecules can be approximately described by the two-level model,<sup>4</sup> in which the ground and first excited states determine the electronic properties of the molecule. In this model, the  $\beta$  value is described as

$$\beta \propto \frac{E_{\text{eg}} f \Delta\mu_{\text{eg}}}{(E_{\text{eg}}^2 - \hbar^2 \omega^2)(E_{\text{eg}}^2 - 4\hbar^2 \omega^2)}, \quad (1)$$

in which  $E_{\text{eg}}$  is the transition energy from the ground state to the first excited state,  $\Delta\mu_{\text{eg}}$  is the difference in the dipole moments between the ground and first excited states,  $f$  is the oscillator strength of the transition, and  $\omega$  is the input laser frequency. Equation 1 implies that molecules with donor and acceptor groups connected by  $\pi$ -conjugated systems tend to have a large  $\beta$  because of an enhanced  $\Delta\mu_{\text{eg}}$ . For that reason, many  $\pi$ -conjugated organic compounds have been studied using both theoretical and experimental methods.

Among organic materials, ionic  $\pi$ -conjugated compounds,<sup>5,6</sup> such as 4-([2-(4-dimethylamino)phenyl]ethenyl)-1-methylpyridinium *p*-toluenesulfonate (DAST),<sup>7,8</sup> have attracted great interest in the field of second-order NLO materials because of their several advantages of use in their crystalline form. Those attributes include crystal-structure controllability by changing the counter ion,<sup>5</sup> as well as a high hardness and melting point that are attributable to the Coulombic interaction together with the van der Waals interaction, and a large  $\beta$  because of charged  $\pi$ -conjugation systems.<sup>9</sup> In particular, DAST, which was first discovered by our group,<sup>7</sup> and then reported by S. R. Marder et al.<sup>8</sup> as a second-order NLO material, shows a very large second-order NLO coefficient ( $d$ ) and an electro-optic (EO) coefficient ( $r$ ):  $d_{11}$  of 330 pm/V at 1907 nm<sup>10</sup> and  $r_{11}$  of 160 pm/V at 820 nm.<sup>11</sup> Crystal-growth proce-

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dures of DAST with higher optical quality and larger size are being investigated, because DAST is a superior crystalline compound for EO device applications.<sup>12</sup> Recently, DAST has also been acknowledged as being an efficient THz-wave generator using difference-frequency generation.<sup>13</sup> Nevertheless, it is still necessary to enhance the second-order NLO properties so that they will be superior to those of DAST. Such an enhancement is an interesting subject for future study.<sup>14,15</sup>

Our investigation by a semiempirical calculation has revealed two strategies to attain large second-order NLO properties for the DAST analogues.<sup>14</sup> One is extended  $\pi$ -conjugation of stilbazolium derivatives through increasing the number of double bonds between two aromatic rings. In this approach, large  $\beta$  values were obtained, but the absorption maximum tended to extend to longer wavelengths. The other strategy is elongated  $\pi$ -conjugation by fused aromatic rings, such as naphthyl and isoquinolinium groups, instead of phenyl and pyridinium groups, respectively. In this case, we expected that these compounds would show a blue shift of the absorption maximum wavelength ( $\lambda_{\text{eg}}$ ), even though the compounds have similar  $\beta$  values in the double-bond extension system. The design of molecules having both a large  $\beta$  value and a short  $\lambda_{\text{eg}}$  presents a difficult trade-off. Therefore, the second approach seemed to be worth investigating, starting from the synthesis of compounds.

This study prepared methoxy-substituted stilbazolium analogues **1** with the conjugated double-bond extension, **2** and **3**, with the extended  $\pi$ -conjugation by a fused aromatic ring and the original salt **4**, as shown in Fig. 1. Although **1** and **2** were prepared in a previous study,<sup>16</sup> their detailed procedures of synthesis have not been reported. Isoquinolinium derivative **3** was synthesized for the first time. Their absorption spectra were compared with those of the simple stilbazolium derivative **4**,<sup>11,17</sup> and their second-order NLO properties are discussed herein based on experimental and theoretical studies using HRS measurements and a semiempirical MO calculation, respectively. The HRS measurements of salts of **1** through **3** using an external reference method have not been reported. These salts have iodide with  $\beta = 0$  as a counter anion. For that reason, only the cation parts contribute to showing HRS signals. The MO calculation was extended to several geometries in this work to show a comparison of the experimental quantities in solution. We chose methoxy derivatives that were all obtainable from commercial reagents, except 6-methyliso-

quinoline (**5**), as precursors. The HRS measurements of these compounds seemed to be possible using a conventional Nd:YAG laser because of their blue-shifted absorption cutoff wavelengths ( $\lambda_{\text{cutoff}}$ s) in comparison with those of dimethylamino derivatives, such as DAST.

## Results and Discussion

**Chromophore Preparation.** The preparation of stilbazolium analogues with iodide anion **1–3** is shown in Fig. 2. Chromophores **1** and **2** were synthesized through a condensation reaction of 1,4-dimethylpyridinium iodide (**7**), and the corresponding aldehyde with piperidine as a base catalyst in the same manner as DAST preparation. In the case of **1**, the reaction gave complicated products when methanol was used as the reaction solvents, and the isolation of **1** was troublesome. On the other hand, the reaction in ethanol–acetone afforded **1** as brownish-yellow needles without a difficult purification process because of the decreased solubility of **1** in the solvent. Regarding chromophore **2**, crystals including one water molecule per ion pair were obtained as hygroscopic yellowish-orange needles through recrystallization of the precipitates, which were obtained from the methanolic reaction mixture. Water-containing crystals were changed into absolute crystals through recrystallization from acetone–ethanol under dried condition. To prepare **3**, **5** was first synthesized according to published references.<sup>18–20</sup> That is, Schiff base **8** was treated with acid to give **5**. 2,6-Dimethylisoquinolinium iodide (**6**) was prepared by the reaction of **5** and methyl iodide in quantitative yield. Under the same conditions as for the preparation of **1** and **2** using piperidine in methanol or ethanol, the desired **3** was not obtained from **6** and *p*-anisaldehyde; the starting materials were almost entirely recovered. The reaction of **6** and the aldehyde in the presence of pyrrolidine,<sup>21</sup> instead of piperidine in ethanol under reflux, gave **3** as a brownish-yellow powder that was inferred to contain one water molecule per ion pair. Their structure and composition were identified by <sup>1</sup>H NMR, IR, and elemental analysis. Furthermore, IR, elemental analysis, and DSC measurements were used to confirm whether water was contained in their crystals or not. In a following investigation, **1** and **2** without water and **3** including water were used.

**Absorption Spectra.** UV–visible absorption spectra of chromophores **1–3** in methanol were measured (Fig. 3). The  $\lambda_{\text{eg}}$ s for **1–3** were 411, 397, and 396 nm, respectively. These

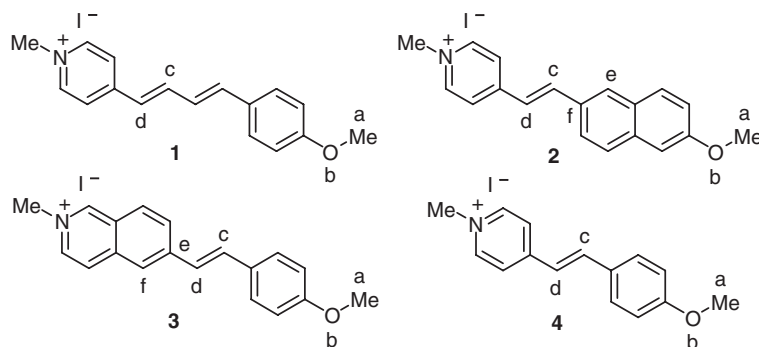


Fig. 1. Structure of stilbazolium analogues investigated in this study. Roman letters indicate atom positions as a reference for Table 2.

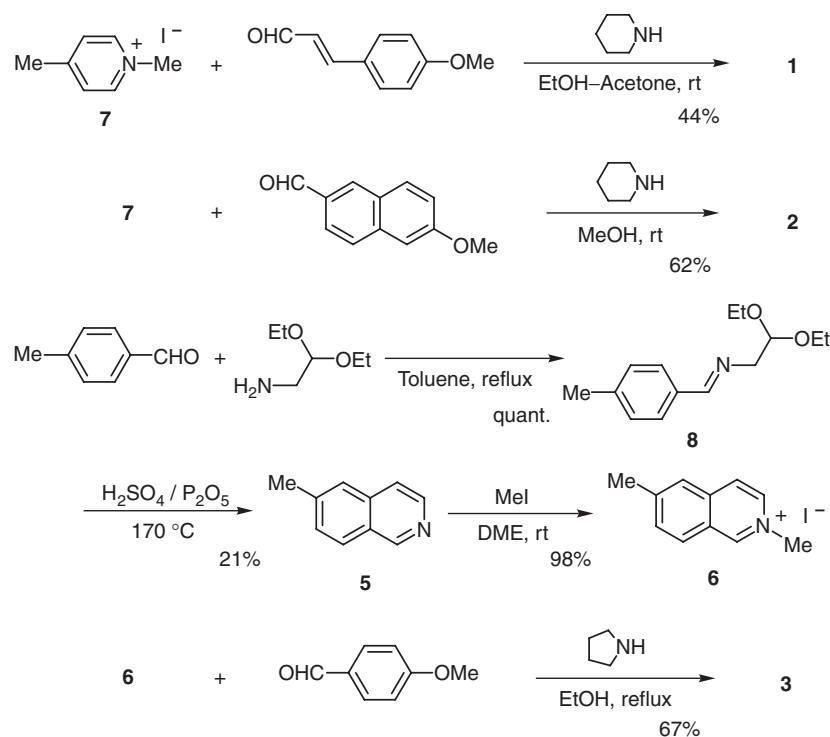
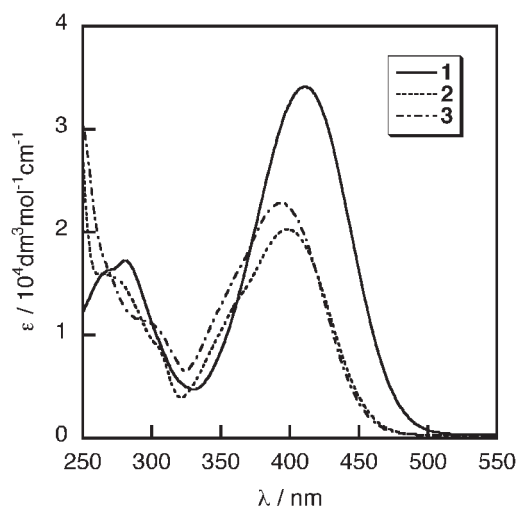


Fig. 2. Synthetic procedure for stilbazolium analogues.

Fig. 3. UV-visible absorption spectra of stilbazolium analogues **1**, **2**, and **3** in methanol.

values can be converted directly into experimental transition energies from the ground to the excited states ( $E_{\text{eg}}$ ) of the stilbazolium cation,  $E_{\text{eg,expt}}$  (Table 1). As anticipated by the calculation results,<sup>14</sup>  $\pi$ -conjugation elongation using fused rings was confirmed to shift  $\lambda_{\text{eg}}$  to shorter wavelengths than in the case of  $\pi$ -conjugation elongation by increasing the double-bond number. The  $\epsilon$  values of **1–3** were  $34100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $20300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , and  $22800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , and those of **2** and **3** were smaller than that of **1** by about 60–67%. Figure 3 shows that it was characteristic that the absorption bands of **2** and **3**, constituted by fused aromatic rings, were slightly broad, indicating that their molecular orbitals

Table 1. Experimental  $\beta_0$  ( $\beta_{0,\text{expt}}$ ) and  $E_{\text{eg}}$  ( $E_{\text{eg,expt}}$ ) Values of Stilbazolium Analogues **1–4**

Compound	$\beta_{0,\text{expt}}/10^{-30} \text{ esu}$	$E_{\text{eg,expt}}/\text{eV}$
<b>1</b>	370	3.02
<b>2</b>	330	3.12
<b>3</b>	350	3.13
<b>4</b>	140 <sup>a)</sup>	3.25 <sup>a)</sup>

a) From Ref. 23.

were split in a complex fashion. The  $\lambda_{\text{cutoff}}$ s of **1–3** were 522, 499, and 497 nm, respectively; the  $\lambda_{\text{cutoff}}$ s of **2** and **3** are also more blue-shifted than those of **1**.

**Hyperpolarizability.** Using the HRS method, the experimental  $\beta$  values ( $\beta_{\text{obs}}$ ) of **1–3** at 1064 nm in methanol were evaluated as  $1090 \times 10^{-30} \text{ esu}$ ,  $870 \times 10^{-30} \text{ esu}$ , and  $900 \times 10^{-30} \text{ esu}$ , respectively. No absorption occurred at 532 nm for these three compounds in methanol. For that reason, the effect from two-photon fluorescence,<sup>22</sup> which enhances the apparent signal intensity at the HRS wavelength, was negligibly small. Therefore, we simply estimated the  $\beta_{0,\text{expt}}$  values—experimental  $\beta$  at zero frequency—from the  $\beta_{\text{obs}}$  values using the two-level model (see Eq. 3 in the Experimental section). Table 1 summarizes these values. For a comparison, data for the simple stilbazolium iodide **4**<sup>23</sup> were also added in addition to data for **1–3**. Figure 4 shows the relation between their values of  $\lambda_{\text{eg}}$  and  $\beta_{0,\text{expt}}$ . The points of **2** and **3** are in the upper area of the straight line through the points of **1** and **2**. Our previous study concerning the double-bond extension system between two aromatic rings of DAST showed that the relation of the calculated  $\beta$  at zero frequency ( $\beta_{0,\text{calc}}$ )<sup>24</sup> and the measured  $\lambda_{\text{eg}}$  in methanol<sup>25</sup> was almost linear up to the compound with a

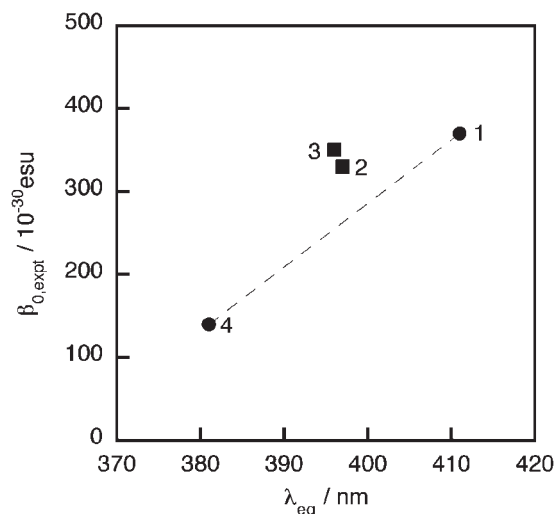


Fig. 4. Experimental  $\beta$  at zero frequency ( $\beta_{0,\text{expt}}$ ) vs absorption maximum wavelength ( $\lambda_{\text{eg}}$ ). Squares are for fused-ring system; circles are for a non-fused-ring system. Numbers in the figure correspond to compounds in Fig. 1. The dashed line shows a hypothetical linear relation for the non-fused-ring system (see text).

double-bond number of four. Applying the linear relationship between  $\lambda_{\text{eg}}$  and  $\beta_{0,\text{expt}}$ , the hypothetical compound, which belongs to a double-bond extension system and has  $\beta_0$  of around  $340 \times 10^{-30}$  esu, should have a  $\lambda_{\text{eg}}$  of about 405 nm. Accordingly, for extended  $\pi$ -conjugation systems with fused aromatic rings, such as **2** and **3**, we clarified that their  $\lambda_{\text{eg}}$  values were about 10 nm shorter than those of a double-bond extension system having the same  $\beta$  value.

The relationship between the molecular structures obtained from the calculation and the calculated physical quantities was investigated to compare these experimental values with the calculated ones. We obtained several optimized structures with the minimum energy for cations **1**<sup>+</sup>–**4**<sup>+</sup>: all of these structures are planar, including two aromatic rings connected to the double bond and oxygen and carbon atoms of the methoxy group.

The HRS method was performed in methanol. Therefore, the obtained  $\beta$  values were considered to be the average ones for several conformers, which are rotation isomers surrounding C–C single bonds. In the case of non-fused-ring systems, such as **1** and **4**, only the methoxy group rotation can generate conformers. On the other hand, for **2** and **3**, belonging to the fused-ring system, rotations about the single bond between the C–C double bond and a fused ring (naphthyl or isoquinolinium group) are also possible to give conformers with minimum energy. Table 2 lists their respective  $\beta_{0,\text{calc}}$  values, calculated  $E_{\text{eg}}$  ( $E_{\text{eg,calc}}$ ), and calculated dipole moment in the ground state ( $\mu_{\text{g}}$ ) of these conformers, together with their calculated heats of formation ( $\Delta H$ ). In that table, angles  $\theta$  and  $\phi$  are defined to be dihedral angles of C<sub>a</sub>–O<sub>b</sub>–C<sub>c</sub>–C<sub>d</sub> and C<sub>a</sub>–O<sub>b</sub>–C<sub>e</sub>–C<sub>f</sub>, respectively, where the subscripts of the atoms indicate atom positions in the cations, as shown in Fig. 1. The differences between the  $\Delta H$  values of the conformers of each ionic species are very small. Consequently, all of the conformers can exist in methanol. In addition, the physical quantities of these species should be the numerical average of the conformers. However, it is noteworthy that the methoxy group rotation shows almost no effect on  $\beta_{0,\text{calc}}$ ,  $E_{\text{eg,calc}}$ , and  $\mu_{\text{g}}$ . Even for rotation of the fused-ring group, the decrease in the  $\beta$  values was calculated to be less than 6%. The differences of  $E_{\text{eg,calc}}$  and  $\mu_{\text{g}}$  among these conformations are either nonexistent or less than those of  $\beta_{0,\text{calc}}$ . These results indicate that the  $\beta_{0,\text{calc}}$  values for those conformers with the lowest energy in Table 2 are useful as representative values for a comparison with the  $\beta_{0,\text{expt}}$  values in Table 1. The ratios of  $\beta_{0,\text{expt}}/\beta_{0,\text{calc}}$  for **1**–**4** are 1.4, 1.7, 2.0, and 1.1, respectively. Because the ratios of **2** and **3** were found to be larger than those of **1** and **4**, peculiar effects may exist for  $\beta$  in the fused-ring system regarding methanol solvation. Moreover, such effects may not have been accounted for in the calculations. On the other hand, the ratios of  $E_{\text{eg,expt}}/E_{\text{eg,calc}}$  were almost constant, around 1.1–1.2.

## Conclusion

This study synthesized novel methoxy-substituted stilbazolium analogues **1**–**3**. Their second-order NLO properties were

Table 2. Calculated  $\Delta H$ ,  $\beta_0$  ( $\beta_{0,\text{calc}}$ ),  $E_{\text{eg}}$  ( $E_{\text{eg,calc}}$ ), and  $\mu_{\text{g}}$  Values of Stilbazolium Cation Conformers **1**<sup>+</sup>–**4**<sup>+</sup>, Whose Structures Are Expressed by the Dihedral Angles  $\theta$  and  $\phi$ <sup>a)</sup>

Cation	$\theta/^\circ$	$\phi/^\circ$	$\Delta H/\text{kJ mol}^{-1}$	$\beta_{0,\text{calc}}/10^{-30}$ esu	$E_{\text{eg,calc}}/\text{eV}$	$\mu_{\text{g}}/\text{Debye}$
<b>1</b> <sup>+</sup>	179.9	—	788.27	266	2.51	17.60
	0.0	—	788.60	264	2.51	17.86
<b>2</b> <sup>+</sup>	179.9	180.0	806.59	218	2.58	18.79
	0.8	0.9	805.80	211	2.60	18.99
	0.1	180.0	806.88	205	2.58	18.77
	179.9	0.0	804.08	199	2.60	18.62
<b>3</b> <sup>+</sup>	180.0	179.9	799.52	176	2.76	17.29
	0.0	0.0	799.86	174	2.76	17.60
	0.0	180.0	799.69	167	2.75	17.11
	180.0	0.0	800.02	166	2.74	17.16
<b>4</b> <sup>+</sup>	180.0	—	731.95	135	2.69	13.59
	0.1	—	732.24	133	2.69	13.75

a) Angles  $\theta$  and  $\phi$  are dihedral angles of C<sub>a</sub>–O<sub>b</sub>–C<sub>c</sub>–C<sub>d</sub> and that of C<sub>a</sub>–O<sub>b</sub>–C<sub>e</sub>–C<sub>f</sub>, respectively. See Fig. 1 for reference on atom positions.



investigated and their absorption spectra in methanol were measured. Thereby, we clarified that the  $\lambda_{\text{eg}}$ s of extended  $\pi$ -conjugation compounds **2** and **3** with fused aromatic rings, such as isoquinolinium and naphthyl groups, became shorter than that of double-bond extension compound **1**. For methoxystilbazolium analogues **1–3**, the  $\beta$  values in methanol were evaluated experimentally using the HRS method. Subsequently, they were compared with the calculated ones using a semi-empirical MO method. The relationship between their  $\lambda_{\text{eg}}$  and  $\beta_{0,\text{expt}}$  showed that extended  $\pi$ -conjugation systems with fused aromatic rings had a shorter  $\lambda_{\text{eg}}$  than a double-bond extension system when compared at the same  $\beta$  value. Namely, the fusion of aromatic rings to stilbazolium analogues is effective to realize chromophores with a large  $\beta$  value within an upper-limited absorption wavelength. The counter-anion exchange of **1** and **2** from iodide to *p*-toluenesulfonate was found to give second-order NLO active crystals, with the  $d$  values expected to be comparable to those of DAST.<sup>16</sup> Current studies are pursuing the crystal growth of these salts and the exploration of more efficient noncentrosymmetric crystal structures for methoxystilbazolium analogues **1–3**.

## Experimental

**General.** The melting points were measured using a Yanaco MP-500 micro melting-point apparatus without any correction. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured with a spectrometer (JNM-LA400; JEOL). <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were expressed as  $\delta$  down-field from internal tetramethylsilane. IR spectra were recorded on a spectrometer (FTIR-8100M; Shimadzu Corp.). Microanalyses were performed at the Microanalytical Room of Institute for Chemical Reaction Science, Tohoku University. UV–visible spectra were measured with a spectrophotometer (V-570; Jasco Inc.). Methanol solutions of about  $1 \times 10^{-5}$  M (1 M = 1 mol dm<sup>-3</sup>) were used to measure  $\lambda_{\text{eg}}$ . Methanol solutions of about  $1 \times 10^{-4}$  M were used to determine  $\lambda_{\text{cutoff}}$  corresponding to the wavelength at which the absorbance was less than  $10^{-3}$ . DSC measurements were made on an instrument (DSC 8240B; Rigaku Corp.) at a heating rate of 10 K/min.

The reagents and solvents were purchased from commercial suppliers, and were used without further purification. Column chromatography was carried out using silica gel (Wakogel C-300; Wako Pure Chemical Industries, Ltd.). 1,4-Dimethylpyridinium iodide (**7**) was synthesized according to a procedure that was reported earlier.<sup>26</sup>

**Synthesis. 4-[4-(4-Methoxyphenyl)-1,3-butadienyl]-1-methylpyridinium Iodide (1):** Piperidine (20 drops) was added to a solution of 1,4-dimethylpyridinium iodide (**7**) (4.01 g, 17.0 mmol) and 4-methoxycinnamaldehyde (3.17 g, 17.0 mmol) in acetone (25 cm<sup>3</sup>) and ethanol (5 cm<sup>3</sup>) at room temperature. The mixture was stirred overnight. The resulting precipitate was then collected by filtration and purified by recrystallization from an ethanol–acetone mixture to obtain **1** (2.87 g, 44%). Brownish yellow needles, mp 224.5–225.5 °C (Found: C, 53.72; H, 4.72; N, 3.52; I, 33.28%. Calcd for C<sub>17</sub>H<sub>18</sub>INO: C, 53.84; H, 4.78; N, 3.69; I, 33.46%); IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  3033, 3007, 1642, 1588, 1557, 1509, 1470, 1291, 1252, 1190, 1175, 1146, 1046, 1007, 862, 812, and 515; UV (MeOH)  $\lambda_{\text{max}}/\text{nm}$  218 (log  $\epsilon$  4.44), 268 (sh, 4.21), 281 (4.24), and 411 (4.53); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  3.83 (3H, s), 4.26 (3H, s), 6.81 (1H, d,  $J$  = 15.3 Hz), 6.95 (2H, d,  $J$  = 8.8 Hz), 7.0–7.1 (2H, m), 7.53 (2H, d,  $J$  = 8.8 Hz),

7.75 (1H, dm,  $J$  = 15.3 Hz), 8.00 (2H, d,  $J$  = 6.8 Hz), and 8.61 (2H, d,  $J$  = 6.8 Hz).

**4-[2-(6-Methoxy-2-naphthyl)ethenyl]-1-methylpyridinium Iodide (2):** Piperidine (5 drops) was added to a solution of **7** (2.01 g, 8.5 mmol) and 6-methoxy-2-naphthaldehyde (1.58 g, 8.5 mmol) in methanol (40 cm<sup>3</sup>) at room temperature. After stirring for 4.5 h, piperidine (5 drops) was added again. The mixture was stirred for 3 days. The resulting precipitate was then collected by filtration and purified by recrystallization from methanol to obtain **2**·xH<sub>2</sub>O (2.12 g, ca. 58%), where  $x$  was determined to be about 1.5 by microanalysis. Anhydrous **2** was obtained by recrystallization from the acetone–ethanol mixture. Yellow needles, mp 244.5–245.5 °C (Found: C, 56.48; H, 4.51; N, 3.29; I, 31.50%. Calcd for C<sub>19</sub>H<sub>18</sub>INO: C, 56.59; H, 4.50; N, 3.47; I, 31.47%); IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  3029, 2938, 1646, 1613, 1561, 1520, 1482, 1395, 1266, 1221, 1192, 1171, 982, 849, 808, and 509; UV (MeOH)  $\lambda_{\text{max}}/\text{nm}$  227 (log  $\epsilon$  4.70), 274 (4.19), and 397 (4.31); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  3.94 (3H, s), 4.29 (3H, s), 7.19 (1H, dd,  $J$  = 9.0, 2.4 Hz), 7.29 (1H, d,  $J$  = 2.4 Hz), 7.46 (1H, d,  $J$  = 16.3 Hz), 7.83 (1H, d,  $J$  = 8.8 Hz), 7.83 (1H, d,  $J$  = 9.0 Hz), 7.88 (1H, dd,  $J$  = 8.8, 1.7 Hz), 8.05 (1H, d,  $J$  = 16.3 Hz), 8.08 (1H, s), 8.15 (2H, d,  $J$  = 6.8 Hz), and 8.67 (2H, d,  $J$  = 6.8 Hz).

**6-Methylisoquinoline (5):** Schiff base **8** (10.0 g, 43 mmol), prepared quantitatively from *p*-tolualdehyde and 2-aminoacetaldehyde diethyl acetal in toluene under reflux,<sup>18</sup> was added dropwise to a mixture of conc. H<sub>2</sub>SO<sub>4</sub> (20 cm<sup>3</sup>) and diphosphorus pentoxide (12.0 g, 85 mmol) at 170 °C under nitrogen and heated for 30 min.<sup>19</sup> The mixture was cooled to room temperature and then poured into an aqueous KOH solution to become basic. The products were extracted several times with ether, washed with saturated NaCl solutions, and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the residue was subjected to column chromatography (ether) to give 1.31 g (21%) of **5**. Pale cream scales (ether), mp 87.0–88.5 °C (lit.<sup>20</sup> 88.5–89.5 °C) (Found: C, 83.60; H, 6.37; N, 9.28%. Calcd for C<sub>10</sub>H<sub>9</sub>N: C, 83.88; H, 6.34; N, 9.78%); IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  3056, 3031, 3006, 2975, 2942, 1630, 1582, 1495, 1399, 1385, 1360, 1275, 1217, 1044, 1028, 970, 957, 891, 839, 801, 777, 646, and 475; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.56 (3H, s), 7.44 (1H, dd,  $J$  = 8.3, 1.5 Hz), 7.57 (1H, d,  $J$  = 5.8 Hz), 7.60 (1H, br s), 7.87 (1H, d,  $J$  = 8.3 Hz), 8.48 (1H, d,  $J$  = 5.8 Hz), and 9.19 (1H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  21.65, 119.58, 124.96, 126.76, 126.95, 129.10, 135.65, 140.25, 142.69, and 151.70.

**2,6-Dimethylisoquinolinium Iodide (6):** Methyl iodide (5.3 cm<sup>3</sup>, 85 mmol) was added to a solution of **5** (8.07 g, 56 mmol) in 1,2-dimethoxyethane (55 cm<sup>3</sup>) at room temperature. The mixture was stirred for 2 days. The resulting precipitate was then collected by filtration to obtain **6** (15.7 g, 98%). Pale yellow needles (dimethoxyethane–methanol), mp 199.0–200.0 °C (Found: C, 46.20; H, 4.09; N, 4.63; I, 44.60%. Calcd for C<sub>11</sub>H<sub>12</sub>IN: C, 46.34; H, 4.24; N, 4.91; I, 44.51%); IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  2977, 1644, 1611, 1512, 1435, 1397, 1370, 1358, 1285, 1188, 1167, 831, 820, and 635; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  2.71 (3H, s), 4.50 (3H, s), 7.92 (1H, dd,  $J$  = 8.5, 1.5 Hz), 8.09 (1H, br s), 8.34 (1H, d,  $J$  = 8.5 Hz), 8.34 (1H, d,  $J$  = 6.8 Hz), 8.51 (1H, dd,  $J$  = 6.8, 1.2 Hz) and 9.74 (1H, br s).

**6-[2-(4-Methoxyphenyl)ethenyl]-2-methylisoquinolinium Iodide (3):** Pyrrolidine as a catalyst<sup>21</sup> (3 drops) was added to a solution of **6** (0.45 g, 1.6 mmol) and *p*-anisaldehyde (0.23 cm<sup>3</sup>, 1.9 mmol) in ethanol (3.6 cm<sup>3</sup>) under reflux. Then reflux was continued for 3 h. Again, pyrrolidine (3 drops) was added to the mix-

ture. After being refluxed for 3 h, the reaction mixture was cooled to room temperature. The resulting precipitate was collected by filtration to obtain  $3 \cdot \text{H}_2\text{O}$  (0.44 g, 67%). Brownish-yellow micro-needles (acetone–ethanol), mp 222.0–222.5 °C (Found: C, 54.02; H, 4.41; N, 3.19; I, 30.43%. Calcd for  $\text{C}_{19}\text{H}_{20}\text{INO}_2$ : C, 54.17; H, 4.79; N, 3.32; I, 30.12%); IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  3004, 2930, 1647, 1619, 1599, 1574, 1509, 1456, 1420, 1402, 1266, 1258, 1244, 1169, 1024, 959, 830, 650, and 556; UV (MeOH)  $\lambda_{\text{max}}/\text{nm}$  222 (log  $\epsilon$  4.66), 247 (4.49), 302 (sh, 4.04), and 396 (4.36);  $^1\text{H}$ NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  3.85 (3H, s), 4.47 (3H, s), 7.00 (2H, d,  $J$  = 8.9 Hz), 7.36 (1H, d,  $J$  = 16.3 Hz), 7.66 (2H, d,  $J$  = 8.9 Hz), 7.68 (1H, d,  $J$  = 16.3 Hz), 8.25 (1H, s), 8.32 (1H, d,  $J$  = 6.8 Hz), 8.33 (2H, m), 8.46 (1H, dd,  $J$  = 6.8, 1.5 Hz), and 9.62 (1H, s).

**HRS Measurement.** The  $\beta$  values of compounds **1**, **2**, and **3** in methanol solution were evaluated experimentally using the HRS technique. The fundamental beam at 1064 nm was obtained from a Q-switched Nd:YAG laser (LS-412; Spectron Laser Systems, Ltd.) with a 10-ns pulse width and about a 10-mJ pulse energy. The beam was irradiated on a small quartz cell containing a methanol solution. The HRS experimental set-up and details to obtain the  $\beta$  value have been described in previous papers.<sup>3,17</sup> *p*-Nitroaniline was used as the external reference with  $\beta$  =  $34.5 \times 10^{-30}$  esu at 1064 nm in methanol.<sup>4</sup> In the external reference method,<sup>27</sup> the  $\beta$  values for the samples were evaluated using

$$\beta_s^2 = \beta_r^2 \left( \frac{a_s}{a_r} \right), \quad (2)$$

in which subscripts s and r indicate the values for the sample and the reference, respectively.  $\beta$  denotes the second-order hyperpolarizabilities at the fundamental wavelength;  $a$  is the slope of the line drawn for the quadratic coefficient  $\text{GB}_2$  vs  $N_{\text{solute}}$  (the number density of the sample or reference in a methanol solution). Then, the  $\beta$  value for the sample by the HRS method ( $\beta_{\text{obs}}$ ) was corrected for any resonance effects using the two-level model to obtain those at zero frequency, namely the static  $\beta$  ( $\beta_{0,\text{expt}}$ ). The  $\beta_{0,\text{expt}}$  is given by

$$\beta_{0,\text{expt}} = \beta_{\text{obs}} \left[ 1 - \left( \frac{\lambda_{\text{eg}}}{\lambda} \right)^2 \right] \left[ 1 - 4 \left( \frac{\lambda_{\text{eg}}}{\lambda} \right)^2 \right], \quad (3)$$

in which  $\lambda$  is the fundamental wavelength of the laser light. The concentrations of sample and reference solutions were changed successively in the order of about  $1 \times 10^{16}$ – $1 \times 10^{17}$  molecules  $\text{cm}^{-3}$ , and about  $1 \times 10^{19}$ – $5 \times 10^{19}$  molecules  $\text{cm}^{-3}$ , respectively. All of the solutions were filtered through filters with 0.1- $\mu\text{m}$  pores to remove dust particles.

**Semiempirical MO Calculation.** The optimized molecular conformations, transition energy ( $E_{\text{eg,calc}}$ ), dipole moment in ground state ( $\mu_g$ ) and  $\beta$  ( $\beta_{0,\text{calc}}$ ) values of compounds **1**, **2**, **3**, and **4** were calculated using the PM3 method<sup>28</sup> in the program system MOPAC 94, provided on a CAChe WorkSystem (ver. 4.1.1; Sony/Tektronix Corp.).

The EF and PRECISE keywords were used as the optimization routine and convergence criterion for calculating, respectively. A finite-field (FF) method, i.e., by treating an external electric field, for the calculation of  $\beta$  was developed based on a dipole-moment expansion.<sup>29</sup> This approach was performed using a POLAR keyword. The vector component of  $\beta$  along the dipole moment is

$$\beta = \frac{3}{5\|\mu\|} \sum_i \beta_i \mu_i, \quad (4)$$

where

$$\sum_i \beta_i \mu_i = \beta_x \mu_x + \beta_y \mu_y + \beta_z \mu_z, \quad (5)$$

and

$$\beta_i = \sum_j \beta_{ijj}. \quad (6)$$

This  $\beta$  value is the vector component in the gas phase at zero frequency, and is abbreviated as  $\beta_{0,\text{calc}}$ .

The transition energy ( $E_{\text{eg}}$ ) in gas phase was also calculated using a multielectron configuration interaction (MECI) treatment, performed by the MECI keyword, as implemented in the MOPAC program. Keywords of 1SCF and C.I. = 5 were added to consider one hundred microstate configurations between the highest three occupied and the lowest three unoccupied molecular orbitals. SINGLET and GEO-OK were also used as keywords only for calculating the singlet states of interest, and for overriding the geometric safety checks, respectively.

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