Synthesis and Crystal Structures of Phenylethynylpyridinium Derivatives for Second-Order Nonlinear Optics

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Several salts of 1-methyl-4-[4-(dimethylamino)phenylethynyl]pyridinium **1**, whose ethenyl analogue **2** is the cation of DAST (1-methyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pyridinium *p*-toluenesulfonate), were synthesized, and these properties were investigated. From a molecular-orbital calculation, the hyperpolarizability (β) of **1** was calculated to be about 80% of that of **2**. The absorption maximum wavelength of **1** is shorter than that of **2**. Six SHG active salts based on cation **1**, including iodide and 4-substituted benzenesulfonates, were obtained in total. Among them, the crystal structures of *p*-chlorobenzenesulfonate salt (**1c**) and *p*-toluenesulfonate salt (**1e**) could be analyzed. As a result, these two have almost the same structures, and the off-diagonal second-order nonlinear optical coefficient (d) values were estimated to be about twice as large as those of DAST.

As second-order nonlinear optical (NLO) chromophores, many organic compounds with polarized π-conjugation systems were found to have potential to exceed inorganic compounds due to their large nonlinear optical coefficients, greater ease for synthetic design, and lower costs.[1] Among them, organic ionic chromophores have several advantages, compared with organic non-ionic species, like a large hyperpolarizability (β) derived from a charged π-conjugation system,[2] crystal-structure controllability by changing the counter ion[3] and high melting points and hardness, originating from the Coulomb interaction. For example, 1-methyl-4-{2-[4-(dimethylamino)-phenyl]ethenyl}pyridinium *p*-toluenesulfonate (DAST: **2e** in Fig. 1)[4–6] has very large NLO properties and its single-crystal growth and applications have been investigated.[7–11] In previous studies, we synthesized DAST analogues with extended π-conjugation systems,[12–14] or a simple substituent[15] for improved NLO properties.

In this work, we investigated cation **1**, which has a triple bond instead of a double bond in cation **2**, i.e., the cation portion of DAST, as shown in Fig. 1. In the case of non-ionic chromophores, a series of tolan derivatives was found to have larger $\mu\beta$ values than a series of stilbene derivatives when compared at the same excitation energy (E_{eg}) up to 3.3 eV.[16] Since a similar effect was expected for DAST analogues, we first confirmed it by a semiempirical calculation. Then, **1a** was synthesized and its UV–visible spectrum was compared with that of **2a**. Although some phenylethynylpyridinium derivatives have been prepared for nonlinear optical properties,[17] the derivatives of cation **1**, whose dimethylamino groups are stronger donors than those of reported compounds, are expected to have large β values and have been reported for the first time. In addition, we performed counter anion exchanges about **1a** to obtain the optimized noncentrosymmetric crystal structure for second-order nonlinear optics. An X-ray crystallographic analysis was carried out for some of the SHG active crystals.

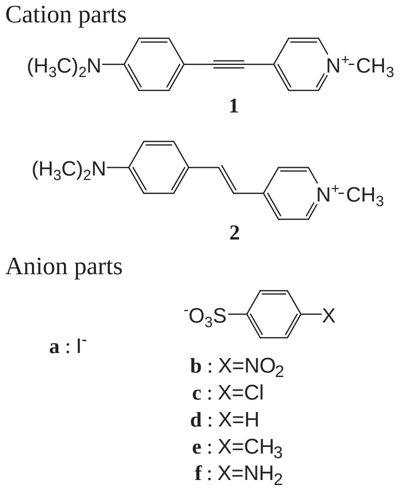

Fig. 1. Chemical structures of **1** and **2** with these derivatives.

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Published on the web February 11, 2005; DOI 10.1246/bcsj.78.344

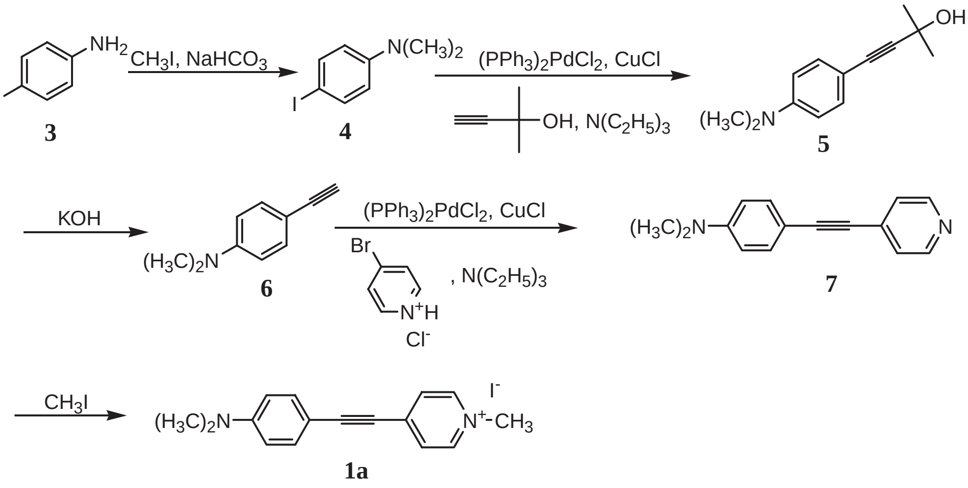


Fig. 2. Synthetic procedure of **1a**.

Experimental

The β values at zero frequency ($\beta_{0,\mathrm{calc}}$), E_{eg}, and dipole moment difference between the ground and excited states ($\Delta\mu_{\mathrm{eg}}$) of series of compounds were obtained by semiempirical molecular orbital (MO) calculations using MOPAC94 PM3 (CAChe ver. 4.1.1) for their optimized structures. Iodide **1a** was synthesized according to Fig. 2. The chemical structures of the obtained compounds were confirmed by ^{1}H NMR spectroscopy (JEOL LAMBDA 400) and elemental analysis (IMRAM, Tohoku University). The melting points were determined by a differential scanning calorimeter (Perkin Elmer Pyres Diamond DSC). Compound **3** was purchased from Aldrich Chemical Co. The synthetic details are described below.

4-Iodo-*N*,*N*-dimethylaniline 4. To a stirred mixture of **3** (40 g), DMF (100 mL), and $NaHCO_3$ (34 g), iodomethane (72 g) was poured dropwise and stirred for 40 h at room temperature, and the resulting mixture was poured into 500 mL of cold water. The obtained precipitate was filtered and dissolved in tetrahydrofuran. It was then filtered off, and the solvent in the filtrate was removed. Recrystallization of the residual solid from methanol gave **4** (25 g, 55%) as white crystals. mp 79 °C; ^{1}H NMR ($CDCl_3$) δ 2.92 (s, 6H), 6.49 (d, $J = 9.0$ Hz, 2H), 7.46 (d, $J = 9.0$ Hz, 2H); Found: C, 38.71; H, 4.34; N, 5.70%. Calcd for $C_8H_{10}NI$: C, 38.89; H, 4.08; N, 5.67%.

4-(3-Methyl-3-hydroxy-1-butynyl)-*N*,*N*-dimethylaniline 5. To a mixture of **4** (40 g), dichlorobis(triphenylphosphine)palladium(II) (1.4 g), copper(I) chloride (0.1 g), and triethylamine (300 mL), 2-methyl-3-butyn-2-ol (23 g) was added and stirred for 2 days at 80 °C under a nitrogen atmosphere. Water (300 mL) was then added and the mixture was extracted with ether (300 mL × 3). The organic phase was dried over Na_2SO_4 and filtered. The solvent in the filtrate was removed under reduced pressure. Purification of the residue on silica gel 60 (eluent: hexane–ethyl acetate 10:1) gave **5** (20 g, 71%) as a yellow powder. mp 88 °C; ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 6H), 2.04 (s, 1H), 2.96 (s, 6H), 6.61 (d, $J = 9.0$ Hz, 2H), 7.29 (d, $J = 9.0$ Hz, 2H); Found: C, 76.70; H, 8.37; N, 6.80%. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89%.

4-Ethynyl-*N*,*N*-dimethylaniline 6. To a mixture of **5** (20 g) and toluene (300 mL), potassium hydroxide (20 g) was added and refluxed for 5 h. After filtration, the solvent was removed under reduced pressure. Purification of the residue on silica gel 60 (eluent: hexane–ethyl acetate 20:1) gave **6** (11 g, 87%) as an orange powder. mp 56 °C; ^{1}H NMR ($CDCl_3$) δ 1.57 (s, 1H), 2.97 (s, 7H), 6.62 (d, $J = 8.5$ Hz, 2H), 7.36 (d, $J = 8.5$ Hz, 2H); Found: C, 82.48; H, 7.68; N, 9.52%. Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65%.

4-[4-(Dimethylamino)phenylethynyl]pyridine 7. To a mixture of **6** (3.8 g), dichlorobis(triphenylphosphine)palladium(II) (0.37 g), copper(I) chloride (0.026 g), and triethylamine (100 mL), 4-bromopyridine hydrochloride (5.1 g) was added and stirred for 2 days at 75 °C under a nitrogen atmosphere. The mixture was then filtered, and solvent in the filtrate was removed under reduced pressure. Purification of the residue by silica-gel column chromatography (eluent: hexane–ethyl acetate 10:1) gave **7** (3.8 g, 65%) as a yellow powder. mp 194 °C; ^{1}H NMR ($CDCl_3$) δ 3.01 (s, 6H), 6.66 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 5.7$ Hz, 2H), 7.42 (d, $J = 8.5$ Hz, 2H), 8.55 (d, $J = 5.7$ Hz, 2H); Found: C, 81.05; H, 6.35; N, 12.60%. Calcd for $C_{15}H_{14}N_2$: C, 81.03; H, 6.71; N, 11.94%.

1-Methyl-4-[4-(dimethylamino)phenylethynyl]pyridinium iodide 1a. To a solution of **7** (0.5 g) and chloroform (50 mL), iodomethane (3 mL) was added and stirred for 24 h. The precipitate was then collected by filtration and recrystallized from methanol gave **1a** (0.715 g, 87%) as orange crystals. mp 227 °C (decomp); ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 6H), 4.30 (s, 3H), 6.76 (d, $J = 9.0$ Hz, 2H), 7.50 (d, $J = 9.0$ Hz, 2H), 7.92 (d, $J = 6.8$ Hz, 2H), 8.69 (d, $J = 6.8$ Hz, 2H); Found: C, 53.08; H, 4.68; N, 7.47%. Calcd for $C_{16}H_{17}IN_2$: C, 52.76; H, 4.70; N, 7.69%.

The counter anion exchange of **1a** was performed as shown in Fig. 3. 4-Substituted benzenesulfonate derivatives were selected as counter anions because many SHG active crystals were obtained in our previous work.[12–15,18] The general procedure of counter anion exchange is as follows.

To a methanol solution of iodide **1a** (10 mmol), a methanol solution of silver salt of benzenesulfonate **b**–**f** (10 mmol) was added. Then, the silver iodide precipitated in the resulting mixture was filtered off. The solvent of the filtrate was removed under reduced pressure and recrystallized from methanol, giving **1b**–**1f** with the yield of 50–80%.

UV–visible absorption spectra in a methanol solution were recorded on a Jasco V-570 spectrophotometer. The SHG activity of powdered crystals was confirmed by the illumination of green light (539.5 nm) when a beam at 1079 nm from an Nd:YAP laser (Elmas L-100) was irradiated. X-ray crystallographic analysis was performed for **1c** and **1e** at 22 °C using a Mac Science MXC3 dif-

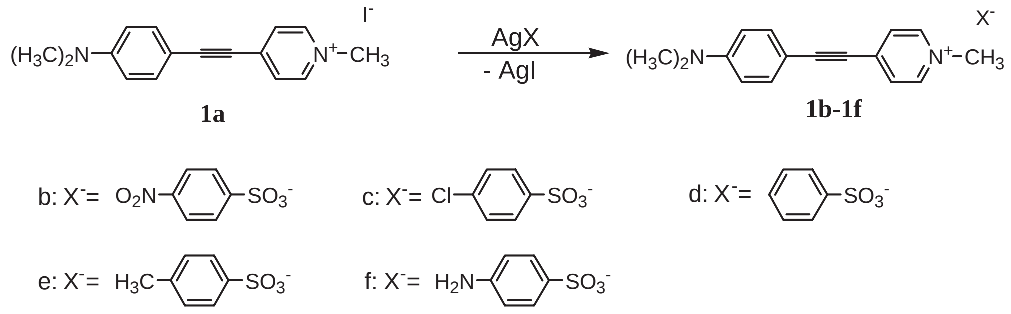
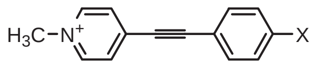
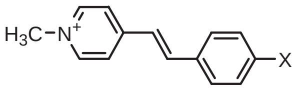


Fig. 3. Counter anion exchanges of **1a** using silver salts of 4-substituted benzenesulfonate.

Table 1. Calculated E_{eg}, $\Delta\mu_{eg}$, and β_0 Values of Series I and II Introducing Various Substituents on X

Series	X	E_{eg}/eV	$\Delta\mu_{eg}$/Debye	$\beta_{0,calc}$/10^{-30} esu
 I	CN	3.39	14.5	60
	H	3.30	12.9	55
	CH_3	3.16	14.2	75
	C_2H_5	3.27	14.4	77
	OH	3.01	14.2	91
	NH_2	2.73	16.1	151
	$N(CH_3)_2$	2.65	17.5	195
 II	CN	3.01	11.2	84
	H	2.94	10.1	76
	CH_3	2.83	11.0	100
	C_2H_5	2.86	10.9	98
	OH	2.72	11.1	191
	NH_2	2.47	13.1	188
	$N(CH_3)_2$	2.38	14.4	241

fractometer with a Mo Kα source ($\lambda = 0.71073$ Å). The cell parameters were determined from the observed setting angles of 22 preliminary reflections. The crystal structure was determined by the direct method and refined by full-matrix least-squares procedures using the CRYSTAN program. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were attached to their parent atoms by fixed bond lengths and idealized bond angles, and were refined isotropically. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-235901–235903. Copies of the data can be obtained free charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; ordeposit@ccdc.cam.ac.uk).

Results and Discussion

At first, we calculated E_{eg}, $\beta_{0,calc}$, and $\Delta\mu_{eg}$ of **1**, **2**, and their derivatives, as shown in Table 1. When a strong donor became attached, E_{eg} became smaller and the β values increased, in general. When compared between the cations with the same subsituent, the β values of series I were smaller than those of series II, while the E_{eg} and $\Delta\mu_{eg}$ values of series I were larger than those of series II. Figure 4 shows the relationship between β_0 and E_{eg} for series I and II. According to this result, the β_0 values of series I, introducing a triple-bond, were larger than those of series II when E_{eg} was roughly larger than 2.38 eV, which was estimated from the intersection point of two correlation lines for series I and II.

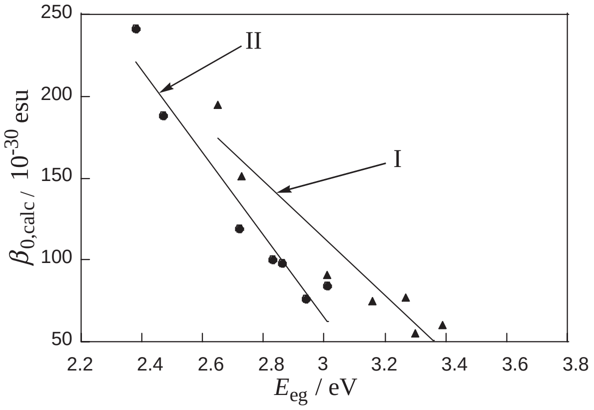


Fig. 4. Relationship between $\beta_{0,calc}$ and E_{eg} for series of I and II.

We successfully synthesized **1a** in a moderate yield. Figure 5 shows the UV and visible absorption spectrum of **1a** together with that of **2a**. The absorption maximum wavelength (λ_{max}) of **1a** was 26-nm shorter than **2a**, while the extinction coefficient and spectral outline were almost the same. This fact that λ_{max} of **1a** was shorter than **2a** coincided with the calculation results that E_{eg} of **1** was larger than that of **2**. The SHG activities of the obtained crystals were checked by the powder test described above. Surprisingly, all of the synthesized crystals (**1a**–**1f**) were SHG active, although the symmetry of the shape of cation **1** was higher than that of cation **2**. However, it is im-

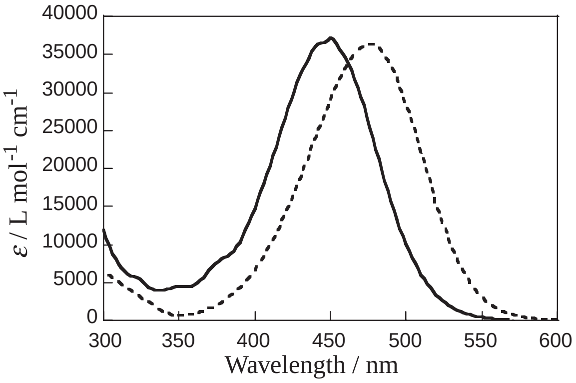


Fig. 5. UV and visible absorption spectra of **1a** (solid line) and **2a** (dotted line) in methanol.

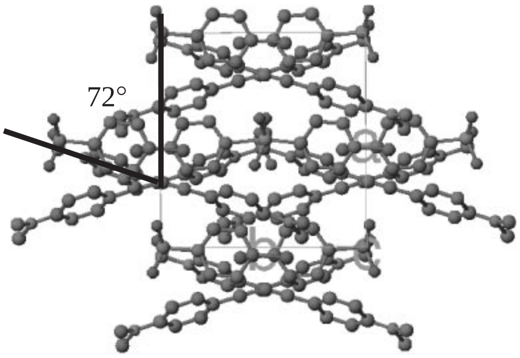


Fig. 6. Crystal structure of **1c** viewed along *c* axis. Hydrogen atoms are omitted.

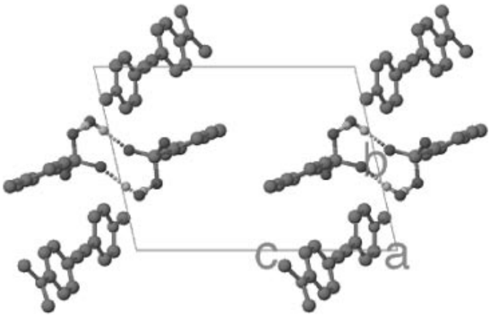


Fig. 7. Crystal structure of water containing **1e** (**1e**$\cdot$$H_2O$) viewed along *a* axis. Hydrogen atoms are omitted except for those with water.

possible to predict the crystal structure clearly. We can just predict empirically.

We tried to prepare their single crystals from methanol solutions by a slow evaporation method under a nitrogen atmosphere. Good-quality single crystals were successfully obtained for **1c** and **1e**. On the other hand, **1e** also gave monohydrate SHG-inactive single crystals when slow evaporation was performed in an ambient atmosphere. The crystallographic data of these three crystals are summarized in Table 2. The **1c** crystal belongs to monoclinic noncentrosymmetric space group *Cc*, and the angle θ between cation's long axis and the polar a axis is about 72°, as shown in Fig. 6. Along the *c* axis, the layer of cations and the layer of anions are alternately piled up in this crystal. The crystal of **1e** was found to have almost the same parameters as **1c**, and these two crystals are isomorphous. This type of phenomenon is sometimes observed between *p*-toluenesulfonate and *p*-chlorobenzenesulfonate anions.[19] DAST (**2e**) also belongs to the same space group, and the cation–anion layered structure is also similar. However, DAST has a smaller angle of θ about 20°. In this connection, direction of the anion's long axis in the DAST crystal is almost parallel to the a axis, while that in the crystals of **1c** and **1e** is almost perpendicular to the a axis, i.e., almost parallel to the b axis. The monohydrated crystal of **1e** (**1e**$\cdot$$H_2O$) belongs to triclinic space group $P\bar{1}$. In this crystal, two water molecules bridge two sulfonate groups of anions due to hydrogen bonding, as shown by the dotted line in Fig. 7, which is the origin of the center of symmetry, resulting in the centrosym-

Table 2. Crystallographic Data of **1c**, **1e**, and **1e**$\cdot$$H_2O$

Compound	**1c**	**1e**	**1e**$\cdot$$H_2O$
Formula	$C_{22}H_{21}ClN_2O_3S$	$C_{23}H_{24}N_2O_3S$	$C_{23}H_{24}N_2O_3S\cdot H_2O$
F.W.	428.9	408.5	426.5
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*Cc*	*Cc*	$P\bar{1}$
a/Å	11.111(7)	11.195(6)	8.254(4)
b/Å	10.456(8)	10.424(5)	10.335(4)
c/Å	18.034(4)	18.10(2)	14.255(6)
α/°	90	90	74.03(3)
β/°	100.60(4)	101.39(6)	75.49(4)
γ/°	90	90	75.23(3)
V/Å^3	2059(2)	2070.6(2)	1109.0(8)
Z	4	4	2
D_x/Mg m^{-3}	1.383	1.310	1.223
μ(Mo Kα)/mm^{-1}	3.057	1.741	1.682
No. of total reflections	2707	2656	5615
No. of unique reflections	2313	2318	4631
No. of reflections with $I > 2\sigma(I)$	2109	2103	3711
R	0.039	0.047	0.056
wR	0.036	0.056	0.050

metric space group. A similar structural motif has been reported for water containing crystals of **2e**[20] and its methoxy derivative.[21]

By using the oriented-gas model,[22] we estimated the d values of **1c** and **1e** compared with those of DAST. MO calculation results for the cation part in the crystal structures were used for the β values. The β values of the cation part of **1c**, **1e**, and **2e** were calculated to be 202×10^{-30} esu, 219×10^{-30} esu, and 255×10^{-30} esu, respectively. Also, the local field factors of **1c** and **1e** were set to be the same as those of the **2e** crystal at a wavelength of 1907 nm. The contribution of the anion to the *d* values is negligible, because the β values of these anions are only several percent of those of the counter cations. As a result, the diagonal components of **1c** and **1e** were calculated to be 51.6 and 65.0 pm/V, respectively, which are one-fortieth to one-thirtieth of those of DAST ($d_{11} = 2010$ pm/V). It is natural that the diagonal component decreased when the angle θ increase. On the other hand, the off-diagonal components were estimated to be 257 and 288 pm/V, respectively, which are more than twice those of DAST ($d_{12} = 124$ pm/V). Also, these values are slightly larger than those of 1-ethyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pyridinium *p*-nitrobenzenesulfonate, studied previously.[23] Large off-diagonal components are valuable for a wide range of applications, like wavelength conversion, because the diagonal component of the d values cannot be used due to a lack of the phase-matching condition.

In conclusion, ethynyl analogue of DAST and its related compounds with cation **1** were prepared and their properties were investigated. All of the salts of cation **1** synthesized (**1a–1f**) were found to have noncentrosymmetric structures. The crystal structures of **1c** and **1e** were analyzed to be isomorphous to each other, and were estimated to have a twice-larger off-diagonal d component compared with that of DAST. These crystals will be good candidates for second-order nonlinear optical materials, especially wavelength conversion purposes.

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