

Synthesis and non-linear optical properties of new ionic species: tolan and diphenylbutadiyne with trimethylammonio and dimethylamino groups

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ABSTRACT: As new ionic organic species for second-order non-linear optical (NLO) materials, 4-[[4-(dimethylamino)phenyl]ethynyl]phenyltrimethylammonium iodide (**1a**), 4-[[4-(dimethylamino)phenyl]butadiynyl]phenyltrimethylammonium iodide (**2a**) and their derivatives with 4-substituted benzenesulfonate instead of iodide were successfully synthesized. The transparent wavelength region of **1a** is wider than that of a typical NLO molecule, *p*-nitroaniline (pNA), whereas **2a** and pNA have similar transparent regions. The experimental and calculated first hyperpolarizabilities (β) of **1a** and **2a** were found to be about 7 and 11 times, respectively, larger than those of pNA. Even when the volume factor was taken into account, the cationic part of **1a** was found to be a better second-order NLO material than pNA derivatives. Four second-order NLO-active crystals were found out of 12 salts synthesized. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: DAST; second-order non-linear optical materials; anilinium salt; organic ionic crystal; hyper-Rayleigh scattering

INTRODUCTION

In the last two decades, organic non-linear optical (NLO) materials have been extensively studied owing to their large optical non-linearity and ultrafast response originating from their π -conjugation systems.^{1–3} For second-order NLO materials, the typical molecular design was established to be π -conjugation systems possessing an electron donor and acceptor at both ends of the systems, and non-ionic species such as *p*-nitroaniline (pNA) derivatives have mainly been investigated. We started a series of studies on organic ionic species for second-order non-linear optics because of their several advantages compared with non-ionic species. First, they have higher melting-points and hardness in general due to the Coulombic intermolecular interaction in crystals. Second, non-centrosymmetric crystal structures with proper molecular alignment can be achieved not by direct modification of the NLO species but by simple exchange of the counter ion, as demonstrated by Meredith.⁴ We found that a combination of *p*-toluenesulfonate with NLO-active stilbazolium often gave non-centrosymmetric structures, e.g. 1-methyl-4-[[2-[4-(dimethylamino)phenyl]-

ethenyl]pyridinium *p*-toluenesulfonate (DAST).^{5–7} Third, large first hyperpolarizabilities (β) are expected owing to the unconventionally polarized structures caused by charged π -conjugation systems. In a previous computational and experimental study, we clarified that the large dipole moment difference between the ground and excited states ($\Delta\mu_{eg}$) resulted in stilbazolium with large β ,⁸ which is proportional to $\Delta\mu_{eg}$ in the two-level model.⁹ Owing these advantageous features of π -conjugated ionic species for second-order NLO properties, we synthesized a variety of stilbazolium analogues.^{10–14}

In the present study, we extended the ionic species by changing the cationic acceptor portion from an *N*-methylpyridinium ring to an *N,N,N*-trimethylanilinium ring. Differences between pyridinium and anilinium cations in electronic resonance structures are shown in Fig. 1, where the left- and right-hand structures have more contributions in the ground and excited states, respectively. Although the two structures for pyridinium can be drawn by just shifting the bonds and charge, those for anilinium cannot be drawn without generating charge separation in the π -conjugated system. This qualitatively indicates that the excited state of the anilinium cation is destabilized compared with the pyridinium cation and a wider HOMO–LUMO gap was expected to break through the trade-off relationship between absorption cutoff and β .¹⁵ We selected the dimethylamino group as a typical donor and tolan (diphenylethyne) and diphenylbutadiyne

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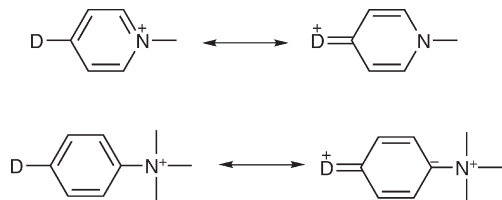


Figure 1. Resonance structures of *N*-methylpyridinium and *N,N,N*-trimethylanilinium with an electron-donating group (D)

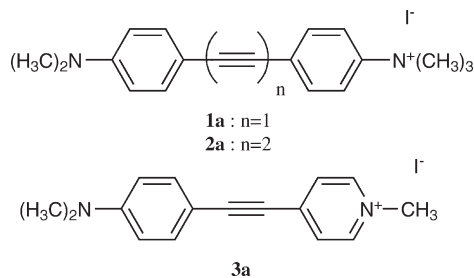


Figure 2. Structures of **1a**, **2a** and **3a**

skeletons as π -conjugation systems. 4-[[4-(Dimethylamino)phenyl]ethynyl]phenyltrimethylammonium iodide (**1a**), 4-[[4-(dimethylamino)phenyl]butadiynyl]phenyltrimethylammonium iodide (**2a**) (shown in Fig. 2) and their derivatives with different counter anions were synthesized to clarify their linear and non-linear optical properties. X-ray crystallographic analysis of **1a** was also investigated. Although tolan^{16–18} and diphenylbutadiyne¹⁹ derivatives have been studied as second-order NLO materials, they were all non-ionic compounds and those with an anilinium-type structure were studied here for the first time.

EXPERIMENTAL

Iodide salts **1a** and **2a** were synthesized according to Fig. 3. 4-Ethynyl-*N,N*-dimethylaniline (**7**) was prepared by the Sonogashira reaction²⁰ of **5** followed by aceto-nolysis.²¹ Compounds **5** and **7** were coupled by the Sonogashira reaction again to give bis[4-(dimethylamino)phenyl]ethyne (**8**). Bis[4-(dimethylamino)phenyl]butadiyne (**9**) was synthesized by the oxidative coupling reaction²² of **7**. Careful asymmetric methylation of **8** and **9** with iodomethane gave salts **1a** and **2a**, respectively. The iodide anions of **1a** and **2a** were converted to other anions such as *p*-aminobenzenesulfonate, *p*-toluenesulfonate, benzenesulfonate, *p*-chlorobenzenesulfonate and *p*-nitrobenzenesulfonate, as shown in Fig. 4. Details of the synthetic procedures are described below.

4-Iodo-*N,N*-dimethylaniline (5). Into a stirred mixture of **4** (40 g), DMF (100 ml) and NaHCO₃ (34 g), iodo-methane (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 precipitate obtained was filtered and dissolved in tetrahydrofuran. Then it was filtered off and solvent in the filtrate was removed. Recrystallization of the residual solid from methanol gave **5** (25 g, 55%) as white crystals, m.p. 79 °C. ¹H NMR (CDCl₃), 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%. Calculated for C₈H₁₀NI: C, 38.89; H, 4.08; N, 5.67%.

4-(3-Methyl-3-hydroxy-1-butynyl)-*N,N*-dimethylaniline (6). To a mixture of **5** (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 added and the mixture

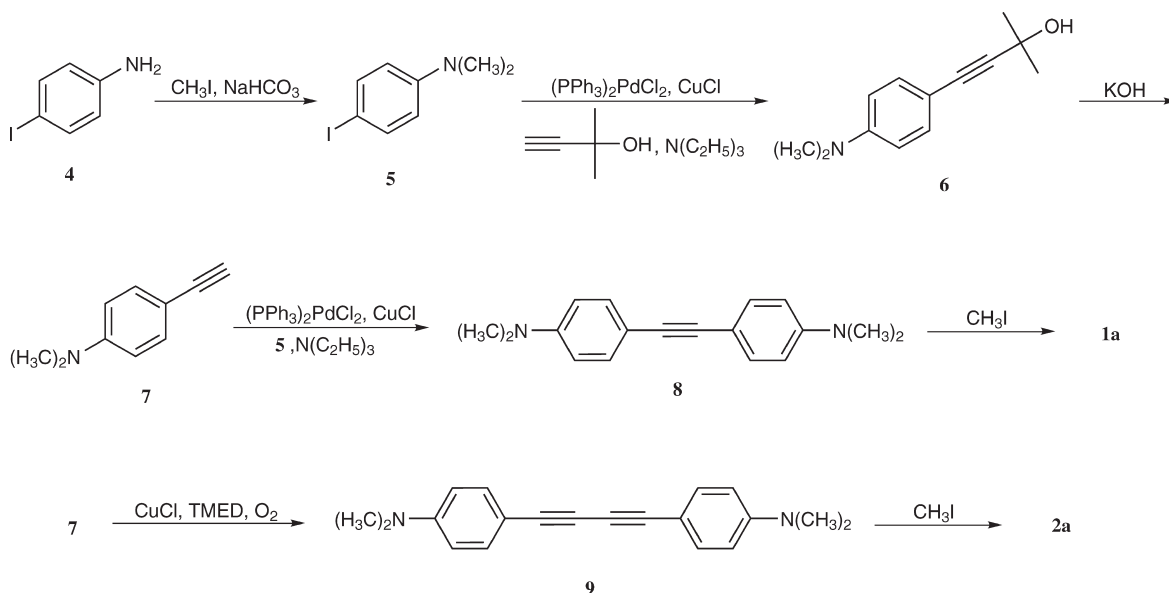


Figure 3. Synthetic procedure for **1a** and **2a**

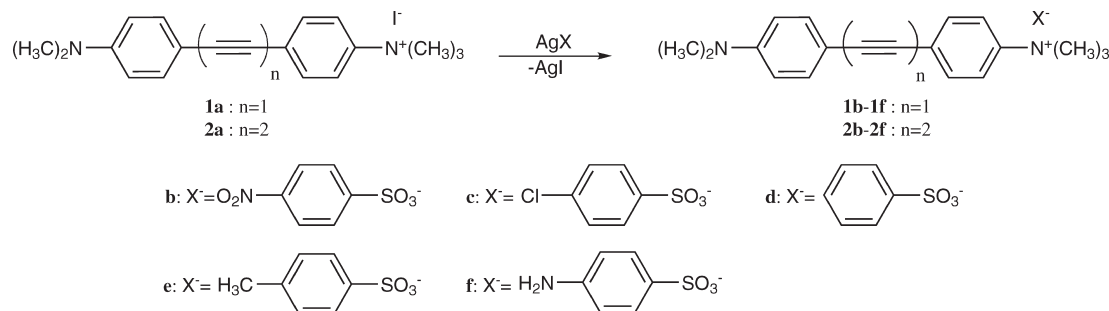


Figure 4. Counter anion exchanges of **1a** and **2a** using silver salts of 4-substituted benzenesulfonate

was extracted with diethyl ether (300 ml $\times$ 3). The organic phase was dried over Na_2SO_4 and filtered. Solvent in the filtrate was removed under reduced pressure. Purification of the residue on silica gel 60 [eluent: hexane–ethyl acetate (10:1)] gave **6** (20 g, 71%) as a yellow powder, m.p. 88 °C. ^1H 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%. Calculated for $\text{C}_{13}\text{H}_{17}\text{NO}$: C, 76.81; H, 8.43; N, 6.89%.

4-Ethynyl-N,N-dimethylaniline (7). To a mixture of **6** (20 g) and toluene (300 ml), potassium hydroxide (20 g) was added and the mixture was 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 **7** (11 g, 87%) as an orange powder, m.p. 56 °C. ^1H 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%. Calculated for $\text{C}_{10}\text{H}_{11}\text{N}$: C, 82.72; H, 7.64; N, 9.65%.

Bis[4-(dimethylamino)phenyl]ethyne (8). To a mixture of **7** (400 mg), dichlorobis(triphenylphosphine)palladium(II) (39 mg), copper(I) chloride (3 mg) and triethylamine (25 ml), **5** (680 mg) was added and the mixture was stirred for 1 day at 80 °C under a nitrogen atmosphere. After filtration, the solvent was removed under reduced pressure. Purification of the residue on silica gel [eluent: hexane–ethyl acetate (10:1)] gave **8** (160 mg, 22%) as a colorless powder, m.p. 196 °C. ^1H NMR (CDCl_3), δ 2.97 (s, 12H), 6.65 (d, $J=9.0$ Hz, 4H), 7.38 (d, $J=9.0$ Hz, 4H). Found: C, 81.32; H, 7.75; N, 10.49%. Calculated for $\text{C}_{18}\text{H}_{20}\text{N}_2$: C, 81.78; H, 7.63; N, 10.60%.

4-[[4-(Dimethylamino)phenyl]ethynyl]phenyltrimethylammonium iodide (1a). Into a mixture of **8** (1.3 g) and chloroform (100 ml), iodomethane (3 g) was poured dropwise and stirred for 4 days at room temperature. Then precipitate was collected by filtration and recrystallized from methanol to give **1a** (1.0 g, 56%) as a light-yellow powder, m.p. 208 °C. ^1H NMR (CD_3OD), δ 2.99 (s, 6H), 3.67 (s, 9H), 6.72 (d, $J=9.1$ Hz, 2H), 7.36 (d, $J=8.6$ Hz, 2H), 7.68 (d, $J=9.1$ Hz, 2H), 7.88 (d, $J=8.6$ Hz, 2H). Found: C, 56.09; H, 5.63; N, 6.86%. Calculated for $\text{C}_{19}\text{H}_{23}\text{IN}_2$: C, 56.17; H, 5.71; N, 6.89%.

Bis[4-(dimethylamino)phenyl]butadiyne (9). Copper(I) chloride (100 mg) was dissolved in 5 ml of acetone and *N,N,N',N'*-tetramethylethylenediamine (116 mg), then acetone (100 ml) and **7** were added and stirred with oxygen bubbling for 6 h. The precipitate was filtered and washed with acetone to give **9** (2.0 g, 84%) as a light-yellow powder, m.p. 216 °C. ^1H NMR (CDCl_3), δ 2.99 (s, 12H), 6.61 (d, $J=8.9$ Hz, 4H), 7.39 (d, $J=8.9$ Hz, 4H). Found: C, 82.69; H, 6.71; N, 9.68%. Calculated for $\text{C}_{20}\text{H}_{20}\text{N}_2$: C, 83.30; H, 6.99; N, 9.71%.

4-[[4-(Dimethylamino)phenyl]butadiynyl]phenyltrimethylammonium iodide (2a). A similar procedure to the synthesis of **1a** was performed using **9** instead of **7** to give **2a** as a light-yellow powder in 68% yield, m.p. 244 °C. ^1H NMR (CD_3OD), δ 3.00 (s, 6H), 3.67 (s, 9H), 6.69 (d, $J=9.0$ Hz, 2H), 7.35 (d, $J=9.0$ Hz, 2H), 7.73 (d, $J=9.3$ Hz, 2H), 7.92 (d, $J=9.3$ Hz, 2H). Found: C, 58.45; H, 5.38; N, 5.97%. Calculated for $\text{C}_{21}\text{H}_{23}\text{IN}_2$: C, 58.61; H, 5.39; N, 6.51%.

General procedure for counter anion exchanges. To a methanolic solution of iodide **1a** or **2a** (10 mmol), a methanolic solution of the silver salt of benzenesulfonates **b-f** (10 mmol) were added. The silver iodide precipitated in the resulting mixture was filtered off. The solvent of the filtrate was removed under reduced pressure and recrystallization from methanol gave **1b-1f** and **2b-2f** in 50–80% yield.

Measurements. Melting-points were determined using a differential scanning calorimeter (Perkin-Elmer pyres diamond DSC). The chemical structures of the compounds obtained were confirmed by ^1H NMR spectroscopy (JEOL Lambda 400) and elemental analysis (IMRAM, Tohoku University). UV–visible absorption spectra in methanolic solution were recorded on a Jasco V-570 spectrophotometer. Hyper-Rayleigh scattering (HRS) measurements²³ for **1a** and **2a** were performed by using a nanosecond Nd:YAG laser (Coherent Infinity 40–100) at 1064 nm. These measurements were executed in the methanolic solution and pNA was used as an external standard,²⁴ whose β value at 1064 nm in methanol is 3.45×10^{-29} esu.⁹ The β values obtained were corrected to β at zero frequency ($\beta_{0,\text{expt}}$) according to the

two-level model. The β values at zero frequency ($\beta_{0,\text{calc}}$) were also obtained together with $\Delta\mu_{\text{eg}}$ by the semi-empirical molecular orbital (MO) calculation using MO-PAC94 PM3 (CACHÉ version 4.1.1) for their optimized structures. SHG activities of crystals were confirmed by irradiation with the Nd:YAP laser beam at 1079 nm from an Elmas L-100. This was conducted only for qualitative purposes to remove the centrosymmetric crystals from further investigation. X-ray crystallographic analysis was performed using a Mac Science MXC3 diffractometer with an Mo $K\alpha$ source ($\lambda = 0.71073 \text{ \AA}$) for a crystal of **1a** grown in methanolic solution by the slow evaporation method. 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.

RESULTS AND DISCUSSION

The UV and visible absorption spectra of iodide salts **1a** and **2a** in methanol are shown in Fig. 5 together with those of pNA in methanol. The longest absorption maximum wavelength (λ_{max}) of **1a** is 21 nm shorter than that of pNA, whereas **2a** has a 7 nm longer λ_{max} compared with pNA. However, the absorption cutoff wavelength (λ_{cutoff}) of **2a** is shorter than that of pNA. Hence the new ionic species **2** can be used in the same wavelength range as pNA derivatives irrespective of the extended π -conjugation system of **2**. Cation **1** has the wider transparent region than pNA. The corresponding pyridinium analogue to **1a**, i.e. 1-methyl-4-[4-(dimethylamino)phenylethynyl]pyridinium iodide (**3a**), has a λ_{max} in methanol at 450 nm which is the 102 nm longer than the λ_{max} of **1a**. Hence the wider HOMO–LUMO gap of **1a** than that of **3a** was confirmed. The molar absorption coefficients at

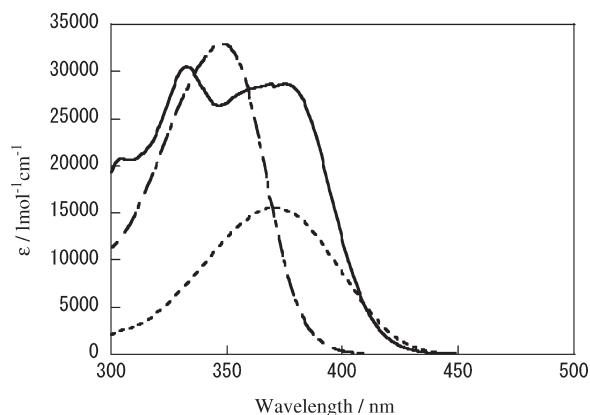


Figure 5. UV and visible absorption spectra of pNA (dotted curve), **1a** (dot-dashed curve) and **2a** (solid curve) in methanol

λ_{max} (ϵ_{max}) of **1** and **2** are about double those of pNA because of the increased number of π -electrons in the conjugation system for **1** and **2**.

Since the λ_{cutoff} values of the related compounds are shorter than 532 nm, their β values could be properly evaluated by the HRS method using a Nd:YAG laser beam at 1064 nm. The $\beta_{0,\text{expt}}$ values obtained for **1a** and **2a** were 1.14×10^{-28} and 1.06×10^{-28} esu, respectively, which are about seven times larger than those of pNA. By MO calculations, we also obtained $\beta_{0,\text{calc}}$ and $\Delta\mu_{\text{eg}}$ values, which are summarized in Table 1 together with the experimental values mentioned above. The $\beta_{0,\text{calc}}$ values of **1** and **2** are about 11 times larger than those of pNA, and a similar tendency was verified by the experimental results. According to the two-level model, β is proportional to $\Delta\mu_{\text{eg}}$, f and E_{eg}^{-3} , where f is oscillator strength and E_{eg} is excitation energy from the ground state to the excited state. Since f is considered to be roughly proportional to ϵ_{max} and E_{eg} is inversely proportional to λ_{max} , we can estimate the enhancement factors of β values of **1** and **2** from the values in Table 1. Among the three parameters, the $\Delta\mu_{\text{eg}}$ values of **1** and **2** are about three to four times larger than those of pNA, the ϵ_{max} values are about double, and the λ_{max}^3 values are almost the same. Hence the largest contribution to enhancing the β values of **1** and **2** comes from $\Delta\mu_{\text{eg}}$. This result is the same as for stilbazolium derivatives studied previously.⁸

Since the bulk NLO property expresses performance in a unit volume, β divided by the molecular volume is a good index to estimate the bulk property. Actually, **1a** and **2a** occupy a larger volume in crystals than pNA, and it is better to take this factor into account. In the present study, the molecular shapes are linear and β divided by the molecular length is also valid for comparison. The calculated molecular lengths (L) of pNA, **1** and **2** are about 6.7, 15.9 and 18.7 Å, respectively. Using $\beta_{0,\text{calc}}$ and L , the $\beta_{0,\text{calc}}/L$ ratios for pNA, **1** and **2** were calculated as 1, 4.5 and 4.2, respectively. In actual crystals, cations **1** and **2** accompany counter anions, and the ratios become lower owing to the counter anion volume. However, when a counter anion possessing a smaller volume than the cation is selected, the ratios become no less than half of the calculated values above. From these results, the order of bulk NLO property was estimated to be **1** > **2** > pNA. Hence **1** is a better ionic species for second-order NLO materials. The π -conjugation elongation effect of the

Table 1. Values related to optical properties

	Experimental values			Calculated values	
	λ_{max} (nm)	ϵ_{max} ($10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$)	$\beta_{0,\text{expt}}$ (10^{-30} esu)	$\beta_{0,\text{calc}}$ (10^{-30} esu)	$\Delta\mu_{\text{eg}}$ (D)
1a	348	3.3	114	88.5	19.5
2a	376	3.1	106	98.0	26.1
pNA	369	1.6	15.7	8.38	6.05

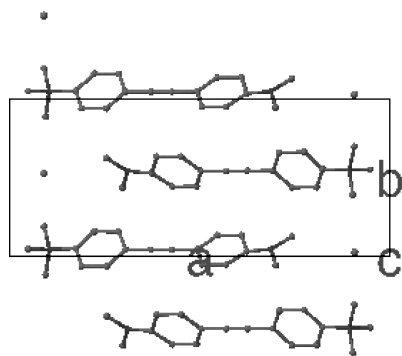
Table 2. Crystallographic data for **1a**

Formula	C ₁₉ H ₂₃ N ₂ I
Formula weight	406.3
Crystal system	Monoclinic
Space group	P2 ₁
<i>a</i> (Å)	19.80(1)
<i>b</i> (Å)	8.017(5)
<i>c</i> (Å)	5.876(5)
β (°)	96.13(6)
<i>V</i> (Å ³)	927.57(1)
<i>Z</i>	2
<i>D_x</i> (mg m ⁻³)	1.454
<i>R</i>	0.037
<i>wR</i>	0.046

anilinium derivatives seemed to be saturated from **1** with one triple bond between two aromatic rings to **2** with two conjugated triple bonds. The smaller $\beta_{0,\text{expt}}$ of **2a** than that of **1a** suggested saturation of the π -conjugation elongation effect even at a molecular level. This tendency is in contrast to the case of stilbazolium, which showed a monotonic increase in $\beta_{0,\text{calc}}$ up to the compound with four double bonds between two aromatic rings²⁵ and $\beta_{0,\text{expt}}$ saturation between the compound with two double bonds and that with three double bonds.²⁶

The counter anion exchange reactions for **1a** and **2a** were performed to modify the crystal structure. The introduced counter anions were benzenesulfonate derivatives, which often gives SHG-active salts with stilbazolium derivatives in our previous studies.^{10–12} Of 12 salts synthesized, **1a**, **1c**, **2c** and **2e** were found to be SHG active.

Among these four compounds, we have been able to obtain single crystals of good quality for x-ray crystallographic analysis only for **1a** so far. Its crystallographic data and crystal structure are shown in Table 2 and Fig. 6, respectively. In the cation structure, two benzene rings are slightly twisted by a dihedral angle of about 9°, which is not so serious enough to decrease the β value owing to lack of π -orbital overlap. Although this crystal belongs to the monoclinic noncentrosymmetric space group P2₁, the

**Figure 6.** Crystal structure of **1a** viewed along the *c* axis. Hydrogen atoms are omitted

angle between the polar *b* axis and the long axis of the cation is unfortunately about 89.9°, with the result that the second-order NLO coefficient of the single crystal is close to zero.

In conclusion, we found that tolan derivatives **1** with trimethylammonio and dimethylamino groups are organic ionic species with better second-order NLO properties than pNA. Further research to optimize the polar alignment of the cations and investigation of cation modification are in progress to improve the optical properties of the anilinium salts.

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