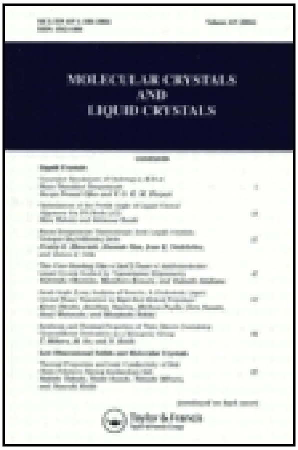

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Synthesis of Phenylbutadiynylpyridinium Derivatives for Nonlinear Optics

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Synthesis of Phenylbutadiynylpyridinium Derivatives for Nonlinear Optics

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1-Methyl-4-{[4-(dimethylamino)phenyl]butadiynyl}pyridinium (PBP) derivatives with iodide or benzenesulfonate anion were synthesized as potential compounds for both second- and third-order NLO applications. PBP shows peculiar absorption spectrum in methanol, in which molar extinction coefficient at absorption maximum (λ_{max}) decrease irrespective of bathochromic shift of λ_{max} compared with the corresponding compound with one triple bond between two aromatic rings. From semiempirical MO calculations, it was explained by aromatic-ring rotation of PBP in methanol. Activity on second-harmonic generation (SHG) was found in four out of thirteen compounds synthesized. Although most of PBP derivatives were found to show exothermic reaction before melting, pure solid-state polymerization was not confirmed in these compounds.

Keywords: DAST; ionic dye; nonlinear optics; organic crystal; solid-state polymerization

INTRODUCTION

Ionic π-conjugated crystals such as 1-methyl-4-{2-[4-(dimethylamino)-phenyl]ethenyl}pyridinium *p*-toluenesulfonate (DAST) [1] are considered to be one of the promising second-order nonlinear optical (NLO) materials used for terahertz-wave generation [2] etc. In this connection, development of high performance second-order NLO materials is still an interesting research subject. In our previous study, we

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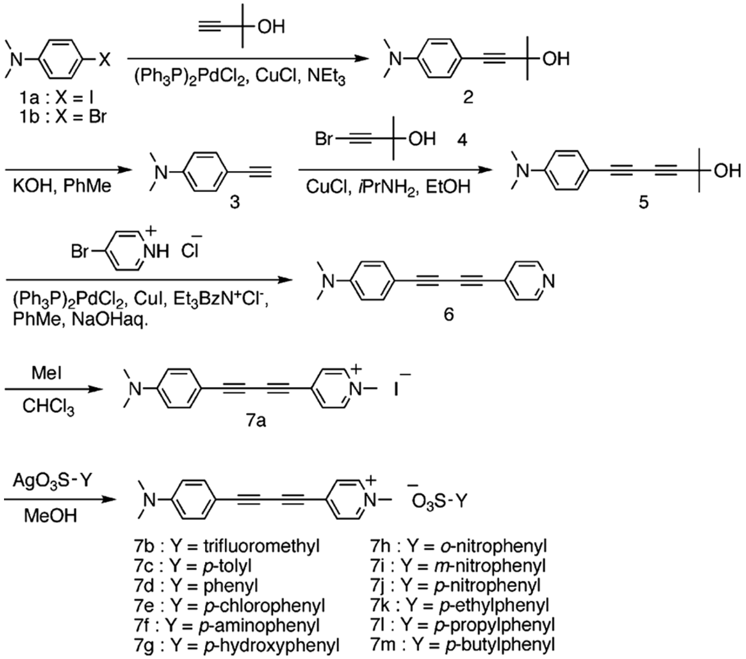


FIGURE 1 Synthesis scheme of PBP derivatives **7a** through **7m**.

have found that increase of double bond number between phenyl and pyridinium rings of DAST cation is quite effective to enhance hyperpolarizability β [3]. Even when a triple bond is used as a π-conjugated bridge between phenyl and pyridinium rings, many compounds with second-harmonic generation (SHG) activity were found irrespective of the symmetrical cationic structure compared with stilbazolium structure [4]. In this study, above two molecular designs were combined, and 1-methyl-4-{[4-(dimethylamino)phenyl]butadiynyl}pyridinium (PBP) derivatives **7a** through **7m** in Figure 1 were prepared and their properties were elucidated. In addition, another interesting point on the PBP molecular structure is possibility of polymerization in solid state because some butadiyne derivatives are known to give polydiacetylenes (PDAs) [5]. This point was also investigated.

EXPERIMENTAL

PBP derivatives were synthesized according to Figure 1. Synthesis procedure of 4-ethynyl-*N,N*-dimethylaniline **3** was reported previously [4]. Cadiot-Chodkiewicz coupling reaction between **3** and **4**

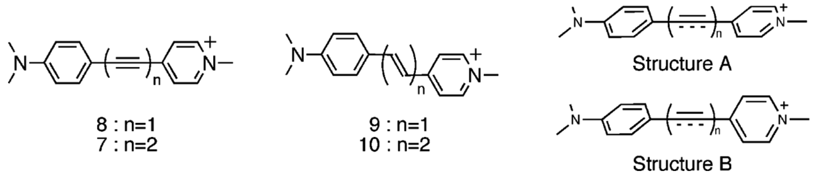
TABLE 1 Melting Points, NMR and IR Spectral Data and Elemental Analyses of **5**, **6** and **7a**

Compound	Mp[a]/°C	^{1}H-NMR[b] δ/ppm	^{13}C-NMR[b] δ/ppm	IR (KBr)/cm^{-1}	Found/% (Calcd/%)
5	106	1.57 (s, 6 H), 2.98 (s, 6 H), 6.60 (d, $J = 8.8$ Hz, 2 H), 7.36 (d, $J = 8.8$ Hz, 2 H)	31.04, 39.93, 65.68, 67.65, 71.21, 80.54, 85.81, 107.60, 111.64, 133.86, 150.66	3392, 3352, 2985, 2224, 2141, 1606, 1523, 1367, 1215, 1157, 818	C, 79.00; H, 7.49; N, 6.14 (C, 79.26; H, 7.54; N, 6.16)
6	201	3.02 (s, 6 H), 6.63 (d, $J = 9.1$ Hz, 2 H), 7.34 (d, $J = 5.8$ Hz, 2 H), 7.42 (d, $J = 9.1$ Hz, 2 H), 8.58 (d, $J = 5.8$ Hz, 2 H)	39.93, 71.59, 77.77, 79.43, 86.17, 106.95, 111.65, 125.96, 130.84, 134,18, 149.87, 151.01	2918, 2200, 1599, 1585, 1522, 1450, 1367, 1182, 816	C, 82.44; H, 5.72; N, 11.27 (C, 82.89; H, 5.73; N, 11.38)
7a	223[c]	3.08 (s, 6 H), 4.40 (s, 3 H), 6.76 (d, $J = 9.4$ Hz, 2 H), 7.46 (d, $J = 9.4$ Hz, 2 H), 8.07 (d, $J = 6.7$ Hz, 2 H), 8.86 (d, $J = 6.7$ Hz, 2 H)	40.08, 72.36, 77.22, 90.26, 94.38, 106.21, 112.83, 130.71, 135.63, 141.06, 146.36, 153.30	3087, 3020, 2195, 1628, 1604, 1510, 1373, 1188, 810	C, 55.55; H, 4.32; N, 7.05 (C, 55.68; H, 4.41; N, 7.22)

[a] Peak temperature measured by DTA.

[b] ^{1}H- and ^{13}C-NMR spectra were measured in $CDCl_3$ for **5** and **6** and in CD_3OD for **7a**. In ^{13}C-NMR data of **7a**, a peak assigned to methyl carbon attached to the pyridinium ring was not clearly detected because of overlap with split peaks of deuterated-methanol carbon.

[c] Exothermic peak due to thermal polymerization.


8 : n=1
7 : n=2

9 : n=1
10 : n=2

Structure A

Structure B

FIGURE 2 Chemical structures of cations with various π-conjugation bridges between pyridinium and (dimethylamino)phenyl groups. Two conformations of cations are displayed as Structure A with a planer form and Structure B in which two aromatic rings are perpendicular.

[6] gave **5** in 92% yield. Elimination of acetone from **5** and the following Sonogashira coupling reaction with 4-bromopyridine hydrochloride were performed in one pot to give **6** in 45% yield [7]. Methylation of **6** by iodomethane in chloroform resulted in **7a** in 98% yield. Melting points, spectroscopic data and elemental analyses of **5**, **6** and **7a** are summarized in Table 1. Anion exchange of **7a** was performed by the reaction with silver sulfonates [8] to give the corresponding PBP sulfonates **7b** through **7m**. The reason why such sulfonates were selected as counter anions was that they gave many SHG active crystals with stilbazolium and its related cations [3,4]. PBP derivatives were finally recrystallized from methanol. Since **7d** and **7g** gave crystals containing water or solvent, they were heated at 120°C for 6 h under reduced pressure to remove the included compounds. Thermogravimetric and differential thermal analyses (TG-DTA) were performed using a Seiko TG/DTA 220U apparatus with temperature increasing rate of 10°C/min. SHG activity was verified by irradiation from a Nd:YAP laser at 1079 nm. Calculations of ionic species **7** through **10** shown in Figure 2 were performed by CAChe WorkSystem Pro Ver. 6.1.12.33. Structures were optimized by PM3 in MOPAC 2002 (Ver. 2.5.0) and structure A in Figure 2 with planer conformation was found to be most stable form for all cations. Calculations for structure B in Figure 2, in which one of the aromatic rings was rotated by 90°, were also executed. The β values at zero frequency (β_0) and UV-Vis spectra were obtained by PM3 and ZINDO, respectively.

RESULTS AND DISCUSSION

In order to find difference in the conjugation effect of the bridging group between pyridinium and (dimethylamino)phenyl groups, UV-Vis absorption spectra of cations **7** through **10** were compared for iodide in methanol (Fig. 3). About absorption maximum wavelength

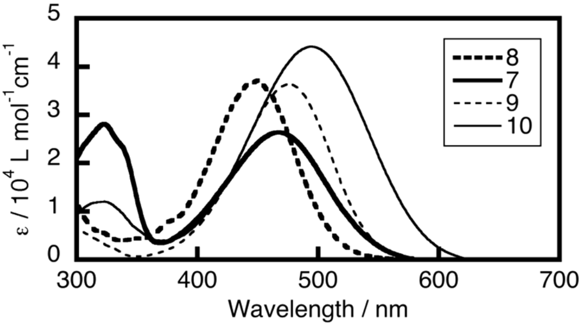


FIGURE 3 UV-Vis spectra of cations **7** through **10** in methanol. All cations were measured in iodide form.

(λ_{max}) in visible region, bathochromic shift of the triple-bond system (from **8** to **7**) is 18 nm, which is the same as the shift in the double-bond system (from **9** to **10**). Namely, similar bathochromic effect originated from conjugation number was observed for both multiple-bond systems. On the other hand, molar extinction coefficient at λ_{max} (ε_{max}) decrease in the triple-bond system (from **8** to **7**) by 29% while ε_{max} increase in the double-bond system (from **9** to **10**) by 24%. In addition to this opposite tendency, **7** shows relatively large absorption at 323 nm whose ε_{max} is larger than that at 468 nm. This difference can be explained by relative stability of the planer structure of the π-conjugation systems compared with the non-planer structures. By using the PM3 method, we calculated difference in heat of formation (ΔH_f) between the optimized planer structure and the structure with 90° rotation of one of the aromatic ring of the optimized structure, i.e., structures A and B in Figure 3. The ΔH_f values for **9** and **10** are 28.4 and 21.5 kJ/mol at least, respectively, indicating that planer structure A is quite stable for the double-bond system. On the other hand, ΔH_f for **8** is reduced to be 7.9 kJ/mol and that for **7** is only 2.1 kJ/mol, which is comparable to the energy of molecular thermal motion at ambient temperature, i.e., about 2.5 kJ/mol. Since triple-bond carbons have two π-orbitals crossed at right angles together with two sp-orbitals, aromatic rings can conjugate with the butadiynyl bridge even in structure B for **7** resulting in small ΔH_f. Accordingly, the structure of **7** at ambient temperature is not fixed as structure A and aromatic rings can rotate each other. When the absorption spectra of **7** calculated by ZINDO were compared between structures A and B, HOMO → LUMO transition at 478 nm for structure A was found to shift to a longer wavelength for structure B but no oscillator strength resulting in no absorption band at longer wavelength than 478 nm. Longest-wavelength absorption for structure B of **7** was calculated to be 372 nm. From these calculation results, peculiar spectral shape of **7** was considered to be due to aromatic ring rotation in methanol solution.

The β_0 values of **8**, **7**, **9** and **10** were calculated to be 190×10^{-30}, 211×10^{-30}, 240×10^{-30} and 417×10^{-30} esu, respectively. The order of β_0 values just corresponds to that of $\lambda_{\max}$ at the longest wavelength. The longer $\lambda_{\max}$ is, the larger β_0 is obtained in these compounds. Emission from the crystals stimulated by irradiation of a Nd:YAP laser is summarized in Table 2. Among synthesized thirteen compounds **7a** through **7m**, **7c**, **7e**, **7f** and **7k** showed clear SHG activity confirmed by green emission. Most of other crystals showed red emission. Since these compounds show red one-photon fluorescence and they have no absorption at 1079 nm of the laser wavelength, we think that the red emission by the laser irradiation was caused by multiphoton fluorescence.

Although PBP has the typical π-conjugation system with a donor and an acceptor for second-order nonlinear optics as mentioned above, it is also interesting for 1,4-addition solid-state polymerization to give polydiacetylenes (PDAs) for third-order NLO materials if PBP alignment is appropriate for polymerization in crystals. When polymerization occurs in the present PBP derivatives, PDAs with (dimethylamino)phenyl groups as electron donors and pyridinium groups as electron acceptors directly attached to the backbone will be obtained. When UV was irradiated to the crystals at ambient temperature, no color changes were observed indicating that photopolymerization did not proceed. On the other hand, many crystals showed an exothermic peak before melting as shown in Table 2, suggesting that thermal polymerization occurred. However, partial melting was observed under an optical microscope in this temperature region and this polymerization seemed to be not pure solid-state polymerization. Solid-state polymerization was reported to occur at high temperature even if butadiyne moieties are not aligned in proper conditions for 1,4-addition in some

TABLE 2 Temperature of Exo- or Endo-Thermic Peaks Observed by DTA and Emission Observed by Nd:YAP Laser Irradiation

Compound	**7a**	**7b**	**7c**	**7d**	**7e**	**7f**	**7g**	**7h**	**7i**	**7j**	**7k**	**7l**	**7m**
Temperature/°C	211[a]	234[a]	228[a]	185[b]	228[a]	196[a]	213[a]	219[a]	223[a]	246[a]	180[a]	232[a]	211[b]
Emission[c]	–	R	G	R	G	G	R	R	R	R	G	R	R

[a] Onset of an exothermic peak.

[b] Onset of an endothermic peak followed by an exothermic peak.

[c] G: Green emission due to SHG, R: Red emission due to multiphoton fluorescence.

cases [9]. Thus, in the present cases, such polymerization was initiated at high temperature below melting point and exothermic polymerization reaction resulted in partial melting.

In conclusion, PBP derivatives, which are potential compounds for both second- and third-order NLO applications, were successfully synthesized. Peculiar absorption spectrum of **7a** in methanol, in which $\varepsilon_{\max}$ decrease although $\lambda_{\max}$ is red-shifted compared with iodide of **8**, was explained by aromatic-ring rotation of **7** in methanol. As a second-order NLO materials, several SHG active crystals were found. Their crystal growth for crystallographic analysis is being progressed. From the thermal study, most of PBP derivatives were found to show exothermic reaction before melting. However, it was not pure solid-state polymerization because partial melting was observed in the exothermic reaction. Further anion exchange to control PBP arrangement seems to be interesting to obtain efficient second-order NLO crystals and solid-state polymerizable crystals. Another possible way to obtain PDAs is hydrogen-bond complex formation [10] of PBP precursor **6**. These studies are in progress.

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