Preparation and Crystal Structures of 4-(4′-Pyridylthio)-1-methylpyridinium Salts: Assembly of a Donor–Acceptor-Type Molecule Containing a Sulfide Bridge

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A series of ionic 4-(4′-pyridylthio)-1-methylpyridinium salts with different counteranions (*1*, I$^-$; *2*, BF$_4^-$; *3*, PF$_6^-$; and *4*, OTf$^-$, where OTf = trifluoromethanesulfonate) have been prepared. Structural analysis reveals that the cation exhibits a variety of stacking structures dependent on the anion. Compound *1* crystallizes in space group $P2_{1/n}$ (#14), with $a = 10.764(3)$ Å, $b = 9.601(5)$ Å, $c = 13.105(3)$ Å, $\beta = 108.35(2)$, $V = 1285.4(8)$ Å^3, and $Z = 4$. In this compound, each cation moiety is stacked in a helical arrangement along the *c*-axis. Compound 2, which is isomorphous to 1, has space group $P2_{1/n}$ (#14), with $a = 11.647(2)$ Å, $b = 9.203(3)$ Å, $c = 13.232(2)$ Å, $\beta = 108.42(2)$, $V = 1345.6(5)$ Å^3, and $Z = 4$. Compound 3 crystallizes in space group $P2_{1/n}$ (#14), with $a = 8.06(1)$ Å, $b = 17.43(1)$ Å, $c = 10.30(1)$ Å, $\beta = 103.0(1)$, $V = 1410(3)$ Å^3, and $Z = 4$. In this salt, the cation molecules assume a head-to-tail stacking arrangement, forming a polar pseudo 1-D chain. Compound 4 crystallizes in space group $P\bar{1}$ (#2), with $a = 7.585(4)$ Å, $b = 15.443(7)$ Å, $c = 6.775(4)$ Å, $\alpha = 99.33(4)$, $\beta = 108.35(2)°$, $\gamma = 98.37(4)$, $V = 756.6(7)$ Å^3, and $Z = 2$. The structure of 4 consists of a columnar stacking of pyridine moieties, with the cation moieties surrounded by the counteranions. Calculations show that the 4-(4′-pyridylthio)-1-methylpyridinium cation may be a good building block for second harmonic generation (SHG) materials, even though salts 1–4 crystallized in centrosymmetric structures and were SHG inactive.   © 2002 Elsevier Science (USA)

*Key Words:* pyridinium cation; crystal engineering; hyperpolarizability calculation.

INTRODUCTION

In recent years, crystal engineering of supramolecular assemblies, using specific intermolecular interactions such as hydrogen bonds or charge transfer forces, has attracted

special attention (1, 2). One of the potential applications of crystal engineering is in the design of organic nonlinear optical (NLO) devices (3,4). Typical examples of organic second harmonic generation (SHG) materials are methyl-4-nitrophenylsulfide (MNS) (5), 3-methyl-4-nitropyridine-1-oxide (POM) (6), and 4-*N*,*N*-dimethylamino-4′-N′-methyl stilbazolium tosylate (DAST) (7). To achieve a high SHG activity, a large second-order hyperpolarizability (β) of the constituent molecule and a polar orientation in the bulk crystal are required (3–8). Recently, organic salts containing the alkylpyridinium group, such as stilbazolium cations, have received much attention, because of their higher heat resistivity versus neutral compounds, and of their usefulness in engineering the molecules into noncentrosymmetric alignment by virtue of complexation with a variety of counterions (9–11).

We focus here on the packing arrangements of the 4-(4′-pyridylthio)-1-methylpyridinium cation in the solid state (Scheme 1). Assembled structures of the sulfur-bridged molecules are of interest from the viewpoint of crystal engineering, because of the twisted molecular conformation (12,13). We have recently reported various supramolecular compounds showing interesting structures based on aromatic disulfides (14,15). The present cation, containing both donor and acceptor moieties, is a possible candidate for SHG materials. An example of 4-amino-4′-nitrodiphenylsulfide (ANDS) is known as a sulfur-bridged SHG-active compound, which is represented as (donor)–S–(acceptor) (16). The donor···acceptor intermolecular interactions, if any, may be advantageous for realizing noncentrosymmetric molecular arrangements in the solid state. We report herein the crystal structures of a series of 4-(4′-pyridylthio)-1-methylpyridinium salts with different counteranions (*1*, I$^-$; *2*, BF$_4^-$; *3*, PF$_6^-$; and *4*, OTf$^-$, where OTf = trifluoromethanesulfonate). We also report the absorption properties and the estimated β-value of the cation.

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$X = I, BF_4, PF_6, OTf$
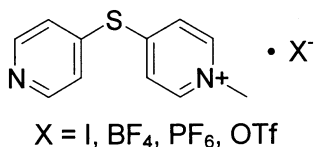
SCHEME 1.

EXPERIMENTAL

General methods. All chemicals and solvents used for the synthesis were commercially available. NMR spectra were recorded on a Bruker AC250 spectrometer. IR spectra were recorded in the range 4000–200 cm^{-1} on a JASCO FT-IR 230 spectrometer using KBr pellets as matrix. UV-vis spectra were recorded in the range 200–800 nm on a JASCO V-570 spectrophotometer. The absorption maxima (λ_{max}) and absorption cut-off ($\lambda_{cut-off}$) wavelengths were measured in methanol solutions of 0.5×10^{-4} mol dm^{-3} and 3.3×10^{-3} mol dm^{-3}, respectively. The solid state UV–vis spectra were measured by the transmission method as KBr pellets. Elemental analyses were performed by using a Yanagimoto C-H-N corder (MT-3). Molecular orbital calculations were carried out using the Fujitsu WinMO-PAC V. 2.0 and MOS-F program packages (17,18). The PM3 parametrization was used for optimizing geometric structures, and the β values for the second harmonic generation (SHG) were calculated by means of the semiempirical INDO/S method.

Preparation of $[(PySPy^+Me)I^-]$ (**1**). Iodomethane (2.8 ml, 45 mmol) was added in one portion to a solution of 4,4′-dipyridylsulfide (1.7 g, 9.0 mmol) in 50 ml of methanol at room temperature, and the solution was stirred for 3 days. The orange reaction solution was concentrated to 5 ml by vacuum evaporation, followed by the addition of CH$_2$Cl$_2$ (200 ml) to precipitate a yellow crystalline solid of *N,N′*-dimethyl-4,4′-thiobispyridinium diiodide (0.66 g, 15%) (19). The precipitate was removed by filtration, and the filtrate was concentrated to about 30 ml under reduced pressure, followed by the addition of hexane to precipitate the pale yellow solid of **1** (1.8 g, 59%). X-ray crystals were grown by slow evaporation of a CH$_2$Cl$_2$ solution at ambient temperature. ^{1}H NMR (ppm), DMSO, 8.80 (d, 2H, $J_{HH} = 6.0$ Hz), 8.70 (d, 2H, $J_{HH} = 6.8$ Hz), 7.83 (d, 2H, $J_{HH} = 7.0$ Hz), 7.72 (d, 2H, $J_{HH} = 6.0$ Hz), 4.21 (s, 3H). IR (cm^{-1}) 3055, 3016, 1626, 1567, 1099, 836, 822, and 710. UV/vis (λ_{max}/nm), MeOH, 203.0, 221.0, 270.0 (sh), 296.0. Anal. Calcd for C$_{11}$H$_{11}$N$_2$IS: C, 40.01; H, 3.36; N, 8.48. Found: C, 39.71; H, 3.34; N, 8.41.

N,N′-dimethyl-4,4′-thiobispyridiniium bisiodide (19). ^{1}H NMR (ppm), DMSO, 8.86 (d, 4H, $J_{HH} = 5.6$ Hz), 8.17 (d,

4H, $J_{HH} = 5.9$ Hz), 4.27 (s, 6H). IR (cm^{-1}) 3012, 1624, 1550, 1493, 1466, 1222, 1194, 1092, 831, 812, and 482. Anal. Calcd for C$_{12}$H$_{14}$N$_2$I$_2$S: C, 30.53; H, 2.99; N, 5.93. Found: C, 30.65; H, 2.93; N, 5.91.

Preparation of $[(PySPy^+Me)BF_4^-]$ (**2**). To a solution in a Schlenk flask containing 110 mg (3.3×10^{-1} mmol) of **1** in 50 ml of CH$_2$Cl$_2$ was added 78 mg (4.0×10^{-1} mmol) of AgBF$_4$. The reaction mixture was stirred at room temperature for 12 h in the dark. The solid AgI was filtered off and the filtrate was concentrated to about 10 ml under reduced pressure, followed by the addition of diethyl ether to precipitate the anion-exchanged salt. Collection by filtration and drying under vacuum gave an off-white crystalline solid of **2** (50 mg, 52%). X-ray crystals were grown by slow diffusion of diethyl ether into **2** dissolved in CH$_2$Cl$_2$ at ambient temperature. Because this complex was found to be isomorphous with **1**, no detailed X-ray analyses were performed. IR (cm^{-1}) 3060, 3015, 1629, 1570, 1101, 1064, 1039, 826, and 493. UV/vis (λ_{max}/nm), MeOH, 203.0, 230.0, 270.0 (sh), 296.0. Anal. Calcd for C$_{11}$BF$_4$H$_{11}$N$_2$S: C, 45.45; H, 3.82; N, 9.66. Found: C, 45.41; H, 3.84; N, 9.56.

Preparation of $[(PySPy^+Me)PF_6^-]$ (**3**). The procedure is similar to that described for the preparation of **2**, except 101 mg (4.0×10^{-1} mmol) of AgPF$_6$ was used instead of AgBF$_4$. The off-white solid of **3** was obtained in a yield of 12%. X-ray crystals were grown by slow diffusion of diethyl ether into **3** dissolved in CH$_2$Cl$_2$ at ambient temperature. IR (cm^{-1}) 3123, 3052, 1627, 1571, 1494, 1404, 887, 832, and 557. UV/vis (λ_{max}/nm), MeOH, 230.0, 265.0 (sh), 298.0. Anal. Calcd for C$_{11}$F$_6$H$_{11}$N$_2$PS: C, 37.93; H, 3.18; N, 8.05. Found: C, 32.27; H, 2.80; N, 6.84. The found values match the calculated values for a AgPF$_6$ contamination of 17 %: C, 32.42; H, 2.72; N, 6.88.; AgPF$_6$ was hard to remove from the reaction product because of the similar solubilities.

Preparation of $[(PySPy^+Me)Otf]$ (**4**). The procedure is similar to that described for the preparation of **2**, except 103 mg (4.0×10^{-1} mmol) of AgOTf was used instead of AgBF$_4$. The off-white solid of **4** was obtained in a yield of 90%. IR (cm^{-1}) 3123, 3080, 3048, 1633, 1571, 1265, 1158, 1028, and 635. UV/vis (λ_{max}/nm), MeOH, 203.0, 231.0, 270.0 (sh), 296.0. Anal. Calcd for C$_{12}$F$_3$H$_{11}$N$_2$O$_3$S$_2$: C, 40.90; H, 3.15; N, 7.95. Found: C, 41.13; H, 3.11; N, 7.90.

X-ray structure analyses. All the X-ray data were collected using Mo($K\acute{a}$) radiation on the Rigaku AFC-5S four-circle diffractometer. Crystal data, data collection parameters, and analysis statistics for **1**–**4** are listed in Table 1. Selected interatomic distances and angles are given in Table 2. Crystallographic data (excluding structure factors) for the structures of **1**, **3**, and **4** have

TABLE 1
Crystallographic Data for 1, 2, 3 and 4

	1	2	3	4
Formula	$C_{11}H_{11}IN_2S$	$C_{11}H_{11}N_2SF_4B$	$C_{11}F_6H_{11}N_2PS$	$C_{12}F_3H_{11}N_2O_3S_2$
Formula weight	330.19	290.08	348.25	352.35
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
$a/\text{Å}$	10.764(3)	11.647(2)	8.06(1)	7.585(4)
$b/\text{Å}$	9.601(5)	9.203(3)	17.43(1)	15.443(7)
$c/\text{Å}$	13.105(3)	13.232(2)	10.30(1)	6.775(4)
$\alpha/°$				99.33(4)
$\beta/°$	108.35(2)	108.42(1)	103.0(1)	100.73(4)
$\gamma/°$				98.37(4)
$V/\text{Å}^3$	1285.4(8)	1345.6(5)	1410(3)	756.6(7)
Z	4	4	4	2
Space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P\bar{1}$ (#2)
$\rho_{calc}/\text{gcm}^{-1}$	1.706		1.602	1.406
μ/cm^{-1}	26.25		4.03	2.56
$2\theta_{max}/°$	55.0		55.0	55.0
Reflections measured	3284		3949	3736
Independent reflections	2944		1865	3474
R_{int}	0.039		0.023	0.021
Used in refinement	2156		2570	2479
Variables	136		226	200
$R_1{}^a$	0.033		0.052	0.056
$R_w{}^a$	0.107		0.153	0.211
S	1.33		2.20	1.80

$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 173573–173575. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44 1223 336033 or e-mail deposit@ccdc.cam.ac.uk). All calculations were performed using the teXsan crystallographic software package (20). These structures were solved by direct methods (SIR92 (21) or SHELXS-97 (22)) and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Absorption correction was applied (ψ scan). Though some of the hydrogen atoms could be located by the Fourier syntheses, all hydrogen atoms were inserted at the calculated positions using a rigid model.

TABLE 2
Selected Bond Distances (Å), Bond Angles (°) and Dihedral Angles (°) with esds in 1, 3, and 4

	1	3	4
C(3)–S	1.777(5)	1.771(4)	1.778(4)
C(8)–S	1.738(6)	1.753(3)	1.751(3)
C(11)–N(2)	1.480(7)	1.495(4)	1.484(4)
C(3)–S–C(8)	102.6(2)	104.3(2)	102.8(1)
Dihedral angle^a	70.6(2)	70.8(2)	62.4(1)

^{a} Dihedral angles between the pyridine and the pyridinium rings.

RESULTS AND DISCUSSION

A. Molecular Structures

The chemical structure of the 4-(4′-pyridylthio)-1-methylpyridinium cation is shown in Scheme 1. The ORTEP drawing of the cation showing the atom-labeling scheme is depicted in Fig. 1. Selected bond distances and angles are listed in Table 2. The cations in all the products have almost the same twisted geometries. Bond angles for C–S–C of 102.6(2), 104.3(2), and 102.8(1)° were observed for compounds 1, 3, and 4, respectively. These are typical values for aromatic disulfides, such as those found for 4-amino-4′-nitrodiphenyl sulfide (C–S–C angle = 103.9(3)°) (16) and 3,3′-dimethylthio-4,4′-diquinolinylsulfide (C–S–C angles = 105.4(1) and 104.8(1)°) (22). An elongation of the C(3)–S bond relative to the C(8)–S bond was observed in all the salts, and the differences for 1, 3, and 4 are 0.039, 0.018, and 0.027 Å, respectively. The dihedral angles between the pyridine ring and the pyridinium ring of compounds 1, 3, and 4 were 70.6(2), 70.8(2), and 62.4(1)°, respectively.

B. Crystal Structures

The crystal packing of compound 1 is shown in Fig. 2a. Each cation moiety is stacked in a helical arrangement
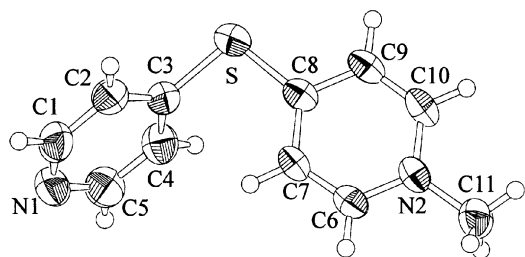
FIG. 1. ORTEP drawing of 4-(4′-pyridylthio)-1-methylpyridinium cation with the numbering scheme.

along the *c*-axis. The assembly of the cation involves face-to-face interactions, such as Py…Py, Py…Py$^+$, and Py$^+$…Py$^+$, as shown in Fig. 2b, with interplanar distances of 3.6, 3.7, and 3.5 Å, respectively. Compound **2**, which contains a slightly larger anion, is isomorphous with compound **1**.
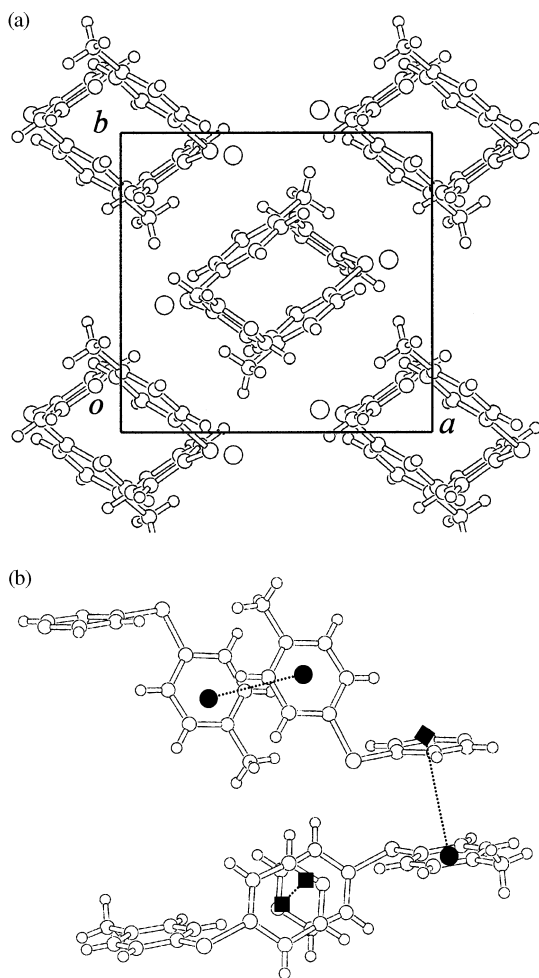

FIG. 2. (a) Packing diagram of **1** viewed along the *c*-axis. (b) Intermolecular interactions of pyridine and pyridinium moieties.
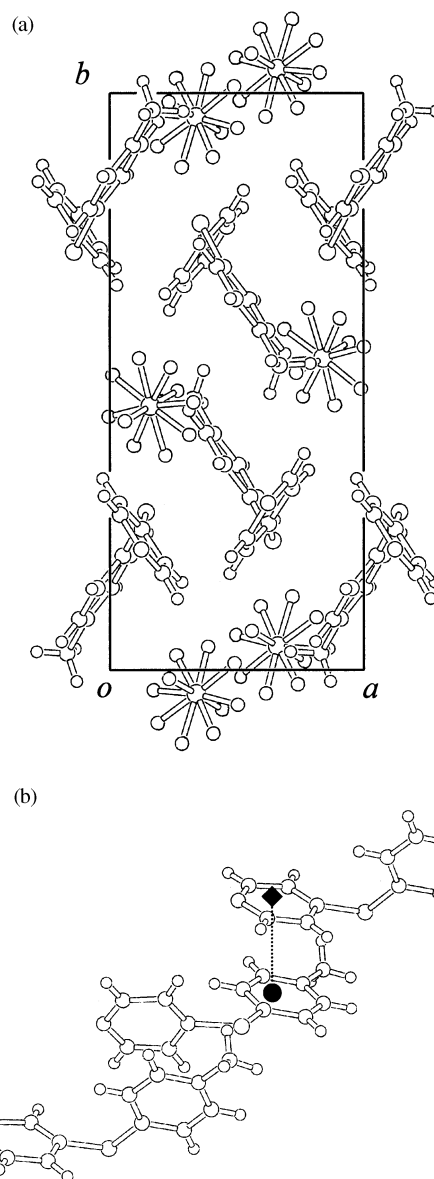

FIG. 3. (a) Packing diagram of **3** viewed along the *c*-axis. (b) Intermolecular interactions of pyridine and pyridinium moieties.

Figure 3a shows the crystal structure of compound **3**. In this salt, the cations are arranged in a head-to-tail manner, and assume a pseudo 1-D chain running along the *c*-axis. The chain involves Py…Py$^+$ face-to-face interactions with an interplanar distance of 3.5 Å. Although each chain is polar, crystals of compound **3** have a center of symmetry with a centrosymmetric space group $P2_1/n$. The PF$_6^-$ anion in this salt is disordered around the F(1)–P–F(2) axis, with a site occupancy ratio of 6:4.

The crystal structure of compound **4** is shown in Fig. 4a. The structure is characterized by the columnar stacking of pyridine rings along the *c*-axis with a Py…Py stacking distance of 3.3 Å. The pyridinium moiety is arranged as a
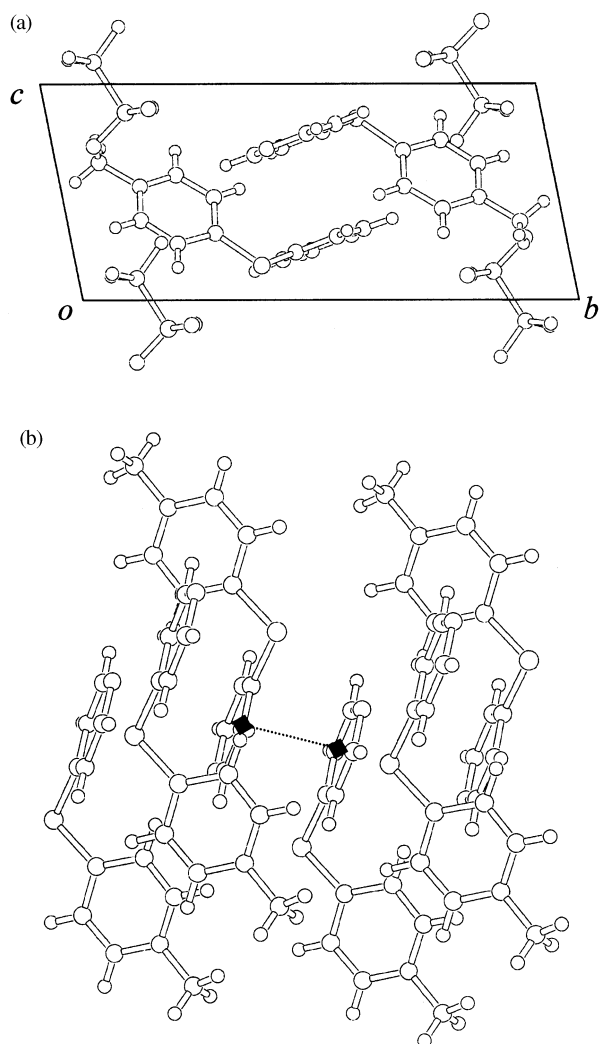
FIG. 4. (a) Packing diagram of **4** viewed along the *a*-axis. (b) Columnar staking of pyridine moieties.

pendent to the column, and is surrounded by the counter anions.

The above structural analyses show that the 4-(4′-pyridylthio)-1-methylpyridinium cation exhibits a variety of packing arrangements, depending on the anion used. The packing structure seems to be influenced by the size of the anion: the salts with small anions of I^- and BF_4^- exhibit the multidimensional π–π interactions, while the salt with a larger anion of PF_6^- shows the one-dimensional structures. Further, in the salt with the largest anion of OTf^-, the π–π interactions exist only between the Py rings. Thus, it may be concluded that a larger anion tends to inhibit intermolecular π–π interactions.

It is noted that the present cation, at least for the above combinations, showed a tendency to crystallize in centro-symmetric structures, which are essentially SHG inactive. Therefore, the so-called salt methodology to realize

noncentrosymmetric molecular arrangement (10,11) turned out to be ineffective for the present cation. To realize noncentrosymmetric structures for the present cation, it may further be necessary to introduce a hydrogen-bonding substituent such as a hydroxyl group into the molecule, because hydrogen bonding is known to be an efficient means to realize polar structures in many SHG-active materials, such as in aminopyridinium benzenesulfonate salts (9, 24) and ANDS (16).

C. Optical Spectra and Calculation of β

The UV–vis spectral data for compounds **1**–**4** are summarized in Table 3. The absorption cut-off wavelength for each salt ($\lambda_{\text{cut-off}}$) is shorter than 400 nm, and thus, the molecule is confirmed to be transparent for an incident light of a YAG laser ($\lambda = 1064$ nm). Slight red-shifts were observed for the absorption maxima (λ_{max}) in the solid state spectra, compared to those obtained in solutions. No fluorescence was observed in the solid state.

The β values for SHG were calculated by means of a Fujitsu MO software package (25,26). The estimated β value for the 4-(4′-pyridylthio)-1-methylpyridinium cation was 8.9×10^{-30} e.s.u. for an incident energy of 1.17 eV ($\lambda = 1064$ nm). The calculations showed that the contributing intramolecular charge-transfer direction was from the sulfur to the pyridinium ring, similar to the case of ANDS (16). The estimated β value of the present cation is comparable to those in SHG active aromatic sulfides such as ANDS (16) and methyl-4-nitrophenylsulfide (MNS) (5). The estimated β values for these molecules are reported to be 14.7×10^{-30} and 7.2×10^{-30} e.s.u., respectively, whereas the experimental β values are about twice the calculated values, 28×10^{-30} and 20×10^{-30} e.s.u., respectively. The estimated β value and the absorption cut-off wavelengths indicate that the 4-(4′-pyridylthio)-1-methylpyridinium cation may be a good building block for SHG materials.

CONCLUSION

The packing structures and molecular properties of a series of 4-(4′-pyridylthio)-1-methylpyridinium salts were

TABLE 3
Absorption Maxima (nm) and Cutoff (nm) for 1, 2, 3, and 4

Compounds	Solid state λ_{max}/nm	Solution state[a] λ_{max}/nm	Solution state[a] $\lambda_{\text{cut-off}}$/nm
1	302, 350	203, 221, 296	380
2	208, 312	203, 230, 296	360
3	206, 308	230, 265, 298	384
4	206, 232, 306	203, 231, 296	387

[a]λ_{max} and $\lambda_{\text{cut-off}}$ are measured in methanolic solutions of 0.5×10^{-4} mol dm^{-3} and 3.3×10^{-3} mol dm^{-3}, respectively.

investigated as possible candidates for SHG materials. It was found that several different molecular arrangements were exhibited by these salts: a helical cation arrangement in compounds **1** and **2**, a head-to-tail 1-D arrangement in compound **3**, and a columnar stacking structure in compound **4**. The estimated β values and the absorption cut-off wavelengths indicate that the cation may be a good building block for SHG materials. However, these salts crystallized in centrosymmetric space groups and were SHG inactive. Therefore, it may be necessary to introduce specific interactions such as hydrogen bonds to obtain SHG-active polar crystals using 4-(4′-pyridylthio)-1-methylpyridinium salts.

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REFERENCES

1. B. Moulton and M. J. Zaworotko, *Chem. Rev.* **101,** 1629–1658 (2001).
2. K. Tanaka, K. Endo, and Y. Aoyama, *Chem. Lett.* 887–888 (1999).
3. D. S. Chemla and J. Zyss, "Nonlinear Optical Properties of Organic Molecules and Crystals," Vol. 1. Academic Press, Orlando, 1987.
4. D. S. Chemla and J. Zyss, "Nonlinear Optical Properties of Organic Molecules and Crystals," Vol. 2, Academic Press, Orlando, 1987.
5. M. Barzoukas, D. Josse, J. Zyss, P. Gordon, and J. O. Morley, *Chem. Phys.* **139,** 359–367 (1989).
6. J. Zyss, I. Ledoux, R. B. Hierle, R. K. Raj, and J. L. Oudar, *IEEE J. Quantum Electron.* **21,** 1286–1295 (1985).
7. U. Meier, M. Bösch, C. Bosshard, and P. Günter, *Synth. Met.* **109,** 19–22 (2000).
8. X. M. Duan, H. Konami, S. Okada, H. Oikawa, H. Matsuda, and H. Nakanishi, *J. Phys. Chem.* **100,** 17780–17785 (1996).
9. Anwar, S. Okada, H. Oikawa, and H. Nakanishi, *Chem. Mater.* **12,** 1162–1170 (2000).
10. G. R. Meredith, *in* "Nonlinear Optical Properties of Organic and Polymeric Materials" (D. J. Williams, Ed.), ACS Symp. Ser. 233, p. 27. *Am. Chem. Soc.*, Washington, DC, 1983.
11. S. R. Marder, J. W. Perry, and W. P. Schaefer, *Science* **245,** 626–628 (1989).
12. L. A. Summers, *J. Heterocyclic Chem.* **24,** 533–544 (1987).
13. M. Kondo, M. Shimura, S. Noro, Y. Kimura, K. Uemura, and S. Kitagawa, *J. Solid State Chem.* **152,** 113–119 (2000).
14. R. Horikoshi, T. Mochida, and H. Moriyama, *Inorg. Chem.* **40,** 2430–2433 (2001).
15. R. Horikoshi, T. Mochida, N. Maki, S. Yamada, and H. Moriyama, *Dalton Trans.* **1,** 28–33 (2002).
16. H. Abdel-Halim, D. O. Cowan, D. W. Robinson, F. M. Wiygul, and M. Kimura, *J. Phys. Chem.* **90,** 5654–5658 (1986).
17. J. J. P. Stewart, MOPAC97, Fujitsu Ltd., Tokyo, Japan, 1998.
18. A. Matsuura, MOS-F 4.1, Fujitsu Ltd., Tokyo, Japan, 1998.
19. D. Jerchel, H. Fischer, and K. Thomas, *Chem. Ber.* **89,** 2921–2933 (1956).
20. teXsan: Crystal Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, 1985 and 1999.
21. A. Altomore, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, and G. Polidori, *J. Appl. Crystallogr.* **27,** 435 (1994).
22. G. M. Sheldrick, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.
23. K. Pluta, A. Maœlankiewicz, and T. Gowiak, *J. Cryst. Spectrosc. Res.* **23,** 285–290 (1993).
24. Anwar, X.-M. Duan, K. Komatsu, S. Okada, H. Matsuda, H. Oikawa, and H. Nakanishi, *Chem. Lett.* 247–248 (1997).
25. J. Abe and Y. Shirai, *J. Am. Chem. Soc.* **118,** 4705–4706 (1996).
26. J. Abe, Y. Shirai, N. Nemoto, and Y. Nagase, *J. Phys. Chem. B* **101,** 1910–1915 (1997).