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Second-Order Optical Nonlinearities and Photostabilities of 2-*N*-Methylstilbazolium Salts

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We have synthesized a number of 2-*N*-methylstilbazolium salts and measured their powder second harmonic generation (SHG) efficiencies. The pale yellow salt 3'-methoxy-2-*N*-methylstilbazolium triflate was found to exhibit an SHG efficiency 24 times that of a urea reference standard at 532 nm, and an X-ray diffraction study showed the crystals to be noncentrosymmetric (space group *Cc*; *a* = 18.126 (4) Å, *b* = 7.040 (1) Å, *c* = 13.315 (2) Å, *β* = 93.46 (1)°, *Z* = 4). These crystals are photochemically stable under visible irradiation. On the other hand, 2'-methoxy-2-*N*-methylstilbazolium triflate shows no SHG signal; it forms centrosymmetric crystals (space group *P*2₁/*n*; *a* = 11.999 (2) Å, *b* = 13.458 (2) Å, *c* = 11.043 (2) Å, *β* = 108.47 (1)°, *Z* = 4) that undergo photochemical 2 + 2 cycloaddition.

Introduction

To design materials with large second-order optical nonlinearities, one must attempt to achieve a large molecular hyperpolarizability (β), alignment of the molecules in the bulk material such that the hyperpolarizability is effectively used, and transparency in the visible region of the spectrum (for near-IR frequency conversion).[1] In this regard we and others have explored the use of unconventional donors such as the $BrC_6H_4^-$,[2,3] pyrenyl,[3] and ferrocenyl[4] moieties with surprising success.

Many chromophores that have been examined for second-order nonlinear optical properties are among the classes of 1,4-disubstituted benzenes, 4,4'-disubstituted stilbenes, and 4,4'-disubstituted tolanes. Their dipole moments and their approximately linear shapes apparently cause most compounds in these classes to crystallize in centrosymmetric space groups. One strategy employed to encourage noncentrosymmetric crystallization of neutral dipolar organic chromophores is to increase their geometrical asymmetry by introducing a substituent in the ortho or meta position of one of the aromatic rings. An alternative approach first explored by Meredith[5] and more recently by us[3] involves the use of ionic chromophores whose counterions can be metathesized, allowing one to vary the orientation of the chromophore in the crystal lattice. In this manner, Meredith[5] and we[3] have demonstrated that a variety of 4-*N*-methylstilbazolium salts can give rise to large powder SHG efficiencies when combined with the correct counterion. These preliminary results suggested that this technique is a promising approach for the synthesis of new materials with large bulk second-order optical nonlinearities. Here we have attempted to further define the scope and limitations of this methodology by studying a number of analogous 2-*N*-methylstilbazolium salts in which the cations are substantially more asymmetric than are the roughly linear 4-*N*-methylstilbazolium ions.

Experimental Section

General Considerations. Reagent grade methanol, acetone, diethyl ether, and dichloromethane were purchased from Fisher

Table I. Summary of Yields for Compounds of the Form $(CH_3)NC_5H_4CH=CHX^+Y^-$

compound	amt, g	% yield
for X = $4\text{-}C_6H_4OCH_3$		
triflate	0.88	40
for X = $4\text{-}C_6H_4\overline{NCH_2CH_2CH_2CH_2}$		
triflate	1.41	78
for X = $4\text{-}C_6H_4N(CH_3)_2$		
triflate	1.69	75
for X = $2,4\text{-}C_6H_3(OCH_3)_2$		
triflate	1.42	65
for X = $2\text{-}C_6H_4OCH_3$		
triflate	0.88	52
for X = $C_5H_5FeC_5H_4$		
triflate	1.88	71
tosylate	0.83	97

Scientific. Methyl tosylate (97%), piperidine (99%), methyl triflate, tetrabutylammonium bromide (97%), tetrabutylammonium iodide (98%), 2-picoline (98%), and sodium tetrafluoroborate were obtained from Aldrich Chemical Co. and were used without purification. Tetrabutylammonium chloride hydrate (97%) was obtained from Fluka Chemie and was used without purification. $[^2H_6]$acetone (99.9% ^2H) and $[^2H_4]$methanol (99.8% ^2H) were obtained from Cambridge Isotope Laboratories and were used without purification. The 2-*N*-methylpicolinium triflate and tosylate salts were prepared by reaction of 2-picoline with methyl triflate and methyl tosylate, respectively, in dichloromethane. Precipitation with ether and isolation by filtration yielded the desired products as white crystalline materials, which were used without further purification.

^1H spectra were recorded on a Bruker AM-500 spectrometer. Chemical shifts were referenced to the chemical shift of the residual protons of the solvent with respect to tetramethylsilane. UV–visible spectra were recorded on a Hewlett-Packard 8154A diode array spectrophotometer. Elemental analyses were performed at the California Institute of Technology.

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[‡] Contribution no. 8126.

(1) See, for example: (a) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690. (b) *Nonlinear Optical Properties of Organic and Polymeric Materials*; Williams, D. J., Ed.; ACS Symposium Series 233; American Chemical Society: Washington, DC, 1983. (c) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: Orlando, 1987; Vols. 1 and 2.
(2) (a) Tam, W.; Wang, Y.; Calabrese, J. C.; Clement, R. A. Nonlinear Optical Properties of Organic Materials. *Proc. SPIE* **1988**, *971*, 107.
(3) Marder, S. R.; Perry, J. W.; Schaefer, W. P. *Science* **1989**, *245*, 626.
(4) Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bandy, J. A.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *Nature* **1987**, *330*, 360.
(5) Meredith, G. In ref 1b, p 27.

Table II. NMR Characterization of Compounds of the Form $(CH_3)NC_5H_4CH=CHX^+CF_3SO_3^-$ (Hydrogen-Labeling Scheme in Figure 1)

for X = 2-$C_6H_4OCH_3$: ^1H NMR (CD_3COCD_3) δ 9.00 (d, J = 6.1 Hz, 1 H, H_a), 8.59 (t, J = 7.9 hz, 1 H, H_c), 8.55 (d, J = 7.0 Hz, 1 H, H_d), 8.08 (d, J = 16.1 Hz, 1 H, H_f), 7.99 (td, J = 6.8, 1.6 Hz, 1 H, H_b), 7.85 (dd, J = 7.7, 1.6 Hz, 1 H, =CHCCH), 7.80 (d, J = 16.1 Hz, 1 H, H_e), 7.49 (td, J = 7.9, 1.6 Hz, 1 H, CHCHCO), 7.17 (d, J = 8.1 Hz, 1 H, CHCO), 7.06 (t, J = 7.3 Hz, 1 H, CHCHCHCO), 4.60 (s, 3 H, Hg), 3.99 (s, 3 H, OCH_3)

for X = 3-$C_6H_4OCH_3$: ^1H NMR (CD_3COCD_3) δ 9.00 (d, J = 6.2 Hz, 1 H, H_a), 8.58 (m, 2 H, H_c and H_d), 7.99 (td, J = 6.2, 3.5 Hz, 1 H, H_b), 7.95 (d, J = 16.0 Hz, 1 H, H_f), 7.77 (d, J = 16.1 Hz, 1 H, H_e), 7.42 (m, 3 H), 7.06 (dt, J = 6.9, 2.4 Hz, 1 H), 4.62 (s, 3 H, H_g), 3.86 (s, 3 H, OCH_3)

for X = 4-$C_6H_4OCH_3$: ^1H NMR (CD_3COCD_3) δ 8.94 (d, J = 6.1 Hz, 1 H, H_a), 8.56 (dd, J = 8.2, 1.7 Hz, 1 H, H_d), 8.53 (t, J = 7.9 Hz, 1 H, H_c), 7.97 (d, J = 16.0 Hz, 1 H, H_f), 7.92 (td, J = 6.7, 1.8 Hz, 1 H, H_b), 7.84 (d, J = 8.8 Hz, 2 H, CHCHCO), 7.61 (d, J = 15.9 Hz, 1 H, H_e), 7.05 (d, J = 8.9 Hz, 2 H, CHCO), 4.58 (s, 3 H, H_g), 3.87 (s, 3 H, OCH_3)

for X = 4-$\overline{C_6H_4NCH_2CH_2CH_2}$: ^1H NMR (CD_3COCD_3) δ 8.55 (d, J = 6.3 Hz, 1 H, H_a), 8.34 (d, J = 8.2 Hz, 1 H, H_d), 8.24 (t, J = 7.8 Hz, 1 H, H_c), 7.83 (d, J = 15.6 Hz, 1 H, H_f), 7.66 (d, J = 8.8 Hz, 2 H, CHCHCN), 7.57 (t, J = 6.5 Hz, 1 H, H_b), 7.15 (d, J = 15.6 Hz, 1 H, H_e), 6.64 (d, J = 8.8 Hz, 2 H, CHCN), 4.28 (s, 3 H, Hg), 3.39 (m, 4 H, NCH_2), 2.06 (m, 4 H, NCH$_2CH_2$)

for X = 4-$C_6H_4N(CH_3)_2$: ^1H NMR (CD_3COCD_3) δ 8.58 (d, J = 6.4 Hz, 1 H, H_a), 8.36 (d, J = 8.5 Hz, 1 H, H_d), 8.27 (t, J = 7.9 Hz, 1 H, H_c), 7.84 (d, J = 15.7 Hz, 1 H, H_f), 7.67 (d, J = 9.0 Hz, 2 H, CHCHCN), 7.61 (t, J = 6.7 Hz, 1 H, H_b), 7.20 (d, J = 15.6 Hz, 1 H, H_e), 6.79 (d, J = 8.8 Hz, 2 H, CHCN), 4.30 (s, 3 H, H_g), 3.07 (s, 6 H, NCH_3)

for X = 2,4-$C_6H_3(OCH_3)_2$: ^1H NMR (CD_3COCD_3) δ 8.92 (d, J = 6.3 Hz, 1 H, H_a), 8.50 (m, 2 H, H_c and H_d), 8.04 (d, J = 16.0 Hz, 1 H, H_f), 7.89 (td, J = 6.2, 2.8 Hz, 1 H, H_b), 7.80 (d, J = 8.6 Hz, 1 H, =CHCCH), 7.66 (d, J = 16.0 Hz, 1 H, H_e), 6.70 (d, J = 2.4 Hz, 1 H, OCCHCO), 6.66 (dd, J = 8.6, 2.4 Hz, 1 H, CHCHCO), 4.54 (s, 3 H, H_g), 4.00 and 3.89 (both s, 3 H, OCH_3's)

for X = $C_5H_4FeC_5H_5$: ^1H NMR (CD_3COCD_3) δ 8.85 (d, J = 6.0 Hz, 1 H, H_a), 8.53 (d, J = 8.2 Hz, 1 H, H_d), 8.45 (t, J = 7.6 Hz, 1 H, H_c), 7.97 (d, J = 15.6 Hz, 1 H, H_f), 7.85 (t, J = 6.5, Hz, 1 H, H_b), 7.25 (d, J = 15.6 Hz, 1 H, H_e), 4.86 and 4.61 (each t, J = 1.8 Hz, 2 H, η-C_5H_4 protons), 4.47 (s, 3 H, H_g), 4.26 (s, 5 H, η-C_5H_5)

Table III. Elemental Analyses of Compounds of the Form $(CH_3)NC_5H_4CH=CHX^+Y^-$

for X = 2-$C_6H_4OCH_3$, triflate: Anal. Calcd for $C_{16}H_{16}F_3NO_4S$: C, 51.20; H, 4.30; N, 3.73. Found: C, 51.46; H, 4.36; N, 3.78.

for X = 3-$C_6H_4OCH_3$, triflate: Anal. Calcd for $C_{16}H_{16}F_3NO_4S$: C, 51.20; H, 4.30; N, 3.73. Found: C, 51.17; H, 4.26; N, 3.73.

for X = 4-$C_6H_4OCH_3$, triflate: Anal. Calcd for $C_{16}H_{16}F_3NO_4S$: C, 51.20; H, 4.30; N, 3.73. Found: C, 51.33; H, 4.30; N, 3.73.

for X = 4-$\overline{C_6H_4NCH_2CH_2CH_2CH_2}$, triflate: Anal. Calcd for $C_{19}H_{21}F_3N_2O_3S$: C, 55.06;, H, 5.11; N, 6.76. Found: C, 55.16; H, 5.14; N, 6.79.

for X = 4-$C_6H_4N(CH_3)_2$, triflate: Anal. Calcd for $C_{17}H_{19}F_3N_2O_3S$: C, 52.57; H, 4.93; N, 7.21. Found: C, 52.57; H, 4.93; N, 7.23. BF_4: Anal. Calcd for $C_{16}H_{19}BF_4N_2$: C, 58.92; H, 5.87; N, 8.59. Found: C, 58.80; H, 5.85; N, 8.64.

for X = 2,4-$C_6H_3(OCH_3)_2$, triflate: Anal. Calcd for $C_{17}H_{18}F_3NO_5S$: C, 50.37; H, 4.48; N, 3.46. Found: C, 50.23; H, 4.59; N, 3.48.

for X = $C_5H_5FeC_5H_4$, triflate: Anal. Calcd for $C_{19}H_{18}F_3FeNO_3S$: C, 50.35; H, 4.00; N, 3.09. Found: C, 50.48; H, 4.07; N, 3.13. tosylate: Anal. Calcd for $C_{25}H_{25}FeNO_3S$: C, 63.16; H, 5.30; N, 2.95. Found: C, 63.10; H, 5.42; N, 3.06. I: Anal. Calcd for $C_{18}H_{18}FeIN$: C, 50.15; H, 4.21; N, 3.25. Found: C, 50.20; H, 4.26; N, 3.28. Br: Anal. Calcd for $C_{18}H_{18}BrFeN$: C, 56.29; H, 4.72; N, 3.865. Found: C, 55.82; H, 4.83; N, 3.64.

Synthesis. The salts in this paper were prepared as described by Phillips.[6] An illustrative example is shown below.

(*E*)-{1-(3-Methoxyphenyl)-2-(2-*N*-methylpyridiniumyl)-ethylene} triflate, 3-$CH_3OC_6H_4CHO$ (1.5 g, 11 mmol), was reacted with (2)-$CH_3C_5H_4NCH_3CF_3SO_3^-$ (1.45 g, 5.64 mmol) in methanol (20 mL) in the presence of piperidine (2 mL) at 60 °C, for 4 h. Addition of ether to the yellow solution yielded (*E*)-{1-(3-methoxyphenyl)-2-(4-*N*-methylpyridiniumyl)ethylene} triflate, which was isolated by filtration and washed with ether (1.11 g, 52% yield). In a similar manner the compounds whose yields are given in Table I were prepared.

Conversion of (*E*)-{1-ferrocenyl-2-(2-*N*-methylpyridiniumyl)ethylene} triflate to the iodide and bromide salts: Tetrabutylammonium iodide or bromide (0.2 M) in acetone was added dropwise with stirring to a nearly saturated solution of the (*E*)-{1-ferrocenyl-2-(2-*N*-methylpyridiniumyl)ethylene} triflate salt in acetone, yielding a precipitate. The addition was continued until an additional drop afforded no more precipitate. The precipitate was isolated by filtration and washed with acetone and dried.

Conversion of (*E*)-{1-(4-(dimethylamino)phenyl)-2-(2-*N*-methylpyridiniumyl)ethylene} triflate to the tetrafluoroborate salt: Tetrabutylammonium chloride (0.2 M) in acetone was added dropwise with stirring to a nearly saturated solution of the (*E*)-{1-(4-(dimethylamino)phenyl)-2-(2-*N*-methylpyridiniumyl)ethylene} triflate salt in acetone, yielding a precipitate. The addition was continued until an additional drop afforded no more precipitate. The precipitate was isolated by filtration and dissolved in water. Addition of a saturated aqueous

solution of sodium tetrafluoroborate yielded a precipitate that was isolated by filtration, washed with water, and dried. The material was purified by recrystallization from acetone/diethyl ether.

NMR characterizations and elemental analyses of stilbazolium salts are given in Tables II and III, respectively.

Solution photolysis of 2'-methoxy-2-*N*-methylstilbazolium triflate (4): A CD_3COCD_3 solution of 4 in a Pyrex NMR tube was photolyzed with a 450-w high-pressure mercury vapor Hanovia lamp for 2 h. A clean trans-to-cis isomerization was observed, forming 5 in greater than 90% yield: ^1H NMR (CD_3COCD_3) δ 9.12 (d, J = 6.1 Hz, 1 H, H_a), 8.38 (t, J = 8.1 Hz, 1 H, H_c), 8.02 (t, J = 6.7 Hz, 1 H, H_b), 7.71 (d, J = 8.0 Hz, 1 H, H_d), 7.42 (d, J = 12.1 Hz, 1 H, H_f), 7.35 (t, J = 7.8, Hz, 1 H, CHCHCO), 7.17 (d, J = 7.7 Hz, 1 H, CHCHCHCO), 7.01 (d, J = 8.8 Hz, 1 H, CHCO), 6.98 (d, J = 12.3 Hz, 1 H, H_e) 6.85 (t, J = 7.5 Hz, 1 H, CHCHCHCO), 4.54 (s, 3 H, NCH_3), 3.67 (s, 3 H, OCH_3).

Solid-state photolysis of 4: A rapidly stirred slurry of 4 (0.100 g, 0.27 mmol) in hexane (20 mL) was photolyzed with a 450-W high-pressure mercury vapor Hanovia lamp for 2 h. The resulting white solid, **6a**, was isolated by filtration and was washed with acetone/ether (0.070 g 70%): ^1H NMR (CD_3OD) δ 8.74 (d, J = 6.1 Hz, 2 H, CHCN), 8.36 (td, J = 8.0, 1.2 Hz, 2 H, CHCHCHCN), 8.23 (dd, J = 7.2, 0.9 Hz, 2 H, CHCHCHCHCN), 7.80 (td, J = 7.5, 1.3 Hz, 2 H, CHCHCN), 7.45 (dd, J = 7.6 1.5 Hz, 2 H, CHCHCHCHCO), 7.24 (td, J = 8.8, 1.5 Hz, 2 H, CHCHCO), 6.94 (td, J = 8.4, 1.2 Hz, 2 H, CHCHCHCO), 6.85 (d, J = 7.9 Hz, 2 H, CHCHCHCHCO), 5.33 and 5.29 (each two protons of AA'BB' pattern, $J_{AB_{cis}}$ = 9.0 Hz, $J_{AB_{trans}}$ = 10.5 Hz, $J_{AA'}$ = $J_{BB'}$ = 3.5 Hz, 4 H cyclobutane H), 4.31 (s, 6 H, H_g), 3.73 (s, 6 H OCH_3).

Powder SHG measurements: Powder SHG efficiencies were determined by using 1064- (SH at 532 nm) and 1907-nm funda-

(6) Phillips, A. P. *J. Org. Chem.* **1947**, *12*, 333.

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**Table IV. Crystallographic Data for
3′-Methoxy-2-N-methylstilbazolium Triflate, 2, and
2′-Methoxy-2-N-methylstilbazolium Triflate, 4**

|	2	4
formula	$C_{15}H_{16}NO\cdot CF_3SO_3$	$C_{15}H_{16}NO\cdot CF_3SO_3$
formula wt	397.37	397.37
space group	Cc (No. 9)	$P2_1/n$ (No. 14)
a, Å	18.126 (4)	11.999 (2)
b, Å	7.040 (1)	13.458 (2)
c, Å	13.315 (2)	11.043 (2)
β, deg	93.46 (1)	108.47 (1)
vol, Å^3	1696.0 (5)	1691.4 (6)
Z; ρ_{calc}, g cm^{-3}	4; 1.470	4; 1.474
no. of reflns; GOF	1493; 3.87	935; 2.15
no. of $F_o{}^2 > 0$; R_F	1464; 0.041	868; 0.029
no. of $F_o{}^2 > 3\sigma(F_0{}^2)$; R_F	1414; 0.040	798; 0.025
T, °C	22	23
λ, Å	0.71073	0.71073
μ, cm^{-1}	2.5	2.5

**Table V. Summary of Powder SHG Values for Compounds of
the Form 2-(CH₃)NC₅H₄CH=CHX⁺Y⁻ (Values Relative to Urea;
Values Less Than 0.5 Times That of Urea Set to Zero)**

compound	1064 nm	1907 nm
X = p-C₆H₄OCH₃		
triflate	0	0
X = p-C₆H₄NCH₂CH₂CH₂CH₂		
triflate	0	0
X = p-C₆H₄N(CH₃)₂		
triflate	0	0
BF₄	0	0
X = 2,4-C₆H₃(OCH₃)₂		
triflate	0	0
X = 2-C₆H₄OCH₃		
triflate	0	0
X = 3-C₆H₄OCH₃		
triflate	24	30
X = C₅H₅FeC₅H₄		
triflate		0
tosylate		0
I		13
Br		1

mental radiation (SH at 953.5 nm) to avoid absorption of the SH by the dark-colored salts. The 1907-nm light was obtained by Raman shifting (first Stokes line of H₂) the 1064-nm output of a Q-switched Nd:YAG laser. The powder SHG measurements were made using the Kurtz powder method.[7] A dual-beam system (using a urea sample in the reference arm) was used to normalize the SH signals for laser shot-to-shot fluctuations. Pulse energies used were in the range 100–500 μJ with spot sizes of 2–3 mm. The diffusely backscattered SH signals were collected and isolated by using filters and a monochromator and detected by using photomultiplier tubes (Hamamatsu R406) whose outputs were amplified and integrated by using 10-ns gate widths. Samples were ground, unsized microcrystalline powders; particle sizes were estimated to range from about 40 to 150 μm. Given the typically broad range of sizes and the possibility of preferential orientation of particles in assembling the samples, the uncertainties in the measured efficiencies can be quite large, perhaps a factor of 2 or more.

Crystal structure determinations: Crystals of 2 and 4 were grown by vapor diffusion of ether into nearly saturated acetone solutions of the compounds and were glued with epoxy to glass fibers. To protect 4 from light, it was coated with India ink. Two equivalent data sets were collected, corrected for a slight decay, and reduced to structure factors. The crystal of 4 proved to be a twin; we collected many worthless data and later had to correct reflections where the twin (about 16% as large as the parent) and the parent reflections superimposed; details are given in the supplementary material (see paragraph at end of paper). The structures were solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms were included

(7) Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798.
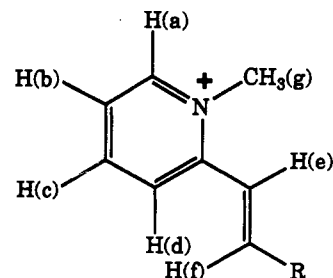
Figure 1. Labeling scheme for hydrogens for 2-stilbazolium salts.
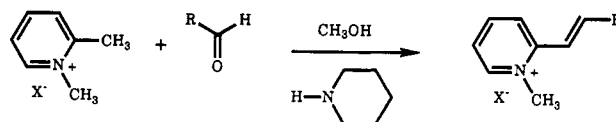
Figure 2. General synthesis of 2-stilbazolium salts.

in the structure factors at calculated positions or, for the methyl groups, at idealized positions based on difference maps calculated in their expected planes. These parameters were refined for 2 but because of a low data:parameter ratio were kept fixed for 4 (Table IV). The final difference maps had features of +0.33 e Å^{-3} (near the triflate oxygens) and −0.20 e Å^{-3} (near nothing) for 2 and featureless excursions of +0.14 and −0.10 e Å^{-3} for 4. Data are summarized in Table IV.

Calculations were done with programs of the CRYM crystallographic computing system, MULTAN, and ORTEP. Scattering factors and corrections for anomalous scattering were taken from a standard reference.[8] $R = \sum|F_o - |F_c||/\sum F_o$, for only $F_o{}^2 > 0$, and the goodness of fit is $[\sum w(F_o{}^2 - F_c{}^2)^2/(n - p)]^{1/2}$, where n is the number of data (2, 1493; 4, 935) and p is the number of parameters refined (2, 291; 4, 227). The function minimized in least squares was $\sum w(F_o{}^2 - F_c{}^2)^2$, where $w = 1/\sigma^2(F_o{}^2)$. Variances of the individual reflections were assigned on the basis of counting statistics plus an additional term, $0.014I^2$. Variances of the merged reflections were determined by standard propagation of error plus another additional term, $0.0014\langle I \rangle^2$. The secondary extinction parameter[9] refined to 0.19 (11) × 10⁻⁶ for 2 and 0.34 (10) × 10⁻⁶ for 4. More complete details of data collection, treatment, structure solution, and refinement are in the supplementary material.

Results and Discussion

2-N-Methylstilbazolium derivatives are readily synthesized by reaction of a 2-N-methylpicolinium salt, 1, and an appropriate aldehyde in the presence of piperidine (Figure 2).[6] Using this reaction, we have synthesized several 2-N-methylstilbazolium derivatives. These compounds have been characterized by ¹H NMR and elemental analysis (see Experimental Section). The salts were examined for second harmonic generation activity by using the Kurtz[7] powder technique. The powder second harmonic generation efficiencies are summarized in Table V.

Whereas more than half of the 43 4-stilbazolium compounds we have examined had powder SHG efficiencies greater than that of urea,[3,10] most of the 2-N-methylstilbazolium compounds gave negligible SHG. Although several samples exhibited strong two-photon fluorescence in the solid state, only 3′-methoxy-2-N-methylstilbazolium triflate, 2, exhibited efficient SHG with an efficiency 24 times that of the urea reference sample by using 1064-nm fundamental light.

(8) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, pp 71, 149.
(9) Larson, E. C. *Acta Crystallogr.* **1967**, *23*, 664, eq 3.
(10) Marder, S. R.; Perry, J. W.; Schaefer, W. P.; Tiemann, B. G. Manuscript in preparation.

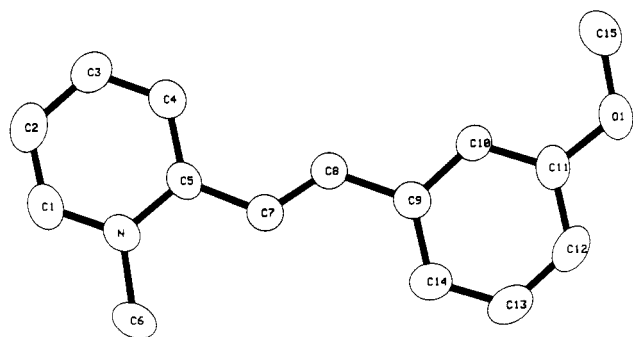688 *Chem. Mater., Vol. 2, No. 6, 1990*

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Figure 3. ORTEP drawing of 3'-methoxy-2-*N*-methylstilbazolium triflate cation with 50% thermal ellipsoids. Hydrogen atoms are not shown.
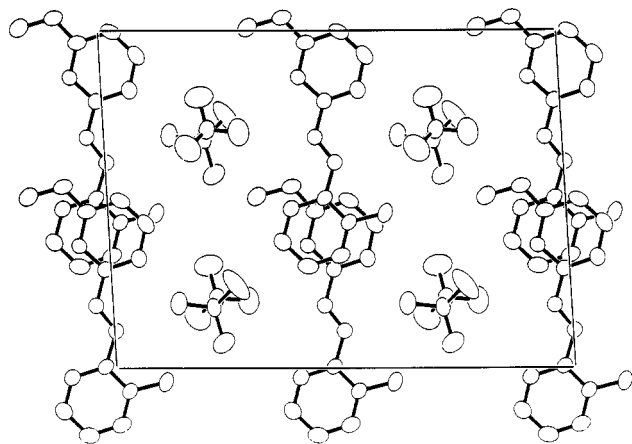
Figure 4. Packing diagram of 3'-methoxy-2-*N*-methylstilbazolium triflate viewed down the *b* axis. Hydrogen atoms are omitted for clarity.

Figure 5. Packing diagram of 3'-methoxy-2-*N*-methylstilbazolium triflate viewed down the *a* axis. Hydrogen atoms are omitted for clarity.

6a   **6b**

Figure 6. Possible structures for 2 + 2 cycloaddition adduct of **4**.

The nonlinear optical properties of this compound are worthy of consideration since, contrary to simple resonance considerations for the design of NLO chromophores, the donor, the methoxy group, and the acceptor, the cationic alkylated nitrogen atom, are cross conjugated. This gives rise to enhanced transparency in the visible in comparison to the isomer 4'-methoxy-2-*N*-methylstilbazolium triflate, **3**, in which the donor and the acceptor are conjugated. In methanol solution, compound **2** has a λ_{max} at 344 nm with a cutoff at 455 nm. In comparison **3** has a charge-transfer band at 368 nm. In the solid state the cutoff (50% transmission) is at ~420 nm (for a ~100-μm thick crystal). Although the molecular hyperpolarizability β of **2** is undoubtedly smaller than that of **3**, its SHG efficiency suggests that it is not necessary to have very strong donors and acceptors or for the donor and the acceptor to be strongly coupled[11] to achieve significant macroscopic nonlinearities.

To better understand the solid-state factors giving rise to the optical nonlinearity of compound **2**, a single-crystal X-ray determination was performed. Suitable crystals were obtained by vapor diffusion of ether into an almost saturated solution of **2** in acetone. The compound crystallizes in the monoclinic space group *Cc*. Bond distances and angles in both the cation and the anion are normal, although the C=C link at 1.310 (6) Å is about 0.02 Å shorter than a normal double bond. The cation is nearly planar and lies in the cell nearly perpendicular to the *b* axis with the N–O vector approximately parallel to *c*. An

ORTEP drawing of the cation is shown in Figure 3, and packing diagrams are in Figures 4 and 5. The structure appears to have π–π stacking interactions with the methoxy phenyl plane lying roughly over the pyridinium plane *of the symmetry-related cation*. The interplanar distance is roughly 3.4 Å. There is excellent alignment of the cations in the cell, with the angle between cations related by the *c*-glide plane being only 10.4 (16)°. This structural motif appears in several of the stilbazolium chromophores for which we have structural information.[12] The carbon-to-sulfur bond of the triflate anion is oriented roughly perpendicular to the plane of the cation.

One concern that must be addressed when considering stilbene and stilbazolium compounds for nonlinear optical application is their photostability with respect to UV–vis and near-IR radiation. The solution photochemistry of stilbenes and stilbazolium salts is well-known.[13] In solution, photolysis of (*E*)-2'-methoxy-2-*N*-methylstilbazolium triflate, **4**, in [²H₆]acetone (Pyrex filtered) led to (*Z*)-2'-methoxy-2-*N*-methylstilbazolium triflate, **5** (in greater than 90% conversion, as shown by ¹H NMR spectroscopy), consistent with previous observations on similar systems.[13] It is interesting to note that one compound in this study, (*E*)-2'-methoxy-2-*N*-methylstilbazolium triflate, **4**, bleaches in the solid state upon exposure to ambient room light, forming the tetrasubstituted cyclobutane **6** (Figure 6).[14] The gross features of the molecular structure of **6** were assigned on the basis of its NMR spectrum. There were two sets of resonances which were indicative of the two sets

(11) This statement is supported by measurements of β on a series methoxynitrostilbenes in which the position of the methoxy group is varied. Cheng, L. T.; Marder, S. R. Manuscript in preparation.
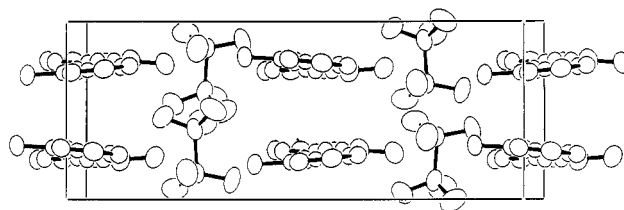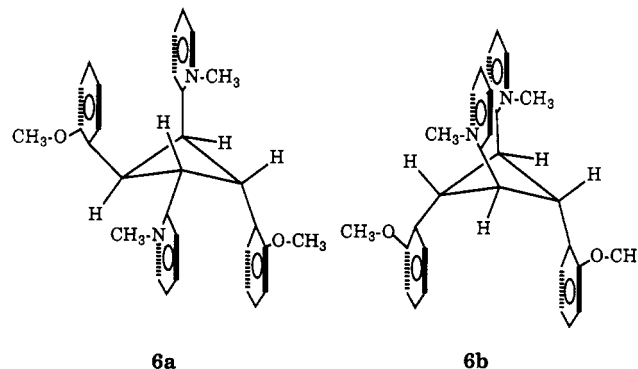
(12) Groves, P. G.; Henling, L.; Marder, S. R.; Marsh, R. E.; Perry, J. W.; Schaefer, W. P.; Tiemann, B. G. Manuscript in preparation.

(13) For leading references on photochemical trans–cis isomerization of stilbenes and stilbazolium salts see: (a) *Modern Molecular Photochemistry*; Turro, N. J.; Benjamin/Cummings: Menlo Park, 1978; pp 473–482. (b) Garner, H.; Gruen, H. *J. Photochem.* **1985**, *28*, 329, and references therein. (c) Gaines, G. L. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 341.

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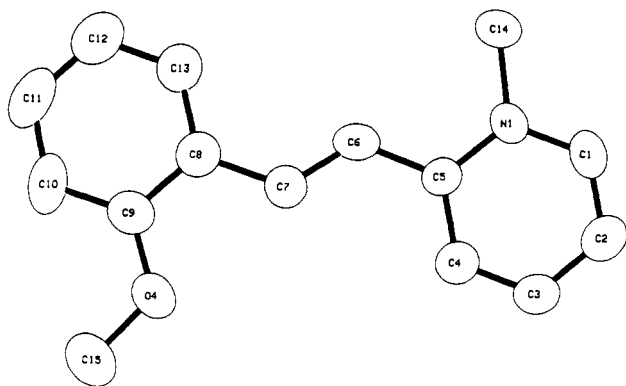
Figure 7. ORTEP drawing of 2'-methoxy-2-*N*-methylstilbazolium triflate cation with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Figure 8. Packing diagram of 2'-methoxy-2-*N*-methylstilbazolium triflate viewed down the *b* axis. The triflate anion and hydrogen atoms are omitted for clarity.

of four adjacent protons of the aromatic rings and two singlets for the methoxy and pyridinium methyl groups, each of which was qualitatively similar to those in the starting compound 4. The most pronounced difference was the disappearance of the resonances assigned to vinyl protons of 4 and the appearance of an AA'BB' set of resonances at δ 5.31 ppm assigned to the protons on the four-membered ring. The reaction was conveniently carried out on a preparative scale by photolyzing a stirred slurry of 4 in hexane for 4 h with a medium-pressure 450-W mercury lamp. After filtration and washing with acetone/ether, the tetrasubstituted cyclobutane 6 was isolated in 70% yield. Several other stilbazolium salts undergo solid-state and/or solution photochemistry, which is the subject of further investigation. Crystals of 2 are substantially more photochemically robust than 4, which is not surprising since the orientation of the chromophore in the crystal lattice precludes overlap of the p-orbitals that would be involved in the 2 + 2 reaction.

If molecules are to undergo an intermolecular 2 + 2 cycloaddition reaction in the solid state, it is necessary for them to stack with double bonds of adjacent molecules within roughly 3.8 Å of one another.[14] In the systems we have examined crystallographically, where π-stacking is important, there is a strong tendency for the donor ring of one molecule to lie over the acceptor ring of another molecule; this observation may have consequences with respect to photostability of SHG-active chromophores. For centrosymmetric systems, this stacking will put the vinylic carbon atoms in roughly the correct region of space for bond formation. But for noncentrosymmetric space groups, in order for the donor ring and acceptor ring to overlap, the molecules must be slip stacked, precluding the 2 + 2 cycloaddition reaction. Thus the SHG-active chromophore may tend to be more stable with respect to photochemical dimerization. Conversely if dimerization is desirable, then counterion variation may lead to a crystal structure that would enable the reaction to occur.

A structural determination of 4 was undertaken to ascertain the orientation of the double bonds involved in the 2 + 2 cycloaddition reaction and to help to assign unambiguously the regiochemistry of the cyclobutane ring. Although the crystal was twinned, it was possible to identify the twin reflections and solve the structure. The compound crystallizes in the centrosymmetric space group $P2_1/n$. Bond lengths and angles are normal. The cation is planar within 0.07 Å except for O4, which is 0.10 Å out of the plane (Figure 7). The parallel cations, related by a center of symmetry at $^1/_2$, 0, $^1/_2$, are separated by about 3.3 Å. The two atoms of the double bond, C6 and C7, are 3.783 (6) Å apart (C6–C7 and C7–C6; Figure 8). Although the carbon–carbon double bonds are not directly above one
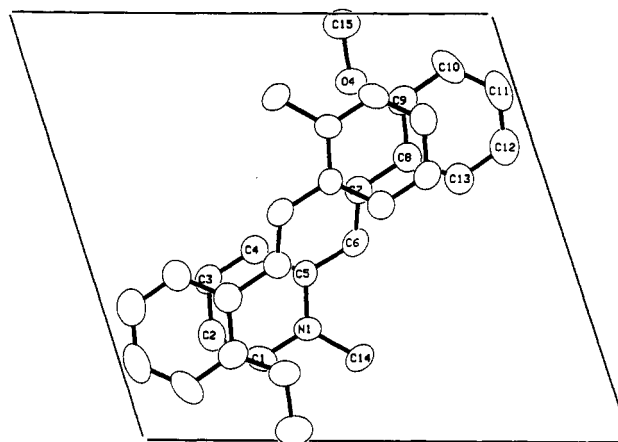
another, they are sufficiently well aligned to facilitate the cycloaddition reaction (note that crystals from the crop grown for the X-ray diffraction study form the cyclobutane upon exposure to light). The crystal structure also allows one to assign the stereochemistry around the cyclobutane ring. The formation of bonds between C6–C7 and C7–C6 would form structure **6a**.

As noted before, neutral dipolar molecules with geometrical asymmetry show a greater tendency to crystallize in noncentrosymmetric space groups than do more linear symmetric analogues. Thus, whereas crystals of 4-nitroaniline are centrosymmetric, 2-methyl-4-nitroaniline crystallizes in the noncentrosymmetric space group *Cc*. Similarly, although crystals of 4-methoxy-4'-nitrostilbene are most likely centrosymmetric (as surmised by no detectible SHG activity), 3-methyl-4-methoxy-4'-nitrostilbene[15] and 2-methoxy-4'-nitrostilbene[16] both crystallize in noncentrosymmetric space groups and both give rise to large SHG efficiencies. The opposite trend is observed with the 2-*N*-methylstilbazolium salts and the 4-*N*-methylstilbazolium salts we have examined. Over half of the 4-*N*-methylstilbazolium salts we have examined exhibit powder SHG efficiencies greater than that of urea, whereas only two of the compounds reported in this paper had powder efficiencies substantially greater than that of urea. Although it is difficult to generalize trends in packing, in the eight crystal structures we determined, a recurring structural motif is alternating parallel rows of cations and rows of anions. Compound 2 follows this motif. It is reasonable to suggest that the ions will more likely form linear rows if the chromophore itself is linear. Thus, whereas molecular asymmetry may tend to favor crystallographic noncentrosymmetry in neutral molecules, it appears from our limited sampling that the opposite is true for rodlike ionic chromophores.

In conclusion, our study demonstrates that cross-conjugated donor/acceptor molecules can give rise to significant SHG efficiencies with improved transparency relative to the fully conjugated systems. In addition, our study has helped to define the scope of counterion variation of crystal structure as an approach to obtain favorable packing of NLO-active chromophores. The results suggest that the probability of isolating ionic chromophores in noncentrosymmetric space groups is higher when the chromophore is approximately linear. This is in contrast to neutral dipolar systems in which geometric asymmetry appears to

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(16) Grubbs, R. B.; Marder, S. R.; Perry, J. W.; Schaefer, W. P. *Chem. Mater.*, submitted.

increase the probability of noncentrosymmetric crystallization.

Molecular and Macroscopic Second-Order Optical Nonlinearities of Substituted Dinitrostilbenes and Related Compounds

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A series of compounds of the form (*E*)-1-(2,4-dinitrophenyl)-2-R-ethylene, where R is a donor group, was prepared, and their molecular hyperpolarizabilities were examined by the dc electric-field-induced second-harmonic generation (EFISH) method. Although the compounds studied had charge-transfer bands at lower energy than their 4-nitrostilbene analogues, the EFISH-determined values of β_μ, the vectorial projection of the hyperpolarizability tensor along the dipole moment direction, were reduced. The powder second harmonic generation efficiencies of these compounds were determined by the Kurtz powder technique.

Introduction

The desire to exploit the second-order optical nonlinearities of conjugated organic materials[1] has led researchers to develop structure–properties relationships for hyperpolarizabilities.[2] Insights from these studies may provide guidelines for the synthesis of new highly nonlinear materials. To develop these relationships, it is important to experimentally determine the molecular hyperpolarizability tensor, β. The vectorial projection of β along the molecular dipole direction, denoted β_μ, can be obtained by electric-field-induced second-harmonic generation (EFISH) experiments with relatively good accuracy.[2,3] Since β_μ is

a frequency-dependent property, comparison of values measured for different molecules must accout for dispersion, typically by using a model. An alternative approach, used in this study, is to perform measurements with sufficiently low frequency radiation so as to obtain an estimate of the limiting nonresonant value.

Second-order optical nonlinearities, such as second harmonic generation (SHG), can be observed only in materials lacking a center of symmetry.[1a] This usually precludes their observation in solutions since they are isotropic in the absence of some external perturbation. If the nonlinear chromophore (solute) is dipolar, application of an electric field causes each dipole to partially align with the field. This alignment removes the center of symmetry, allowing for the observation of second harmonics. If the ground-state dipole is oriented in a direction along which the projection of β contains the dominating components, then analysis of data from the EFISH experiment will provide a meaningful measure of the quadratic optical nonlinearity of the molecule. These measurements, coupled with theoretical models, facilitate a better understanding of the factors that lead to large hyperpolarizability.

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(3) (a) Oudar, J. L.; Le Person, H. *Opt. Commun.* **1975**, *15*, 268. (b) Levine, B. F.; Bethea, C. G. *Appl. Phys. Lett.* **24**, 445. (c) Singer, K. D.; Garito, A. F. *J. Chem. Phys.* **1981**, *75*, 3572.