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Second-Order Optical Nonlinearities of β-Sulfonylstyrene Derivatives

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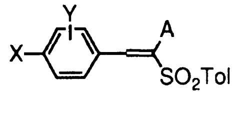
Synopsis. The second-order optical nonlinearities and transparencies of eight substituted styrenes containing at least one sulfonyl group at the β-position, as the electron-withdrawing group, were examined. Oxidation at a sulfur atom (SMe→SOMe→SO_2Me) brings about increases in the β and λ_{max} values.

Second-harmonic generation materials convert the light of semiconductor lasers (800 nm band) into blue laser light (400 nm band). It is well known that molecules containing electron-donating and electron-withdrawing groups separated by a large π-electron conjugated system possess large second-order molecular hyperpolarizabilities (β).[1)]

Here, we report on the second-order optical nonlinearities and transparencies of a new system represented by a general formula (**I**) which has a ketene dithioacetal *S*,*S*-dioxide, *S*,*S*,*S*′-trioxide, or *S*,*S*,*S*′,*S*′-tetraoxide group[2)] as an electron-withdrawing part (Chart 1).

Results and Discussion

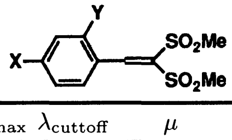
Table 1 summarizes the nonlinearities β (10^{-30} esu) measured by the EFISH technique, SHG (XUrea), and the transparencies (λ_{max} (nm) and λ_{cutoff} (nm)) of two β,β-bis(methylsulfonyl)styrenes (**1**[2)] and **2**) having a 4- or 2-methoxyl as the electron-donating group. SHG (XUrea) means the relative intensity of SHG. The measured molecular dipole moments (in units of 10^{-18} esu=1 Debye=3.3356×10^{-30} C m) of these compounds are also given in Table 1. Contrary to our expectation,



I

Chart 1.

Table 1. Nonlinearities and Transparencies of β,β-Bis(methylsulfonyl)styrenes



Compound			λ_{max}	$\lambda_{cuttoff}$	μ	β	SHG
	X	Y	nm	nm	10^{-18} esu	10^{-30} esu	(×Urea)
1[2)]	MeO	H	325	377	6.1	6.4	8.6
2	H	MeO	333	402	—	—	0.000

β (m^4 V^{-1})=4.1888×10^{-10}β (esu).

the methoxyl-group substitution at the ortho position, not at the para position, as for compound **1**, makes the relative intensity of the SHG of **2** zero.

In order to determine the effect of a *p*-tolylsulfonyl group, not a methylsulfonyl group, on the β, SHG (XUrea), and λ_{max}, nine *p*-tolylsulfonyl-substituted styrenes, **3**—**11**, were synthesized and examined, as listed in Table 2. Compound **3** has no substituents in the benzene ring. The oxygen coordination at a sulfur atom (**4** SMe→**5** SOMe→**6** SO_2Me; **8** SMe→**9** SOMe→**10** SO_2Me) brings about increases of β (**4**→**5**→**6**; **8**→**9**→**10**) and λ_{max}(**4**→**5**→**6**; **8**→**9**→**10**). The introduction of a methoxyl group as the electron-donating group also increases β (**3**→**5**; **4**→**8**; **5**→**9**; **6**→**10**) and λ_{max} (**3**→**5**; **4**→**8**; **5**→**9**; **6**→**10**). The increase in the electron-donating ability (**4** MeO→**11** Me_2N) results in those of β (**4**→**11**) and λ_{max} (**4**→**11**). It coincides with an estimation from a two-level model,[1a)] in which increasing λ_{max} tends to increase β. The introduction of a *p*-tolylsulfonyl group, not a methylsulfonyl group (**6**→**7**), leads to a decrease in β (**6**→**7**). The introduction of various kinds of substituents (**3**—**11**) has no ability to increase the relative intensity of SHG (<1), contrary to our expectation.

In this study, we examined the second-order optical nonlinearities and transparencies of eleven (eight new and the reported three (**1**, **6**, **10**)[2)]) substituted styrenes containing at least one sulfonyl group as the electron-withdrawing group. The oxidation at a sulfur atom (SMe→SOMe→SO_2Me) and the electron-donating ability (H<MeO<Me_2N) in these eleven styrene derivatives bring about increases of the β and λ_{max} values.

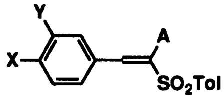
Experimental

Compounds **1**—**11** were prepared as described below; the other compounds were commercially available.

The melting points were determined on a hotstage microscope apparatus (Yanagimoto) and were uncorrected. ^{1}H NMR spectra were obtained on a JEOL (JNM-FX 270) spectrometer. Infrared spectra were measured with a JASCO (A-200) spectrometer; the data are presented for important diagnostic absorptions. Elementary analyses were provided by the chemical analysis center of Chiba university.

Measurements of the absorption maximum wavelength (λ_{max}), the absorption cutoff (λ_{cutoff}) evaluated based on the wavelength, the transmittance of which was 95% in an ethanol solution, the second-order molecular hyperpolarizability (β), the molecular dipole (μ), and the relative in-

Table 2. Nonlinearities and Transparencies of β-(p-Tolylsulfonyl)styrenes



Compound				λ_{max}	$\lambda_{cuttoff}$	μ	β	SHG
	X	Y	A	nm	nm	10^{-18} esu	10^{-30} esu	(×Urea)
3	H	H	SOMe	280	377	4.9	3.8	0.004
4	MeO	H	SMe	314	386	5.9	4.6	0.000
5	MeO	H	SOMe	324	398	5.1	6.0	0.000
6[2)]	MeO	H	SO_2Me	330	—	6.6	8.3	0.000
7	MeO	H	SO_2Tol	337	—	6.5	6.4	0.000
8	MeO	MeO	SMe	336	397	5.6	6.5	0.000
9	MeO	MeO	SOMe	347	421	5.2	7.3	0.08
10[2)]	MeO	MeO	SO_2Me	352	—	6.8	10.6	0.000
11	Me_2N	H	SMe	381	457	6.7	10.3	0.000

tensity of SHG were described in a previous paper.[3)] The solubilities of compounds **6**, **7**, and **10** in ethanol and that of compound **2** in dioxane were poor. Therefore, the λ_{cutoff}, μ, and β of those compounds could not be measured, as given in Tables 1 and 2.

Preparation of 4-Methoxy-β,β-bis(methylsulfonyl)styrene (1). A Typical Procedure: This compound was prepared by the oxidation of 4-methoxy-β-methylsulfinyl-β-methylthiostyrene[4)] (1.07 g; 4.41 mmol) with m-chloroperbenzoic acid (MCPBA) (2.72 g; 14.77 mmol) in dichloromethane (50 ml) at −20 °C (5 h) and then at room temperature (60 h). The usual workup and separation by column chromatography on silica gel [eluent: benzene–ethyl acetate (2 : 1)] gave **1** (1.23 g; 97% yield). Colorless crystals; mp 164—165 °C (from $CHCl_3$/hexane); ^{1}H NMR ($CDCl_3$) δ=3.35 (6H, d), 3.89 (3H, s), 6.99 (2H, d, J=9.0 Hz), 7.89 (2H, d, J=9.0 Hz), 8.29 (1H, s). IR (KBr) 2900, 1605, 1580, 1560, 1420, 1300, 1280, 1180, 1140, 1030, 980, 950, 830, 780 and 760 cm^{-1}.

Found: C, 45.40; H, 4.83%. Calcd for $C_{11}H_{14}O_5S_2$: C, 45.50; H, 4.86%.

2-Methoxy-β,β-bis(methylsulfonyl)styrene (2): Yellow crystals; mp 146—148 °C (from $CHCl_3$/hexane); ^{1}H NMR ($CDCl_3$) δ=3.36 (6H, d, J=4.0 Hz), 3.91 (3H, s), 6.91—7.64 (4H, m), 8.62 (1H, s). IR (KBr) 3000, 2925, 1585, 1470, 1455, 1320, 1295, 1240, 1130, 1010, 970, 950, 940, 925, 765, 740, 570, 560, 530, and 505 cm^{-1}.

Found: C, 44.79; H, 4.87%. Calcd for $C_{11}H_{14}O_5S_2$: C, 44.81; H, 4.96%.

Preparation of β-Methylsulfinyl-β-(p-tolylsulfonyl)styrene (3). A Typical Procedure: Oxidation of β-methylthio-β-(p-tolylsulfonyl)styrene[5)] (996 mg; 3.28 mmol) with MCPBA (728 mg; 4.22 mmol) in dichloromethane (40 ml) was performed at −20 °C (4 h) to give **3** (796 mg; 76% yield). Colorless crystals; mp 134—135 °C (from benzene/hexane); ^{1}H NMR ($CDCl_3$) δ=2.42 (3H, s), 3.17 (3H, s), 7.34 (2H, d, J=7.4 Hz), 7.50 (5H, s), 7.96 (2H, d, J=8.6 Hz), 8.28 (1H, s). IR (KBr) 3000, 1580, 1560, 1510, 1480, 1440, 1400, 1300, 1280, 1200, 1140, 1060, 950, 930, 910, 810, 750, 690, 660, 600, 550, and 500 cm^{-1}.

Found: C, 59.88; H, 4.94%. Calcd for $C_{16}H_{16}O_3S_2$: C, 59.97; H, 5.03%.

4-Methoxy-β-methylsulfinyl-β-(p-tolylsulfonyl)styrene (5): Colorless crystals; mp 115—116 °C; ^{1}H NMR ($CDCl_3$) δ=2.40 (3H, s), 3.13 (3H, s), 3.84 (3H, s), 7.06 (2H, d, J=8.6 Hz), 7.40 (2H, d, J=8.2 Hz), 7.72 (2H, d, J=8.6 Hz), 7.95 (2H, d, J=8.2 Hz), 8.28 (1H, s). IR (KBr) 3450, 3000, 1600, 1508, 1458, 1420, 1300, 1260, 1180, 1145, 1070, 1025, 960, 910, 830, 770, 660 cm^{-1}.

Found: C, 58.24; H, 5.06%. Calcd for $C_{17}H_{18}O_4S_2$: C, 58.26; H, 5.18%.

3,4-Dimethoxy-β-methylsulfinyl-β-(p-tolylsulfonyl)styrene (9):[5)] Pale yellow crystals; mp 145—146 °C (from benzene/hexane); ^{1}H NMR ($CDCl_3$) δ=2.42 (3H, s), 3.10 (3H, s), 3.89 (3H, s), 3.92 (3H, s), 6.92 (1H, d, J=8.0 Hz), 7.11—7.50 (2H, m), 7.64 (1H, d, J=8.0 Hz), 7.54—8.04 (3H, m), 8.19 (1H, s). IR (KBr) 1510, 1265, 1140, 1080, 1065, 550 cm^{-1}.

Found: C, 56.92; H, 5.28%. Calcd for $C_{18}H_{20}O_5S_2$: C, 56.82; H, 5.30%.

Preparation of 4-Methoxy-β-methyllthio-β-(p-tolylsulfonyl)styrene (4). A Typical Procedure: To a solution of (methylthio)methyl p-tolyl solfone[6)] (1.01 g; 4.66 mmol) in THF (15 ml), were added successively trimethylsilyl chloride (1.30 ml; 10.3 mmol) and a 1.58 mol dm^{-3} hexane solution of butyllithium (6.45 ml; 10.3 mmol) at −78 °C. After the resulting solution had been stirred at the same temperature for 2 h, and then p-methoxybenzaldehyde (0.68 ml; 5.6 mmol) was added at −78 °C. The reaction temperature was then slowly raised to room temperature, and the reaction mixture stirred for 2 h. Quenching with an aqueous solution of ammonium chloride, extraction with diisopropyl ether and chloroform, and column chromatography on silica gel [hexane–ethyl acetate (5 : 1)] gave **4** (1.01 g; 65% yield). Colorless crystals; mp 123—125 °C (from $CHCl_3$/hexane); ^{1}H NMR ($CDCl_3$) δ=2.18 (3H, s), 2.41 (3H, s), 3.84 (3H, s), 6.95 (2H, d, J=9.0 Hz), 7.32 (2H, d, J=8.0 Hz), 7.90 (2H, d, J=8.2 Hz), 7.98 (2H, d, J=8.2 Hz), 8.21 (1H, s). IR (KBr) 1600, 1500, 1440, 1340, 1280, 1260, 1170, 1140, 1080, 1020, 905, 840, 750, 650, 580, 560, and 530 cm^{-1}.

Found: C, 61.04; H, 5.45%. Calcd for $C_{17}H_{18}O_3S_2$: C, 61.05; H, 5.42%.

3,4-Dimethoxy-β-methythio-β-(p-tolylsulfonyl)styrene (8):[5,7)] Pale yellow crystals; mp 119—120 °C (from benzene/hexane); ^{1}H NMR ($CDCl_3$) δ=2.19 (3H, s), 2.39 (3H, s), 3.85 (3H, s), 3.88 (3H, s), 6.90 (1H, d, J=8.0

Hz), 7.30 (2H, d, J=8.0 Hz), 7.52 (1H, dd, J=1.0, 8.0 Hz), 7.80 (1H, d, J=1.0 Hz), 7.87 (2H, d, J=8.0 Hz), 8.18 (1H, s). IR (KBr) 1585, 1510, 1310, 1260, 1140, 1085 cm^{-1}.

Found: C, 59.36; H, 5.50%. Calcd for $C_{18}H_{20}O_4S_2$: C, 59.32; H, 5.53%.

4-Dimethylamino-β-methythio-β-(*p*-tolylsulfonyl)-styrene (11): Yellow crystals; mp 114—116 °C (from benzene/hexane); ^{1}H NMR ($CDCl_3$) δ=2.16 (3H, s), 2.40 (3H, s), 3.02 (6H, s), 6.68 (2H, d, J=9.0 Hz), 7.29 (2H, d, J=7.9 Hz), 7.82 (2H, d, J=7.4 Hz), 8.00 (2H, d, J=8.6 Hz), 8.16 (1H, s). IR (KBr) 2900, 1600, 1560, 1510, 1420, 1370, 1360, 1290, 1220, 1180, 1170, 1140, 1080, 910, 820, 720, 650, 580, 550, 520, 470 cm^{-1}.

Found: C, 62.12; H, 6.07; N, 3.99%. Calcd for $C_{18}H_{21}O_2NS_2$: C, 62.22; H, 6.09; N, 4.03%.

Preparation of 4-Methoxy-β-methysulfonyl-β-(*p*-tolylsulfonyl)styrene (6): A Typical Procedure: This compound was produced by the oxidation of **4** (330 mg; 1.02 mmol) with excess MCPBA (535 mg; 3.09 mmol) in dichloromethane (10 ml) at −20 °C (3 h) and at room temperature (17 h). The usual workup and separation by column chromatography on silica gel [eluent: benzene–ethyl acetate (3 : 1)] gave **6** (235 mg; 64% yield). This product was shown by ^{1}H NMR to consist of two geometric isomers in the ratio of 8 : 2. Their geometry was not determined. Colorless crystals; mp 168—170 °C (from CH_3Cl/hexane); ^{1}H NMR ($CDCl_3$) δ=2.38 (3H, s), 2.43 (3H, s), 3.22 (3H, s), 3.48 (3H, s), 3.87 (3H, s), 3.89 (3H, s), 6.98 (2H, d, J=9.2 Hz), 7.33 (2H, d, J=8.6 Hz), 7.84 (2H, d, J=8.2 Hz), 7.90 (2H, d, J=8.6 Hz), 8.29 (1H, s), 8.54 (1H, s). IR (KBr) 1590, 1570, 1540, 1500, 1440, 1420, 1360, 1300, 1270, 1180, 1140, 1080, 1020, 950, 930, 840, 820, 750, 700, 670, 585, 570, 535, 510 cm^{-1}.

Found: C, 55.52; H, 4.89%. Calcd for $C_{17}H_{18}O_5S_2$: C, 55.72; H, 4.95%.

3, 4-Dimethoxy-β-methysulfonyl-β-(*p*-tolylsulfonyl)styrene (10): Pale yellow crystals; mp 160—161 °C (from CH_3Cl/hexane); ^{1}H NMR ($CDCl_3$) δ=2.38 (3H, s), 2.43 (3H, s), 3.19 (3H, s), 3.48 (3H, s), 3.88 (3H, s), 3.91 (3H, s), 3.95 (3H, s), 3.97 (3H, s), 6.95 (1H, d, J=8.0 Hz), 7.35 (2H, d, J=8.2 Hz), 7.48 (1H, dd, J=12.9 Hz), 7.76 (1H, d, J=2.4 Hz), 7.85 (2H, d, J=8.2 Hz), 8.23 (1H, s), 8.55 (1H, s). IR (KBr) 1570, 1555, 1500, 1450, 1360, 1320, 1270, 1240, 1140, 1080, 1010, 970, 800, 770, 640, 560 cm^{-1}.

Found: C, 54.29; H, 5.08%. Calcd for $C_{17}H_{20}O_6S_2$: C, 54.53; H, 5.08%.

4-Methoxy-β,β-bis(*p*-tolylsulfonyl)styrene (7): Compound **7** was prepared by the oxidation of 4-methoxy-β-(*p*-tolylsulfonyl)-β-(*p*-tolylthio)styrene in an analogous manner to **1**. Colorless crystals; mp 176—177 °C (from CH_3Cl/hexane); ^{1}H NMR ($CDCl_3$) δ=2.30 (3H, s), 2.40 (3H, s), 3.80 (3H, s), 6.80—7.97 (12H, m), 8.54 (1H, s). IR (KBr) 2900, 1600, 1570, 1550, 1500, 1460, 1420, 1365, 1320, 1300, 1260, 1180, 1150, 1080, 1030, 930, 760, 710, 690, 660, 620, 590, 550, 520, 480 cm^{-1}.

Found: C, 62.24; H, 4.93%. Calcd for $C_{23}H_{22}O_5S_2$: C, 62.41; H, 5.01%.

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