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Second-Order Optical Nonlinearities of Substituted Stilbenes and the Related Compounds Containing a Trifluoromethyl as the Electron-Withdrawing Group

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The second-order optical nonlinearities and transparencies of seventeen 4,4′-disubstituted stilbenes and ten related compounds containing a trifluoromethyl group at the para position, as the electron-withdrawing group, were examined. The introduction of a trifluoromethyl group produces a shorter-wavelength shift of the UV-vis absorption spectra without any decrease in the magnitude of the second-order molecular hyperpolarizability (β), as compared with the corresponding nitro-derivatives. The absorption cutoff (λ_{cutoff}) of 4-methoxy-4′-trifluoromethylstilbene (**1**) was observed at 375 nm, which is by ca. 90 nm shorter than that (463 nm) of *p*-nitroaniline (***p*-NA**); the β value (12.2×10^{-30} esu) of **1**, however, is almost equal to that (12.6×10^{-30} esu) of ***p*-NA**. The bromo- or methylthio-substituted stilbenes (**12** and **16**) with a cyano group on the central double bond show SHG activity. The relative intensities of SHG are 3.0 and 1.5, respectively.

The growing need for fast, efficient optical devices has made nonlinear optics a frontier field of science. The potential of organic materials for this purpose has recently come into prominence. The efficiency of second harmonic generation (SHG) can exceed that of currently used inorganic materials by several orders of magnitude.[1] SHG materials convert the light produced by semiconductor lasers (800 nm band) into blue laser light (400 nm band) for high-density optical recording.

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. Many SHG studies[1] have been carried out concerning molecules having a nitro group as the electron-withdrawing group, such as 2-methyl-4-nitroaniline (**MNA**),[2] 4-(*N,N*-dimethylamino)-3-acetylamino-1-nitrobenzene (DAN),[3] and 3-methyl-4-methoxy-4′-nitrostilbene (MMONS).[4] Their transparencies, however, are usually poor. The absorption cutoff wavelengths of those molecules are longer than 450 nm, since the nitro group has a strong electron-withdrawing property and conjugates with π-electron conjugated systems.

Therefore, much research has been carried out to obtain SHG molecules with high transmittance for blue light i.e., a λ_{cutoff} that is less than 450 nm. For example, Nogami et al. reported that the absorption cutoff wavelength (λ_{cutoff}) of a 1,3-dithiole derivative was 415 nm.[5] Gotoh et al. found a thienyl chalcone of 390 nm λ_{cutoff}.[6] Stilbenes having various kinds of substituents, (such as a nitro, cyano, perfluoroalkylsulfonyl, or trifluoroacetyl as the electron-withdrawing group and a dimethylamino, methoxyl, hydroxyl, or methylthio as the electron-donating group) have also been studied.[7,8]

In order to optimize the nonlinearity and transparency trade-off, we introduced a trifluoromethyl group at the para position of stilbenes. The trifluoromethyl group has an electron-withdrawing nature caused by the great electronegativity of the fluorine atom. In addition, the trifluoromethyl group conjugates with the π-electron conjugated system to a lesser extent than does the nitro group.

We report here on the second-order optical nonlinearities and transparencies of seventeen 4,4′-disubstituted stilbenes and ten related compounds containing a trifluoromethyl as the electron-withdrawing group.

Experimental

Compounds **1**—**27** and (*E*)-4-hydroxy-4′-nitrostilbene (**N-SD**) were prepared as described below; the other compounds were commercially available.

^{1}H NMR spectra were obtained on a JEOL GSX 270 or JEOL EX 400, and the chemical shifts (δ) in parts per million (ppm) units are referenced to the TMS internal standard. The melting points are not corrected.

UV-vis spectra were recorded on a Hitachi U-4000 instrument equipped with a quartz cell of 10 mm optical path length in 10^{-3} mol dm^{-3} ethanol solutions. $\lambda_{\max}$ is the absorption maximum wavelength; λ_{cutoff} was evaluated from the wavelength with a transmittance of 95%.

Second-Order Molecular Hyperpolarizability Measurements. Second-order molecular hyperpolarizability (β) measurements were performed by an electric-field-induced second-harmonic generation technique (EFISH), as described in Ref. 9. Dioxane was used as the solvent. Pulses of 1064 nm light (ca. 8 ns duration) from a 10-pps Spectron SL401 Nd: YAG laser were used for Maker fringes measurements. The refractive indices of the solutions were measured with a Atago Abbe refractometer 1 T. The dielectric constants were measured with a Yokogawa Hewlett Packard Impedance Analyzer 4191A. The process used to determine β gave the molecular dipole moment (μ).

Relative Intensity of SHG Measurements. The relative intensity of SHG was determined by using the abovementiond Nd: YAG laser with a fundamental wavelength of 1064 nm, according to the Kurtz powder method.[10] Samples purified by recrystallization from various solvents at the end of the synthetic procedure were unsized microcrystalline powders. They were measured as obtained. The crystals of three compounds (**3**, **4**, and **5**) shown in Table 2 were also prepared by a solvent-evaporation method. EtOH/H_2O and toluene were used as the solvents. The particle sizes ranged from 75 to 125 μm. Urea was used as a reference compound.

Syntheses. The *E*-configurations of the compound **1**—**9** were confirmed by the coupling constants ($J_{\mathrm{HH}}=$ 15.9—18.1 Hz) of double-bond positions and synthetic methods.

(*E*)-4-Methoxy-4′-(trifluoromethyl)stilbene (1): Compound **1** was prepared by methylation of 4-hydroxy-4′-trifluoromethyl-(*E*)-stilbene (**2**), referred to the literature.[11] White plate crystals; mp 171—172°C (from methanol); ^{1}H NMR ($CDCl_3$) $\delta=3.83$ (3H, s), 6.91 (2H, d, $J=8.91$ Hz), 6.97 (1H, d, $J=16.7$ Hz), 7.14 (1H, d, $J=16.7$ Hz), 7.47 (2H, d, $J=8.64$ Hz), and 7.57 (4H, s).

(*E*)-4-Hydroxy-4′-(trifluoromethyl)stilbene (2): Compound **2** was prepared with reference to the literature[12] as follows. A mixture of 10.2 g (0.05 mol) of 2-(4-trifluoromethylphenyl)acetic acid and 6.1 g (0.05 mol) of 4-hydroxybenzaldehyde in 30 ml of piperidine was stirred at 110°C for 8 h. After removing piperidine by evaporation in vacuo, the mixture was diluted with chloroform, washed with a 3% aqueous HCl solution, and concentrated in vacuo. The oily residue was chromatographed (silica gel, $CHCl_3$) and recrystallized from acetone to give 3.2 g (24%) of **2** as pale-yellow granular crystals; mp 159—160°C, ^{1}H NMR (acetone-d_6) $\delta=6.88$ (2H, d, $J=8.37$ Hz), 7.11 (1H, d, $J=16.7$ Hz), 7.32 (1H, d, $J=16.5$ Hz), 7.49 (2H, d, $J=8.37$ Hz), 7.65 (2H, d, $J=8.37$ Hz), and 7.71 (2H, d, $J=8.37$ Hz).

In a similar manner as that described for the preparation of **2**, compounds **3**—**6** were obtained.

(*E*)-4-Hydroxy-3-methyl-4′-(trifluoromethyl)stilbene (3): White needle crystals; mp 136—137°C (from chloroform), ^{1}H NMR ($CDCl_3$) $\delta=2.28$ (3H, s), 6.76 (1H, d, $J=8.29$ Hz), 6.94 (1H, d, $J=16.58$ Hz), 7.09 (1H, d, $J=16.58$ Hz), 7.25 (1H, d, $J=7.72$ Hz), 7.31 (1H, s), and 7.56 (4H, s).

(*E*)-4-Hydroxy-3-methoxy-4′-(trifluoromethyl)stilbene (4): White needle crystals; mp 133—134°C (from toluene), ^{1}H NMR ($CDCl_3$) $\delta=3.94$ (3H, s), 5.74 (1H, s), 6.91—7.14 (5H, m), and 7.56 (4H, s).

(*E*)-3-Ethoxy-4-hydroxy-4′-(trifluoromethyl)stilbene (5): White needle crystals; mp 142—143°C (from chloroform), ^{1}H NMR ($CDCl_3$) $\delta=1.47$ (3H, t), 4.17 (2H, q), 5.79 (1H, s), 6.89—7.12 (5H, m), and 7.56 (4H, s).

(*E*)-2-Chloro-4-hydroxy-4′-(trifluoromethyl)stilbene (6): Pale-yellow plate crystals; mp 105—107°C (from hexane), ^{1}H NMR ($CDCl_3$) $\delta=6.77$ (1H, d, $J=8.32$ Hz), 6.91 (1H, s), 6.95 (1H, d, $J=17.06$ Hz), 7.50 (1H, d, $J=16.61$ Hz), 7.57 (1H, d, $J=8.29$ Hz), and 7.58 (4H, s).

(*E*)-4-Methoxy-3-methyl-4′-(trifluoromethyl)stilbene (7): In a similar manner as that described for the preparation of **1**, compound **7** was obtained. White plate crystals; mp 105—106°C (from methanol), ^{1}H NMR ($CDCl_3$) $\delta=2.25$ (3H, s), 3.85 (3H, s), 6.82 (1H, d, $J=8.37$ Hz), 6.96 (1H, d, $J=16.74$ Hz), 7.12 (1H, d, $J=16.47$ Hz), 7.32 (1H, d, $J=8.37$ Hz), 7.35 (1H, s), 7.56 (4H, s).

(*E*)-3-Fluoro-4-methoxy-4′-(trifluoromethyl)stilbene (8): 3-Fluoro-4-hydroxybenzaldehyde was prepared from 3-fluoro-4-methoxybenzaldehyde by the reference to the literature.[13] (*E*)-3-Fluoro-4-hydroxy-4′-(trifluoromethyl)stilbene was prepared as described for the preparation of **2**. In a similar manner as that described for the preparation of **1**, compound **8** was obtained. White needle crystals; mp 98—100°C (from hexane), ^{1}H NMR ($CDCl_3$) $\delta=3.90$ (3H, s), 6.92 (1H, d, $J=8.91$ Hz), 6.94 (1H, d, $J=18.09$ Hz), 7.07 (1H, d, $J=15.93$ Hz), 7.19 (1H, d, $J=8.64$ Hz), 7.31 (1H, m), 7.54 (2H, d, $J=8.64$ Hz), 7.59 (2H, d, $J=8.64$ Hz).

(*E*)-2-Chloro-4-methoxy-4′-(trifluoromethyl)stilbene (9): In a similar manner as that described for the preparation of **1**, the compound **9** was obtained. White granular crystals; mp 77—80°C (from hexane), ^{1}H NMR ($CDCl_3$) $\delta=3.80$ (3H, s), 6.82 (1H, d, $J=8.64$ Hz), 6.84—7.28 (2H, m), 7.51 (1H, d, $J=15.93$ Hz), 7.58 (4H, s), 7.59 (1H, d, $J=8.91$ Hz).

4-Trifluoro-α-cyanostilbene (10): Compound **10** was prepared with reference to the literature[14] as follows. A mixture of 1.85 g (10 mmol) of 2-(4-trifluoromethylphenyl)acetonitrile and 1.06 g (10 mmol) of benzaldehyde in 1.0 g of piperidine and 50 ml of ethanol was stirred at 75°C for 14 h. After pouring the solution into 300 ml of water, it was extracted with chloroform, washed with water, dried over Na_2SO_4, and concentrated in vacuo. Recrystallization from ethanol gave 1.85 g (77%) of pale-yellow needle crystals; mp 142—143°C; ^{1}H NMR (acetone-d_6) $\delta=7.56$—8.12 (10H, m).

In a similar manner as that described for the preparation of **10**, compounds **11**—**27** were obtained.

4-Chloro-4′-trifluoromethyl-β-cyanostilbene (11): Pale-yellow needle crystals; mp 80—82°C (from hexane), ^{1}H NMR (acetone-d_6) $\delta=7.61$ (2H, d, $J=8.79$ Hz), 7.81—8.09 (5H, m), 8.06 (2H, d, $J=8.79$ Hz).

4-Bromo-4′-trifluoromethyl-β-cyanostilbene (12): Pale-yellow needle crystals; mp 84—85°C (from hexane), ^{1}H NMR (acetone-d_6) $\delta=7.76$ (2H, d, $J=8.79$ Hz), 7.72—8.02 (5H, m), 8.05 (2H, d, $J=8.79$ Hz).

4-Methyl-4′-trifluoromethyl-β-cyanostilbene (13): Pale-yellow needle crystals; mp 150—151°C (from ethanol), ^{1}H NMR (acetone-d_6) $\delta=2.42$ (3H, s), 7.39 (2H, d, $J=7.82$ Hz), 7.80—7.90 (5H, m), 8.02 (2H, d, $J=7.82$ Hz).

4-Methoxy-4′-trifluoromethyl-β-cyanostilbene (14): Pale-yellow needle crystals; mp 127—128°C (from ethanol), ^{1}H NMR ($CDCl_3$) $\delta=3.89$ (3H, s), 7.00 (2H, d, $J=8.79$ Hz), 7.54 (1H, s), 7.69 (2H, d, $J=8.79$ Hz), 7.77 (2H, d, $J=8.79$ Hz), 7.93 (2H, d, $J=8.79$ Hz).

4-Hydroxy-4′-trifluoromethyl-β-cyanostilbene (15): Yellow needle crystals; mp 198—199°C (from ethanol).

4-Methylthio-4′-trifluoromethyl-β-cyanostilbene (16): Pale-yellow needle crystals; mp 138—139°C (from ethanol), ^{1}H NMR (acetone-d_6) $\delta=2.59$ (3H, s), 7.43 (2H, d, $J=8.79$ Hz), 7.79—7.98 (5H, m), 8.00 (2H, d, $J=8.79$ Hz).

4-Dimethylamino-4′-trifluoromethyl-β-cyanostilbene (17): Yellow needle crystals; mp 178—179°C (from ethanol/water).

1-Cyano-1-[4-(trifluoromethyl)phenyl]-2-(2-furyl)-ethylene (18): Pale-yellow needle crystals; mp 120—121°C (from chloroform/hexane), ^{1}H NMR ($CDCl_3$) $\delta=$ 6.61—6.63 (1H, m), 7.27 (1H, d, $J=3.90$ Hz), 7.46 (1H, s), 7.65 (1H, d, $J=0.97$ Hz), 7.69 (2H, d, $J=8.30$ Hz), 7.76 (2H, d, $J=8.79$ Hz).

1-Cyano-1-[4-(trifluoromethyl)phenyl]-2-(3-furyl)-ethylene (19): Pale-yellow needle crystals; mp 91—92°C (from hexane), ^{1}H NMR ($CDCl_3$) $\delta=7.27$ (1H, s), 7.50 (1H, s), 7.55 (1H, s), 7.69 (2H, d, $J=8.79$ Hz), 7.74 (2H, d,

J=8.78 Hz), 7.99 (1H, s).

1-Cyano-1-[4-(trifluoromethyl)phenyl]-2-(2-thienyl)-ethylene (20): Pale-yellow plate crystals; mp 166—167°C (from hexane/dichloromethane), ^{1}H NMR (CDCl$_3$) δ=7.18—7.20 (1H, m), 7.62 (1H, d, J=4.88 Hz), 7.68—7.77 (6H, m).

1-Cyano-1-[4-(trifluoromethyl)phenyl]-2-(3-thienyl)ethylene (21): Pale-yellow needle crystals; mp 133—136°C (from ethanol), ^{1}H NMR (CDCl$_3$) δ=7.45 (1H, dd, J=2.93 and 4.89 Hz), 7.62 (1H, s), 7.69 (2H, d, J=8.30 Hz), 7.76 (2H, d, J=8.30 Hz), 7.81 (1H, dd, J=0.97 and 5.37 Hz), 8.02 (1H, d, J=2.93 Hz).

1-Cyano-1-[4-(trifluoromethyl)phenyl]-2-(2-pyrrolyl)ethylene (22): Yellow needle crystals; mp 149—151°C (from hexane/chloroform), ^{1}H NMR (CDCl$_3$) δ=6.38 (1H, m), 6.76 (1H, s), 7.12 (1H, s), 7.47 (1H, s), 7.64—7.69 (4H, m), 9.81 (1H, s).

1-Cyano-1-[4-(trifluoromethyl)phenyl]-2-(1-methyl-2-pyrrolyl)ethylene (23): Yellow plate crystals; mp 175—176°C (from ethanol), ^{1}H NMR (CDCl$_3$) δ=3.77 (3H, s), 6.34 (1H, m), 6.87 (1H, s), 7.43 (1H, s), 7.56 (1H, d, J=3.81 Hz), 7.66 (2H, d, J=8.79 Hz), 7.71 (2H, d, J=8.79 Hz).

1-Cyano-1-[4-(trifluoromethyl)phenyl]-2-(2-imidazolyl)ethylene (24): Pale-yellow needle crystals; mp 209—210°C (from ethanol), ^{1}H NMR (CDCl$_3$) δ=7.36 (2H, s), 7.71—7.78 (5H, m).

1-Cyano-1-[4-(trifluoromethyl)phenyl]-2-(2-pyridyl)ethylene (25): White needle crystals; mp 141—142°C (from hexane/chloroform), ^{1}H NMR (CDCl$_3$) δ= 7.35—7.38 (1H, m), 7.72—7.96 (7H, m), 8.78—8.80 (1H, m).

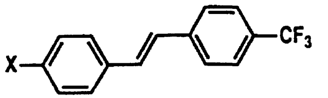
1-Cyano-1-[4-(trifluoromethyl)phenyl]-2-(3-pyridyl)ethylene (26): Pale-yellow needle crystals; mp 115—116°C (from hexane/chloroform), ^{1}H NMR (CDCl$_3$) δ=7.47 (1H, dd, J=4.83 and 8.30 Hz), 7.62 (1H, s), 7.53 (2H, d, J=8.30 Hz), 7.83 (2H, d, J=8.79 Hz), 8.69 (1H, d, J=1.47 Hz), 8.70 (1H, d, J=1.46 Hz), 8.88 (1H, d, J=1.95 Hz).

1-Cyano-1-[4-(trifluoromethyl)phenyl]-2-(4-pyridyl)ethylene (27): White needle crystals; mp 109—110°C (from ethanol), ^{1}H NMR (CDCl$_3$) δ=7.56 (1H, s), 7.72—7.84 (6H, m), 8.79 (2H, d, J=6.34 Hz).

(*E*)-4-Hydroxy-4′-nitrostilbene (N-SD): The compound was prepared according to the literature.[12] Orange granular crystals; mp 208—209°C (form chloroform) (lit,[12] mp 205°C (from ethanol)), ^{1}H NMR (acetone-d_6) δ=6.90 (2H, d, J=8.91 Hz), 7.18 (1H, d, J=16.47 Hz), 7.44 (1H, d, J=16.2 Hz), 7.54 (2H, d, J=8.64 Hz), 7.78 (2H, d, J=8.91 Hz), 8.20 (2H, d, J=8.91 Hz).

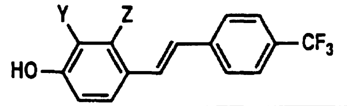
Results and Discussion

Table 1. Nonlinearities and Transparencies of Trifluoromethyl-Substituted Stilbenes



Compound X	λ_{max} nm	$\lambda_{cuttoff}$ nm	μ 10^{-18} esu	β 10^{-30} esu	SHG (×Urea)
1 MeO	323	375	4.32	12.2	0.18
2 HO	327	406	4.74	12.7	0.00
N-SD	380	548	6.90	23.4	0.00
***p*-NA**	372	463	5.54	12.6	0.00
MNA	374	468	5.82	13.3	40

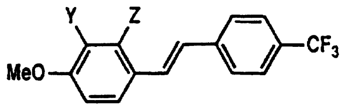
Table 2. Nonlinearities and Transparencies of Trifluoromethyl-Substituted Stilbenes



Compound		λ_{max}	$\lambda_{cuttoff}$	SHG (×Urea)		
Y	Z	nm	nm	As prepared	EtOH/H$_2$O	Toluene
3 Me	H	330	395	0.09	0.08	0.07
4 MeO	H	333	423	0.33	0.31	0.28
5 EtO	H	333	413	0.14	0.17	0.16
6 H	Cl	324	419	0.00	—	—

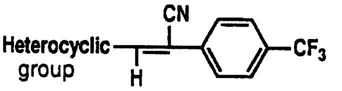
Table 1 summarizes the second-order molecular hyperpolarizabilities (β(10^{-30} esu) and SHG (×Urea)) and transparencies (λ_{max} (nm) and λ_{cutoff} (nm)) of two trifluoromethyl-containing stilbenes (**1** and **2**) with methoxyl or hydroxyl as the electron-donating group. SHG (×Urea) represents the relative intensity of SHG. The measured molecular dipole moments (in unit of 10^{-18} esu=1 Debye) of two compounds are also shown in Table 1. Those data concerning (*E*)-4-hydroxy-4′-nitrostilbene (**N-SD**), *p*-nitroaniline (***p*-NA**), and 2-methyl-4-nitroaniline (**MNA**) are also included in the table for the sake of comparison. The μ and β values of ***p*-NA** and **MNA** are in good agreement with the reported ones[9] of those compounds, respectively. The magnitude of β (12.7×10^{-30} esu) of the trifluoromethyl-containing stilbene **2** is nearly equal to that of ***p*-NA** or **MNA**, and about half that of **N-SD**. The λ_{cutoff} (406 nm) of **2** is by ca. 60 nm shorter than that of ***p*-NA** or **MNA**, and by ca. 140 nm shorter than that of nitro-substituted compound **N-SD**. The λ_{cutoff} (375 nm) of **1**, having a methoxyl as the electron-donating group, is by ca. 30 nm shorter than that of the corresponding hydroxy-substituted compound **2** without decreasing the β value. Thus, the trifluoromethyl-containing stilbene **1** with a methoxyl used as the electron-donating group has a β value (12.2×10^{-30} esu) comparable to that of ***p*-NA** and a λ_{cutoff} (375 nm) ca. 90 nm shorter than that of ***p*-NA**. The relative intensity of SHG of **1**, however,

Table 3. Nonlinearities and Transparencies of Trifluoromethyl-Substituted Stilbenes



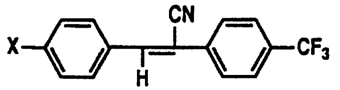
Compound		λ_{max}	$\lambda_{cuttoff}$	μ	β	SHG
Y	Z	nm	nm	10^{-18} esu	10^{-30} esu	(×Urea)
7 Me	H	326	379	5.51	12.8	0.00
8 F	H	321	369	5.44	12.9	0.19
9 H	Cl	313	373	6.27	11.8	0.00

Table 5. Nonlinearities and Transparencies of Heterocycle Analogues of Stilbene Derivatives



Compound	Heterocyclic group	λ_{max} nm	$\lambda_{cuttoff}$ nm	μ 10^{-18} esu	β 10^{-30} esu	SHG (×Urea)
18	2-Furyl	345	411	5.74	7.7	0.46
19	3-Furyl	314	373	5.42	7.1	0.23
20	2-Thienyl	346	418	6.82	6.6	0.22
21	3-Thienyl	321	388	6.68	5.4	0.22
22	2-Pyrrolyl	376	477	5.75	10.9	0.00
23	1-Methyl-2-pyrrolyl	381	454	7.21	11.8	0.65
24	2-Imidazolyl	346	428	5.46	4.3	0.28
25	2-Pyridyl	312	369	6.18	4.3	0.00
26	3-Pyridyl	309	365	5.46	4.4	0.00
27	4-Pyridyl	307	365	5.13	4.2	0.00

Table 4. Nonlinearities and Transparencies of 4-Trifluoromethyl-α-cyano-Substituted Stilbenes



Compound	X	λ_{max} nm	$\lambda_{cuttoff}$ nm	μ 10^{-18} esu	β 10^{-30} esu	SHG (×Urea)
10	H	314	372	4.71	4.5	0.00
11	Cl	318	382	4.22	5.1	0.00
12	Br	320	380	4.63	8.1	3.0
13	Me	323	385	4.79	7.4	0.00
14	MeO	340	412	5.31	14.6	0.00
15	HO	348	484	5.53	15.8	0.00
16	MeS	362	437	4.98	15.5	1.5
17	Me_2N	410	499	6.43	28.9	0.00

is very small, and compound **2** is SHG-inactive.

In order to determine the effect of the kind of substituent groups and the substituent positions on the relative intensity of SHG, all of the following compounds **3**—**27** given in Tables 2, 3, 4, and 5 were synthesized and examined.

Table 2 lists compounds **3**, **4**, **5**, and **6** prepared by introducing a substituent (methyl, methoxyl, or ethoxyl) at the ortho or a substituent (chloro) at the meta position of the hydroxyl group of **2**. The relative intensities of SHG of those compounds (**3**, **4**, **5**, and **6**) are smaller than that of 1. The relative intensities of SHG of the compounds **3**, **4**, and **5** prepared by the solvent-evaporation method (EtOH/H_2O and toluene in Table 2) are also smaller than that of 1. The λ_{max} and λ_{cutoff} of compounds **3**—**6** are roughly the same as those of compound **2**.

As shown in Table 3, methyl-group substitution at the ortho position of a methoxyl group of **1** makes the relative intensity of SHG of **7** zero, contrary to our expectation. The fluoro or chloro substituent at the ortho or meta position (**8** or **9**) doesn't increase the relative intensity of SHG. The λ_{max}, λ_{cutoff}, and β of compounds **7**, **8**, and **9** are about the same as those of compound **1**.

The nonlinearities and transparencies of eight substituted stilbenes having the cyano group at the double-bond position are shown in Table 4. Introduction of a cyano group substituent at the double bond has no effect on the increase of the relative intensities of SHG (**1** 0.18→**14** 0.00, **2** 0.00→**15** 0.00). It, however, increases μ (**1** 4.32×10^{-18} esu→**14** 5.31×10^{-18} esu, **2** 4.74×10^{-18} esu→**15** 5.53×10^{-18} esu) by ca. 1×10^{-18} esu, and β (**1** 12.2×10^{-30} esu→**14** 14.6×10^{-30} esu, **2** 12.7×10^{-30} esu→**15** 15.8×10^{-30} esu) by 2—3×10^{-30} esu, respectively.

The introduction of a bromo or methylthio group (**12** or **16**) results in an SHG intensity that is 3.0- or 1.5-times as large as that of urea, respectively, while that of a chloro, methyl, methoxyl, hydroxyl, or dimethylamino group (**11**, **13**, **14**, **15**, or **17**) results in SHG inactivity. It coincides with an estimation from a two-level model[7)] that increasing λ_{max} (**10** 314 nm→**11** 318 nm→**12**···→**17** 410 nm) usually, but not always, tends to increase β (**10** 4.5×10^{-30} esu→**11** 5.1×10^{-30} esu→**12**···→**17** 28.9×10^{-30} esu).

Table 5 presents nonlinear optical and transparency data concerning ten stilbene-related compounds with heterocyclic and cyano groups. The heterocyclic groups are furyl (**18** and **19**), thienyl (**20** and **21**), pyrrolyl (**22**), 1-methyl-2-pyrrolyl (**23**), imidazolyl (**24**), and pyridyl (**25**, **26**, and **27**) ones. The relative intensities of SHG of six compounds (**18**, **19**, **20**, **21**, **23**, and **24**) are smaller than that of 1. Four compounds (**22**, **25**, **26**, and **27**) are SHG-inactive. This means that the introduction of heterocyclic and cyano groups has no effect to increase the relative intensitiy of SHG. Although the λ_{cutoff} of compounds **19**, **21**, **25**, **26**, and **27** are shorter than 400 nm. But, β values of these compounds are much smaller than that of *p*-**NA**.

Conclusion

In this study we examined the second-order optical nonlinearities and transparencies of seventeen substituted stilbenes as well as ten related compounds containing a trifluoromethyl group at the para position of the double bond as the electron-withdrawing group.

The introduction of a trifluoromethyl as the electron-withdrawing group to a stilbene with a methoxyl as the electron-donating group produces a shorter-wavelength shift of the UV-vis absorption spectra, compared with the corresponding nitro-derivatives, that is to say, the blue light region transparency. The λ_{cutoff} (375 nm) of **1** is ca. 90 nm shorter than that of *p*-**NA** without any decrease in the β value (12.2×10^{-30} esu) of **1**, compared to that of *p*-**NA**.

The bromo or methylthio substituted stilbenes (**12** and **16**) with a cyano group at the double bond show SHG activity. The relative intensities of SHG are 3.0 and 1.5, respectively.

References

1) J. F. Nicoud and R. J. Twieg, "Nonlinear Optical Properties of Organic Molecules and Crystals," ed by D. S. Chemla and J. Zyss, Academic Press Inc., Orlando (1987), Vol. 1, Chap. II-3 and Vol. 2, Appendix I, II; S. Umegaki, *Erekutoronikusu*, **1991**, 76; T. Kondo, N. Ogasawara, and R. Ito, *Oputoronikusu*, **1990**, 132.

2) C. C. Teng and A. F. Garito, *Phys. Rev. B*, **28**, 6766 (1983).

3) P. Kerkoc, M. Zgonik, K. Sutter, Ch. Bosshard, and P. Günter, *Appl. Phys. Lett.*, **54**, 2062 (1989); J. C. Baumert, R. J. Twieg, G. C. Bjorklund, J. A. Logan, and C. W. Dirk, *Appl. Phys. Lett.*, **51**, 1484 (1987).

4) W. Tam, B. Guerin, J. C. Calabrese, and S. H. Stevenson, *Chem. Phys. Lett.*, **154**, 93 (1989).

5) T. Nogami, H, Nakano, Y. Shirota, S. Umegaki, Y. Shimizu, T. Uemiya, and N. Yasuda, *Chem. Phys. Lett.*, **155**, 338 (1989).

6) Y. Goto, A. Hayahsi, Y. Kimura, and M. Nakayama, *J. Cryst. Growth*, **108**, 688 (1991).

7) J. L. Oudar, *J. Chem. Phys.*, **67**, 446 (1977).

8) L. T. Cheng, W. Tam, G. R. Meredith, G. L. J. A. Rikken, and E. W. Meijer, *Proc. SPIE-Int. Soc. Opt. Eng.*, **1147**, 61 (1989); L. T. Cheng, W. Tam, A. Feiring, and G. L. J. A. Rikken, *Proc. SPIE-Int. Soc. Opt. Eng.*, **1337**, 203 (1990); S. N. Oliver, P. Pantelis, and P. L. Dunn, *Appl. Phys. Lett.*, **56**, 307 (1990).

9) S. Umegkai, *Ôyoubuturi*, **57**, 1429 (1988).

10) S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, **39**, 3798 (1968).

11) G. S. Hiers and F. D. Hager, *Org. Synth.*, Coll. Vol. 1, 58 (1932).

12) I. A. Mcculloch and R. T. Bailey, *Mol. Cryst. Liq. Cryst.*, **200**, 157 (1991).

13) H. T. Clarke and E. R. Taylor, *Org. Synth.*, Coll. Vol. 1, 150 (1932).

14) R. Merckx, *Bull. Soc. Chim. Berg.*, **58**, 460 (1949); Y. Wang, W. Tam, S. H. Stevenson, R. A. Clement, and J. Calabrese, *Chem. Phys. Lett.*, **148**, 136 (1988).