mixing speed, catalyst amount, or the cation used (for nucleophilic substitution). An investigation on the effect of the water content in any reaction should account for these variables at least.

Experimental Section

Materials. *n*-Chlorodecane, Aliquat 336, *o*-dichlorobenzene (anhydrous), and sodium and potassium formates were purchased from Aldrich and were used without further purification. The molar concentration of the onium salt was determined by titration.

Trioctylmethylammonium formate was prepared from Aliquat 336 by ion exchange as described by Bar et al.[19] Complete substitution of the chloride was checked by titration.

Calcium formate and lithium formate were prepared by titration of the corresponding hydroxides with analytical grade formic acid (Merck).

Hydranal reagents and solvent for Karl Fischer titration were purchased from Riedel de Haen.

All reagents were dried under reduced pressure (0.5 mbar): the onium salts (to 0.15% (w/w) water) and the ammonium formate (to 1%) in a rotavapor at 80 °C and the other formates (to 0.02%) in a vacuum oven at 140 °C.

Analysis. The conversion of chlorodecane to decyl formate was determined by gas chromatographic analysis.

A solution of trioctylmethylammonium chloride in *o*-dichlorobenzene can be titrated argentometrically (0.02 N $AgNO_3$) when a mixture of acetone, ethanol, and water (equal weights of each) containing sodium bicarbonate (10 mM) and potassium chromate (indicator, 2 mM) is used as the medium. The trioctylmethylammonium formate concentration is obtained by subtracting the titrated value from the initial quat concentration.

The water determination by Karl Fischer titration was precise to 30 ppm. All reagents were titrated prior to the experiments. At the end of each experiment, after the solids had settled, the water content of the liquid phase and of the solid–liquid mixture was determined. Afterward the solid fraction of the mixture was measured (60–80%), and the water content of the solid was calculated.[18]

Water Addition. In all the heterogeneous reactions water was added to the solid by means of a 10-μL syringe. The mixture was allowed to equilibrate overnight in a closed vial. With potassium formate the equilibration time was shortened, by allowing the hygroscopic solid to absorb the required amount of water (indicated by the gain in the weight (analytical balance)) from the air.

In the homogeneous reaction water was added to the solution of the onium salt in *o*-dichlorobenzene, and the mixture was stirred for 30 min.

Reactions. The reactions were carried out in a closed system, consisting of a round-bottom flash (20 mL) equipped with a stoppered side arm and a small condenser through which a mechanical glass stirrer was introduced (Teflon seal).

Heterogeneous Reactions. The dried Aliquat had a gelatinous constitution. Thus, in order to ensure identical initial composition of the organic phase, large batches of solvent, catalyst, and substrate were prepared in advance. This mixture (12 mL) and the contents of one vial of formate salt (27 mmol) were poured into the reaction flask, which was immediately closed. The system was placed in a thermostated bath (±0.5 °C) and stirred at 800 rpm. Samples were withdrawn at fixed time intervals and the liquid phase composition was determined by GC. In order to exclude initial irregularities, the kinetic behavior was investigated only above 5% conversion.

Ion Exchange of Quat Chloride and Solid Formates. The formates were premixed with water as before and added to the solution (12 mL) of trioctylmethylammonium chloride (3.5 mmol) in *o*-dichlorobenzene. The system was held at constant temperature and stirred at 800 rpm. Samples of the liquid phase alone were withdrawn, immediately filtered (GF/A paper, Whatman), and analyzed by argentometric titration. At the end of each run the water content was determined.

Ultrasonic Mixing. An ultrasonic generator (W-375, Heat Systems-Ultrasonics Inc.) with a flat tip was used at an output level of 50 W. The experimental procedure was identical with the mechanically agitated heterogeneous reactions, except for two things:

(1) Since the ultrasonic head had to be immersed in the reaction medium, the reaction had to be performed in an open system. (It is strictly forbidden to introduce the tip through any kind of seal.) Therefore an open vial was used as the reaction vessel.

(2) In order to account for the heat released by the ultrasonic source, the thermostated bath was held at 65 °C. The reaction temperature, which was measured inside the vessel with a thermocouple, varied between 72 and 74 °C but 75 °C was never reached.

Regioselective Trans–Cis Photoisomerization of *m*-Styrylstilbenes

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Abstract: Trans–cis photoisomerizations of *m*-styrylstilbenes, i.e., 2,4,6-triisopropyl-3′-styrylstilbene (TISS), 2,4,6-trimethyl-3′-styrylstilbene (TMSS), and 3-styrylstilbene (SS), and of stilbenes, i.e., 2,4,6-triisopropylstilbene (TIS), 2,4,6-trimethylstilbene (TMS), and stilbene (S), are studied under direct or benzophenone-sensitized irradiation in hexane. Measurements of quantum yields for isomerization have revealed that although the styrylstilbene molecule bears two styryl groups, the reaction is highly regioselective, depending upon the excitation conditions and reactant structures. For example, isomerizations of *trans,trans*-TISS and *trans,cis*-TISS occurred either at the 2,4,6-trisubstituted styryl side upon direct excitation or at the unsubstituted styryl side upon sensitized excitation. When the starting material carries an unsubstituted *cis*-styryl group, the major isomerization always occurred at this moiety by either direct or sensitized excitation, e.g., *cis,trans*-TISS → *trans,trans*-TISS, *cis,cis*-TISS → *trans,cis*-TISS, and *cis,trans*-SS → *trans,trans*-SS. Furthermore, the photoisomerization of *cis,cis*-SS was found to be one-way. These results are interpreted in terms of the usual "energy sink" concept: the excited-state energies (E_S and E_T) of the stilbene chromophores depend on molecular distortion in a subtle manner. It seems that an extremely rapid cis → trans isomerization rate of the unsubstituted *cis*-styryl group is also responsible for the observed preferential photoisomerization of this group. Finally, the cis,cis isomers of TISS, TMSS, and SS underwent upon sensitized excitation minor but substantial one-photon two-double-bond isomerization (cis,cis → trans,trans) in addition to major one-double-bond isomerization. This reaction is not common, since the two isomerizing double bonds are cross-conjugated.

Energy-transfer processes in molecular assemblies such as solids, membranes, and polymers, where electronic interactions between chromophores are frequently strong, can be very rapid (even $>10^{12}$ s^{-1}).[1] As a result, photochemical reactions in these organized

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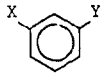
media may often be preceded by the occurrence of rapid energy-transfer processes. In such cases the energy transfer should be of primary importance in determining the photoreactivity of the systems. There is a current interest in the photochemistry of organized systems from synthetic, biological, and practical viewpoints.[2] For example, investigation in this field may contribute to better understanding of the primary photochemical events of photosynthesis and vision and to the invention of the next generation of electronic devices for information storage, switching, and energy conversion.

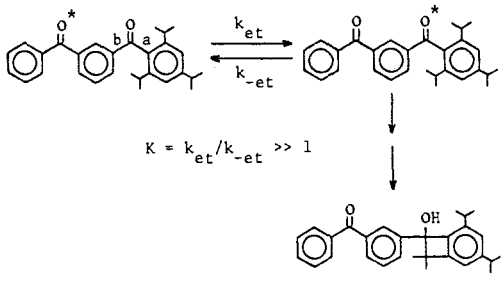
We consider that *m*-phenylene-linked bichromophoric molecules of type A are a simple model for the molecular assembly in a sense that interchromophoric interaction is expected to be strong. Therefore, we are interested in the systematic photochemical study of this type of compounds.



A

X and Y = benzoyl, styryl, or phenylazo

We have already reported the photocyclization reaction of 2,4,6-triisopropylbenzophenone (TIB) and its polycarbonyl derivatives [e.g., a benzoylbenzophenone TIBB (eq 1)] into the corresponding benzocyclobutenols in great detail.[3] Spectroscopic



$K = k_{et}/k_{-et} \gg 1$ (1)

and photokinetic examinations of this reaction have led to the conclusion that excited states of meta-substituted aromatic polyketones can be represented by rapid intramolecular energy migration between the component carbonyl groups (i.e., by pseudoequilibration of localized electronic excitation) and, furthermore, that the electronic excitation resides predominantly at the strained carbonyl group ($K = k_{et}/k_{-et} \gg 1$). The preferential energy migration toward the strained carbonyl group was ascribed to the entropy factor associated with the hindered rotation around bond a. The importance of entropy terms in reversible energy transfer involving a benzophenone triplet was then clearly demonstrated by a laser spectroscopic technique.[4]

We regarded the above excitation-energy localization effect induced by the bulky isopropyl groups as a new steric effect in photochemistry.[3a] In general, steric effects of bulky substituents are known for a wide variety of photochemical reactions. For example, the fundamental principles associated with dynamic stereochemistry, such as steric approach and product development controls[5] and ground-state conformational control (NEER principle),[6] are influenced by steric hindrance to result in change in reaction efficiencies and products. Steric hindrance to energy transfer affects triplet sensitization and quenching efficiencies.[7] Sometimes photoreaction efficiencies are increased as a result of steric congestion, e.g., release of steric strain,[8] loose-bolt effect,[9] steric inhibition of free-rotor radiationless decay,[10] and conformational effect.[3b,11] Excited-state energies are altered by molecular distortion,[12] and this effect was utilized for selective photosensitized trans to cis isomerization.[13] Bulky groups are also useful for asymmetric induction[14] and stabilization of unstable molecules.[8,15] However, in none of these cases has it been noticed that an entropy effect originating in hindered rotation can control the photoreaction.

Table I. Quasi-Photostationary-State Compositions[a]

compd	direct,[b] %	sens,[c] %
TISS	tt, 16; tc, 53; ct, 26; cc, 5	tt, 39; tc, 8; ct, 44; cc, 9
TMSS	tt, 12; tc, 73; ct, 13; cc, 2	tt, 25; tc, 28; ct, 22; cc, 25
SS	tt, 11; tc, 89; cc, 0; **2**, 0	tt, 41; tc, 55; cc, 0; **2**, 4
TIS	t, 2; c, 98	
TMS	t, 8; c, 92[d]	
S	t, 7; c, 93[d]	t, 40; c, 60[e]

[a] A hexane solution ($\sim 5 \times 10^{-3}$ M) was irradiated through Pyrex under bubbling nitrogen. [b] Direct excitation. [c] Benzophenone-(BP-) sensitized excitation; [BP] = 0.1 M. [d] Reference 21. [e] Reference 22.

By means of a variable-temperature NMR spectroscopy a rotational barrier of *cis*-2,4,6-triisopropylstilbene (*c*-TIS) [$\Delta G^{\ddagger}_{26.4}$ = 16.28 kcal/mol, E_a = 15.17 kcal/mol, log A = 12.00 (A in s^{-1})[16a]] is estimated to be approximately equal to that of 2,4,6-triisopropylbenzophenone (TIB) [$\Delta G^{\ddagger}_{31}$ = 16.16 kcal/mol, E_a = 17.07 kcal/mol, log A = 13.45 (A in s^{-1})[16b]]. [The rotations of *trans*-2,4,6-triisopropylstilbene (*t*-TIS) are not hindered at room temperature on the NMR time scale.] Therefore, we expected that investigation of the photoisomerization of four isomeric 2,4,6-triisopropyl-3′-styrylstilbenes (TISS) might also serve, like TIBB, to disclose the role of the entropy factor (hindered rotation) in the reaction. As will subsequently be described,[17] the photoisomerization regioselectivities of TISS can be understood by rapid intramolecular energy migration in their excited states, as in the case of TIBB (eq 1). However, consideration of the entropy factor in the energy migration is not required in the case of TISS. Probably, the excited-state energy difference between the constituent chromophores overshadows the effect of hindered rotation.

(1) (a) Lamola, A. A. In *Energy Transfer and Organic Photochemistry*; Leermakers, P. A., Weissberger, A., Eds.; Wiley: New York, 1969; Chapter 2. (b) Turro, N. J. *Pure Appl. Chem.* **1977**, *49*, 405.

(2) An extensive compilation of research papers in this field can be found in: (a) *Organic Phototransformations in Nonhomogeneous Media*; Fox M. A., Ed. ACS Symposium Series 278; American Chemical Society: Washington, DC, 1985. (b) Scheffer, J. R.; Ramamurthy, V., Turro, N. J., Eds. *Tetrahedron* **1987**, *43*, No. 7. (c) Ramamurthy, V. *Tetrahedron* **1986**, *42*, 5753 (a review).

(3) (a) Ito, Y.; Kawatsuki, N.; Giri, B. P.; Yoshida, M.; Matsuura, T. *J. Org. Chem.* **1985**, *50*, 2893. (b) Ito, Y.; Nishimura, H.; Umehara, Y.; Yamada, Y.; Tone, M.; Matsuura, T. *J. Am. Chem. Soc.* **1983**, *105*, 1590. (c) Ito, Y.; Matsuura, T. *Ibid.* **1983**, *105*, 5237.

(4) Gessner, F.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 7206.

(5) For example: (a) Bryce-Smith, D.; Drew, M. G. B.; Fenton, G. A.; Gilbert, A. *J. Chem. Soc., Chem. Commun.* **1985**, 607. (b) Baldwin, S. W.; Mazzuckelli, T. J. *Tetrahedron Lett.* **1986**, *27*, 5975. (c) Becker, D.; Haddad, N. *Ibid.* **1986**, *27*, 6393. (d) Wolff, S.; Agosta, W. C. *J. Org. Chem.* **1985**, *50*, 4707.

(6) (a) Dauben, W. G.; Rabinowitz, J.; Vietmeyer, N. D.; Wendschuh, P. H. *J. Am. Chem. Soc.* **1972**, *94*, 4285. (b) Jacobs, H. J. C.; Havinga, E. *Adv. Photochem.* **1979**, *11*, 305.

(7) (a) Herkstroeter, W. G.; Jones, L. B.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4777. (b) Froehlich, P. M.; Morrison, H. A. *Ibid.* **1974**, *96*, 332. (c) Wamser, C. C.; Medary, R. T.; Kochevar, I. E.; Turro, N. J.; Chang, P. L. *Ibid.* **1975**, *97*, 4864. (d) Cheung, S. T.; Ware, W. R. *J. Phys. Chem.* **1983**, *87*, 466.

(8) (a) Mandella, W. L.; Franck, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 971. (b) Gusten, H.; Mintas, M.; Klasinc, L. *Ibid.* **1980**, *102*, 7936.

(9) Sakurai, H.; Yoshida, H.; Kira, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1780.

(10) Zimmerman, H. E.; Schissel, D. N. *J. Org. Chem.* **1986**, *51*, 196.

(11) Ito, Y.; Umehara, Y.; Hijiya, T.; Yamada, Y.; Matsuura, T. *J. Am. Chem. Soc.* **1980**, *102*, 5917.

(12) This effect is subtle, as is mentioned later.

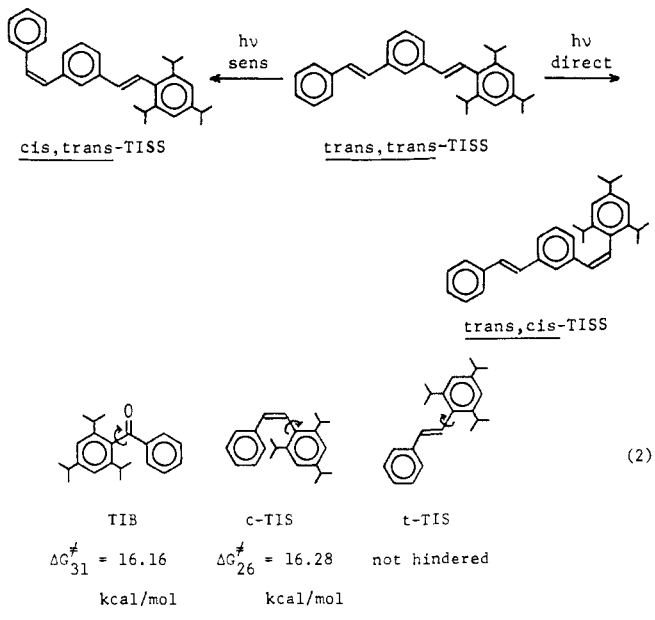
(13) (a) Ramamurthy, V.; Liu, R. S. H. *J. Am. Chem. Soc.* **1976**, *98*, 2935. (b) Kini, A.; Liu, R. S. H. *J. Org. Chem.* **1979**, *44*, 4725. (c) Ramamurthy, V.; Butt, Y.; Yang, C.; Yang, P.; Liu, R. S. H. *Ibid.* **1973**, *38*, 1247.

(14) (a) Lauge, G. L.; Decicco, C.; Tan, S. L.; Chamberlain, G. *Tetrahedron Lett.* **1985**, *26*, 4707. (b) Koch, H.; Scharf, H.-D.; Runsink, J.; Leismann, H. *Chem. Ber.* **1985**, *118*, 1485. (c) Tolbert, L. M.; Ali, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 1742. (d) Sudhakar, A.; Katz, T. J. *Ibid.* **1986**, *108*, 179. (e) Okada, K.; Samizo, F.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1986**, 1044. (f) Inoue, Y.; Kunitomi, Y.; Takamuku, S.; Sakurai, H. *Ibid.* **1978**, 1024.

(15) Tamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 6129.

(16) (a) Ito, Y.; Uozu, Y.; Matsuura, T., unpublished data. (b) Ito, Y.; Umehara, Y.; Yamada, Y.; Matsuura, T.; Imashiro, F. *J. Org. Chem.* **1981**, *46*, 4359.

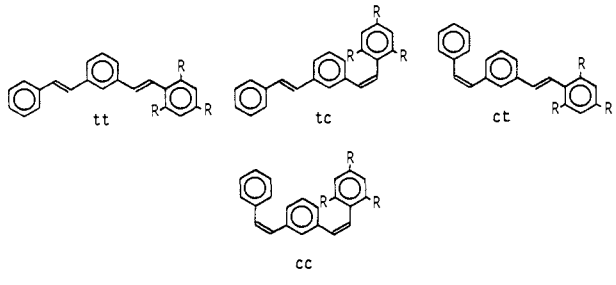
(17) A part of this paper was published in a preliminary form: Ito, Y.; Dote, T.; Uozu, Y.; Matsuura, T. *J. Am. Chem. Soc.* **1986**, *108*, 841.



(2)

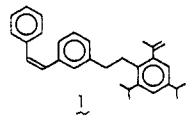
Results

Product Analyses. The trans,trans isomer of 2,4,6-triisopropyl-3′-styrylstilbene (*tt*-TISS) was irradiated in hexane (0.01 M) under bubbling nitrogen with Pyrex-filtered light (>290 nm), and the progress of the reaction was followed by HPLC analyses (silica gel column, 2600:1 hexane–ethyl acetate). Isomerization



TISS, R = i-Pr; TMSS, R = Me; SS, R = H

to the major trans,cis isomer *tc*-TISS and the minor cis,trans isomer *ct*-TISS occurred immediately after exposure to light. Accumulation of the cis,cis isomer *cc*-TISS started only after significant amounts of *tc*-TISS and *ct*-TISS were formed. These compounds eluted in the order cc (retention time 9.9 min), tc (12.7 min), ct (14.2 min), and tt (18.5 min). A quasi-photostationary state was achieved after 1 h of irradiation, and it consisted of tt (16%), tc (53%), ct (26%), and cc (5%) (Table I). Further irradiation increased the proportion of *cc*-TISS (e.g., tt 8%, tc 20%, ct 31%, and cc 41% after 4 h of irradiation), but several byproducts were slowly formed. The structure of a major byproduct was assigned as **1**. The other byproducts were not characterized. Formation of **1** (isolation yield, 45%) indicates that intramolecular hydrogen abstraction[18] is the main competing reaction.



1

A photostationary state was achieved more readily by sensitization with benzophenone (BP). The photostationary-state composition reached after 12 min of irradiation was tt 39%, tc 8%, ct 44%, and cc 9% (Table I). The major product is *ct*-TISS, unlike the direct irradiation where the major product is *tc*-TISS.

(18) (a) Pratt, A. C. *J. Chem. Soc., Chem. Commun.* **1974**, 183. (b) Hornback, J. M.; Barrows, R. D. *J. Org. Chem.* **1982**, *47*, 4285. (c) Padwa, A.; Terry, L. W. *Ibid.* **1986**, *51*, 3738.

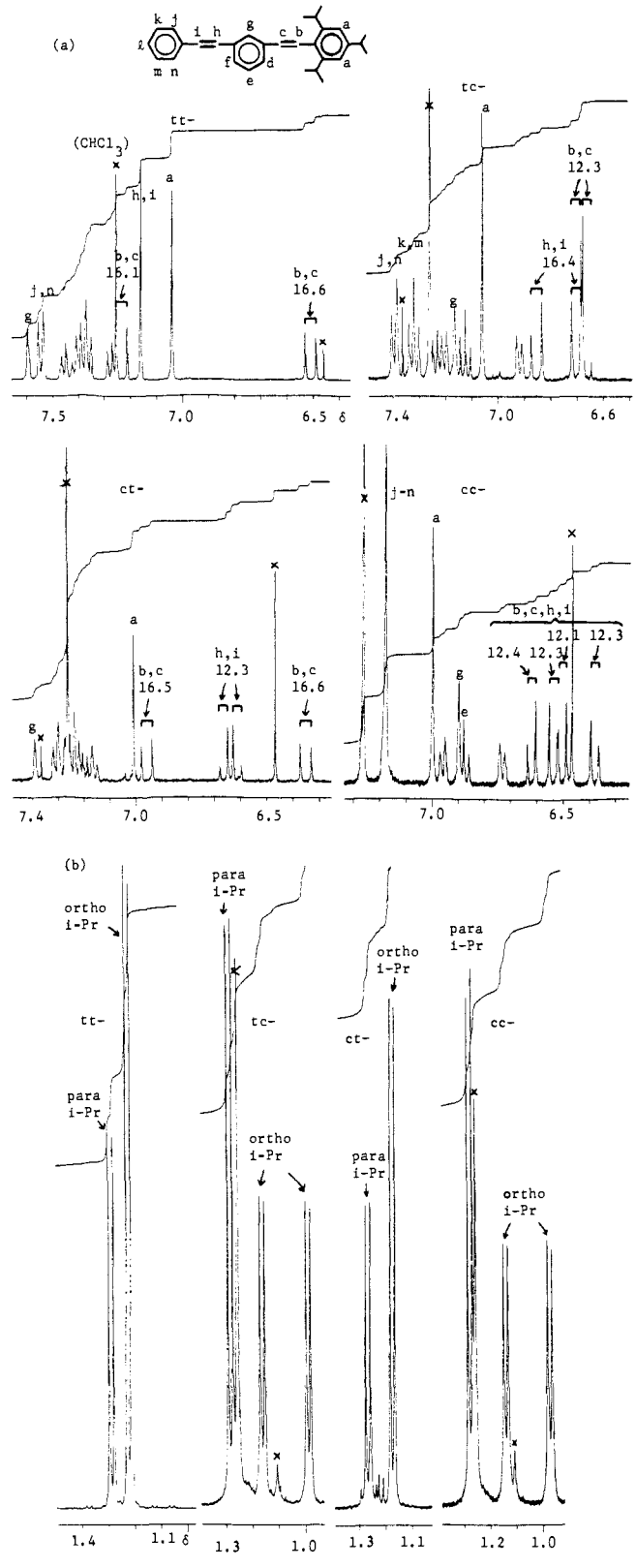


Figure 1. 400-MHz NMR spectra for four isomeric TISS: (a) aromatic and olefinic regions; (b) isopropyl methyl regions.

Formation of byproducts was not observed even after prolonged irradiation.

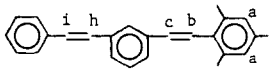
The four isomers of TISS were separated by column chromatography on silica gel. Their 400-MHz NMR signals for olefinic and ortho isopropyl methyl protons are as follows (Figure 1): *tt*-TISS, δ 7.16 (2 H, s, trans CH_h=CH_i), 7.23 and 6.51 (2 H, AB q, J = 16.4 Hz, trans CH_b=CH_c), 1.22 (12 H, d, J = 7.0 Hz, ortho $CHMe_2$); *tc*-TISS, δ 6.85 and 6.70 (2 H, AB q, J = 16.4 Hz, trans CH_h=CH_i), 6.69 and 6.67 (2 H, AB q, J = 12.3

Table II. Quantum Yields (Φ) for Trans-Cis Photoisomerization of *m*-Styrylstilbenes (TISS, TMSS, SS)[a]

config of reactant	reaction[b]	TISS		TMSS		SS	
		direct[c]	sens[d]	direct[c]	sens[d]	direct[c]	sens[d]
tt	tt → tc (S)	0.34	0.026	0.25	0.26	0.038	0.35
	tt → ct (U)	0.026	0.49	0.02	0.24		
	tt → cc (B)	0.00	0.00	0	0	0	0
tc	tc → tt (S)	0.16	0.08	0.17	0.15	see below (*tc*-SS = *ct*-SS)	
	tc → cc (U)	~0	0.39	~0	0.40		
	tc → ct (B)	~0	0.03	~0	0.05		
ct	ct → cc (S)	0.001	0.003	0.005	0.050	0	0
	ct → tt (U)	0.14	0.40	0.070	0.24	0.11	0.42
	ct → tc (B)	~0	0	0	0.12		
cc	cc → ct (S)	0.016	0.20	0.025	0.15	0.20	0.45
	cc → tc (U)	0.16	0.30	0.11	0.28		
	cc → tt (B)	0.007	0.13	0	0.13	0.008	0.35

[a] A degassed hexane solution (~5 × 10^{-3} M) was irradiated at 25 °C. Irradiation wavelength: 313 nm (for direct excitation) or >350 nm [for benzophenone- (BP-) sensitized excitation, [BP] = 0.1 M]. [b] S, U, and B denote the isomerization reactions at the 2,4,6-trisubstituted styryl side, at the unsubstituted styryl side, and at both of these sides, respectively. [c] Direct excitation. [d] BP-sensitized excitation.

Hz, cis CH_b=CH_c), 1.16 and 0.99 (each signal is 6H, d, J = 6.8 Hz, ortho $CHMe_2$); *ct*-TISS, δ 6.95 and 6.35 (2 H, AB q, J = 16.5 Hz, trans CH_b=CH_c), 6.66 and 6.62 (2 H, AB q, J = 12.3 Hz, cis CH_h=CH_i), 1.17 (12 H, d, J = 6.8 Hz, ortho $CHMe_2$); *cc*-TISS, δ 6.62 and 6.54 (2 H, AB q, J = 12.4 Hz, cis CH=CH), 6.50 and 6.38 (2 H, AB q, J = 12.2 Hz, cis CH=CH), 1.14 and 0.97 (each signal is 6 H, d, J = 6.8 Hz, ortho $CHMe_2$).



The geometrical configuration of the four isomeric TISS can be unequivocally determined on the basis of the above NMR data. The methyl signal of the ortho isopropyl group for *tc*-TISS and *cc*-TISS appeared as two doublets owing to slow rotation of the triisopropylphenyl ring on the NMR time scale, supporting the cis configuration of the 2,4,6-triisopropylstyryl unit.[16b] The ortho isopropyl methyls of *cis*-2,4,6-triisopropylstilbene (*c*-TIS) also exhibited magnetic nonequivalence, while those of the trans isomer *t*-TIS were magnetically equivalent: *t*-TIS (60-MHz) δ 7.19 and 6.49 (2 H, AB q, J = 16 Hz, trans CH=CH), 1.20 (12 H, d, J = 7 Hz, ortho $CHMe_2$); *c*-TIS (400-MHz) δ 6.64 and 6.63 (2 H, AB q, J = 12.5 Hz, cis CH=CH), 1.14 and 0.96 (each signal is 6 H, d, J = 6.8 Hz, ortho $CHMe_2$). The coupling constants and chemical shifts of olefinic protons observed for TISS and TIS are consistent with their assigned configurations: it is well-known[19] that the trans coupling (~17 Hz) is larger than the cis (~10 Hz) and that the olefinic proton of *trans*-stilbene (*t*-S, δ 6.99) is less shielded than that of *cis*-stilbene (*c*-S, δ 6.55).

The absorption spectra of the isomeric TISS are displayed in Figure 2. The isomers *ct*-TISS and *cc*-TISS, which lack the unsubstituted *trans*-styryl unit, underwent a significant blue shift.

Direct and BP-sensitized irradiations of less bulky (than TISS) *trans,trans*-2,4,6-trimethyl-3′-styrylstilbene (*tt*-TMSS) gave similar results. By using 2600:1 hexane–ethyl acetate as eluent of HPLC, the four isomers were eluted in the order cc (14.7 min), tc (18.8 min), ct (20.3 min), and tt (27.6 min). The quasi-photostationary-state composition is listed in Table I. Both of the 400-MHz NMR and absorption spectra for each isomeric TMSS are analogous to those of the corresponding isomer of TISS. The fact that the ortho methyl of *cis*-2,4,6-trimethylstilbene (*c*-TMS, δ 2.09) is more shielded than that of the trans isomer *t*-TMS (δ 2.30) is used to confirm the geometrical configuration of the 2,4,6-trimethylstyryl unit of TMSS (see the Experimental Section).

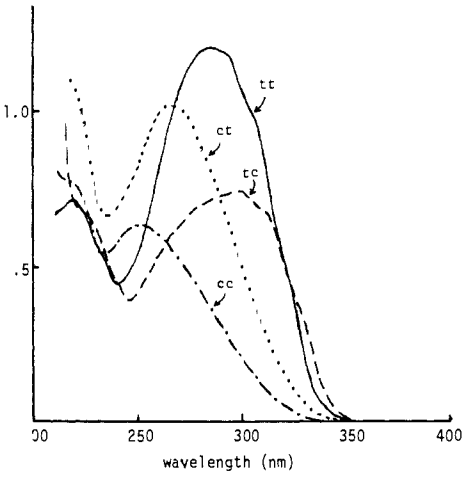
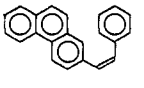


Figure 2. Absorption spectra for four isomeric TISS in *n*-hexane: tt, 3.0 × 10^{-5} M (—); tc, 2.5 × 10^{-5} M (---); ct, 3.1 × 10^{-5} M (···); cc, 2.7 × 10^{-5} M (·–·).

trans,trans-3-Styrylstilbene (*tt*-SS) showed a somewhat different photochemical behavior from that of *tt*-TISS and *tt*-TMSS. Quasi-photostationary-state mixtures that were obtained from direct or BP-sensitized irradiation (1 h or 10 min of irradiation, respectively) contained no cis,cis isomer as summarized in Table I. Furthermore, *cis*-2-styrylphenanthrene (**2**) was formed in a 4% yield by the sensitized excitation. Photocyclization of stilbenes from the triplet state rather than the singlet state is unexpected.[23] The HPLC retention times of these compounds (1400:1 hexane–ethyl acetate as eluent) were as follows: cc, 11.4 min; **2**, 13.3 min; ct, 14.8 min; tt, 19.7 min.



2

It is not likely that **2** is produced via *cc*-SS, since BP-sensitized excitation of *cc*-SS yielded only a small amount of **2**, i.e., tt 42%, ct 58%, cc 0%, and **2** 0.4% after 20 min of irradiation. While not confirmed, **2** was probably produced through photocyclization of *ct*-SS. Prolonged irradiation of SS in benzene solution has previously been performed, and many products arising from trans–cis isomerization, cyclodimerization, and dehydrogenative cyclization were isolated.[20] In the present case, such complete photolysis was not attempted.

Quantum Yields. Quantum yields for trans–cis photoisomerization of *m*-styrylstilbenes (TISS, TMSS, SS) were determined

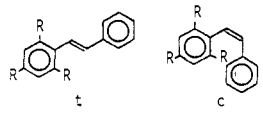
(19) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1974.
(20) (a) Zertani, R.; Meier, H. *Chem. Ber.* **1986**, *119*, 1704. (b) Morgan, D. D.; Horgan, S. W.; Orchin, M. *Tetrahedron Lett.* **1970**, 4347. (c) Dietz, F.; Scholtz, M. *Tetrahedron* **1968**, *24*, 6845. (d) Laarhoven, W. H.; Cuppen, T. J. H. M.; Nivard, R. J. F. *Ibid.* **1970**, *26*, 1069.
(21) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 3907.
(22) Valentine, D., Jr.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 3449.
(23) Mazzucato, U. *Pure Appl. Chem.* **1982**, *54*, 1705.
(24) Fischer, G.; Seger, G.; Muszkat, K. A.; Fischer, E. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1569.

Table III. Quantum Yields (Φ) for Trans–Cis Photoisomerization of Stilbenes (TIS, TMS, S)[a]

compd	reactn	direct[b]	sens[c]
TIS	t → c	0.35	0.47,[d] 0.22,[e] 0.023[f]
	c → t		0.36,[d] 0.057,[e] 0.0006[f]
TMS	t → c	0.47[g]	0.33[d]
	c → t	0.39[g]	0.38[d]
S	t → c	0.50[g]	0.50,[d,h] 0.50,[e] 0.065[f]
	c → t	0.35[g]	0.40[d,h]

[a] A degassed hexane solution (~5 × 10^{-3} M) was irradiated at 25 °C. Irradiation wavelength: 313 nm (for direct excitation) or >350 nm or 366 nm [for sensitized excitation, [sensitizer] = 0.03–0.1 M]. [b] Direct excitation. [c] Sensitized excitation. [d] Benzophenone (E_T = 68.6 kcal/mol). [e] Benzil (E_T = 53.4 kcal/mol). [f] Pyrene (E_T = 48.1 kcal/mol). [g] Reference 21. [h] Reference 22.

in degassed hexane at 25 °C. The reaction was effected either by direct irradiation at 313 nm or by benzophenone-(BP-) sensitized irradiation at >350 nm, to the low conversion (<4%). HPLC analyses showed that trans–cis photoisomerization was the only reaction observed under these conditions. The results are summarized in Table II. The results of the same experiments performed for stilbenes (TIS, TMS, and S) are summarized in Table III.



TIS, R = i-Pr; TMS, R = Me; S, R = H

Table III reveals that trans–cis interconversions of TIS, TMS, and S by direct or BP-sensitized excitation are all efficient and proceed with comparable quantum efficiencies (Φ = 0.33–0.50). On the other hand, perusal of Table II shows that the quantum yields for photoisomerization of *m*-styrylstilbenes depend strongly on the geometrical configuration of the reactant (tt, tc, ct, or cc), the excitation method (direct or sensitized), and the size of the ring substituent R (*i*-Pr, Me, or H). The following five features are noticeable.

(1) The sensitized photoisomerization is more efficient than the direct photoisomerization, as is commonly the case for stilbene-like molecules.[23]

(2) The efficiency for two-double-bond isomerization by absorption of one photon (this reaction is symbolized by B in Table II) is usually negligible except for the sensitized cc → tt isomerization: $\Phi(cc \rightarrow tt)^{sens}$ = 0.13 (TISS), 0.13 (TMSS), and 0.35 (SS). The $\Phi(cc \rightarrow tt)^{sens}$ value for TISS was found to be independent of the conversion (0.5–3%), confirming that the isomerization cc → tt is a one-photon process.

(3) The direct or sensitized photoisomerization of *cc*-SS into the major ct and the minor tt isomers is one-way. In other words, the quantum yields for formation of *cc*-SS from *tt*-SS or *ct*-SS are zero.

Although unsymmetrical styrylstilbenes such as TISS, TMSS, and *ct*-SS have two distinct isomerization centers in the molecule, they exhibited a surprisingly simple pattern of regioselectivity as the following two statements describe.

(4) When the unsymmetrical styrylstilbenes bear an unsubstituted *cis*-styryl group (i.e., *ct*- and *cc*-TISS, *ct*- and *cc*-TMSS, and *ct*-SS), cis-to-trans isomerization of this moiety always predominates, regardless of their excitation method (direct or sensitized). Thus, the main photoisomerization reaction for *ct*-TISS, *ct*-TMSS, and *ct*-SS was ct → tt and that for *cc*-TISS and *cc*-TMSS was cc → tc.

(5) When the unsymmetrical styrylstilbenes do not have an unsubstituted *cis*-styryl group (i.e., *tt*- and *tc*-TISS and *tt*- and *tc*-TMSS), their direct photoisomerization occurs at the 2,4,6-trisubstituted stilbene side with high regioselectivity. By contrast, the sensitized photoisomerization of *tt*- and *tc*-TISS occurs almost exclusively at the unsubstituted stilbene side. In the case of *tt*-TISS, for example, Φ(tt → tc) = 0.34 and Φ(tt → ct) = 0.026 for direct excitation and Φ(tt → tc) = 0.026 and Φ(tt → ct) = 0.49 for sensitized excitation. The regioselectivity for sensitized isomerization of *tt*- and *tc*-TMSS, however, is much lower than that of *tt*- and *tc*-TISS. In general, the isomerization regioselectivity is higher for the isomeric TISS than for the isomeric TMSS, and hence, the effect of 2,4,6-trialkyl substitution is probably steric in nature.

Table IV. Summary of Regioselectivity for Unsymmetrical *m*-Styrylstilbenes

	config of major product[a] (% regioselectivity)	
reactant	singlet	triplet
tt-TISS	tc (93)	ct (95)
tc-TISS	tt (~100)	cc (78)
ct-TISS	tt (99)	tt (99)
cc-TISS	tc (87)	tc (48)[b]
ct-SS	tt (100)	tt (100)

[a] Calculated on the basis of the quantum yields listed in Table II. [b] Other products: ct (32%), tt (20%).

Table V. Absorption Maxima of *m*-Styrylstilbenes and Stilbenes in Hexane[a]

(a) *m*-Styrylstilbenes

	TISS	TMSS	SS
tt	285 (39000)[b]	294 (45000)[b]	296 (48000)[b]
tc	2.4 (30000)[b]	294 (32000)[b]	
ct	266 (33000)	280 (27000)	292 (38000)[b]
cc	253 (24000)	252 (24000)	265 (24000)

(b) Stilbenes

	TIS	TMS	S
t	262 (18000)	280 (23000)	294 (26000)[b]
c	240 (14300)	239 sh (17000)	273 (10500)
	250 sh (13400)	250 sh (15700)	

[a] λ_{max}, nanometers (ε). [b] A vibrational structure is visible in the first absorption band.

Table VI. Fluorescence Maxima of *m*-Styrylstilbenes and Stilbenes in Methylcyclohexane at Room Temperature and at 77 K

compd	λ_{max}^{fl}, nm	rel intens[a]	compd	λ_{max}^{fl}, nm	rel intens[a]
		Room Temperature			
tt-TISS	381	2.8	*t*-TIS	373	0.077
tt-TMSS	380	6.0	*t*-TMS	366	0.30
tt-SS	376	7.7	*t*-S	350[b]	1.0
		77 K			
tt-TISS	370	0.84	*c*-TIS	377	0.14
tt-TMSS	378	0.64	*t*-TMS	362	1.1
tt-SS	380[b]	1.2	*t*-S	350[b]	1.0
t-TIS	369	1.3	*c*-S	440[c]	1[c]

[a] *trans*-Stilbene (*t*-S) = 1.0. [b] A vibrational structure is visible. [c] Reference 24.

Table IV summarizes the photoisomerization regioselectivities observed for unsymmetrical *tt*-, *tc*-, *ct*-, and *cc*-TISS and *ct*-SS. The data are derived from Table II. As will be stated later, these regioselectivities are qualitatively rationalizable by consideration of the usual "energy sink" concept.

Spectra. The absorption maxima (at room temperature) and the fluorescence maxima (at room temperature and 77 K) for *m*-styrylstilbenes and stilbenes are summarized in Tables V and VI. The spectra for a few of these compounds are shown in Figure 3.

Inspection of Figure 3 is informative. Comparison of the absorption spectra of *t*-TIS and *t*-S demonstrates that 2,4,6-triisopropyl substitution produces a considerable hypsochromic and hypochromic shift [*t*-TIS, λ_{max} 262 nm (ε 18000); *t*-S, λ_{max} 294 nm (ε 26000), 307 (24000), 320 sh (14000)]. The absorption spectrum for *tt*-TISS [λ_{max} 285 nm (ε 39000), 307 sh (32000), 323 sh (17000)] is approximately the sum of the spectra for *t*-TIS and *t*-S, indicating that the two olefinic moieties in the *tt*-TISS molecule are relatively independent because of their cross-con-

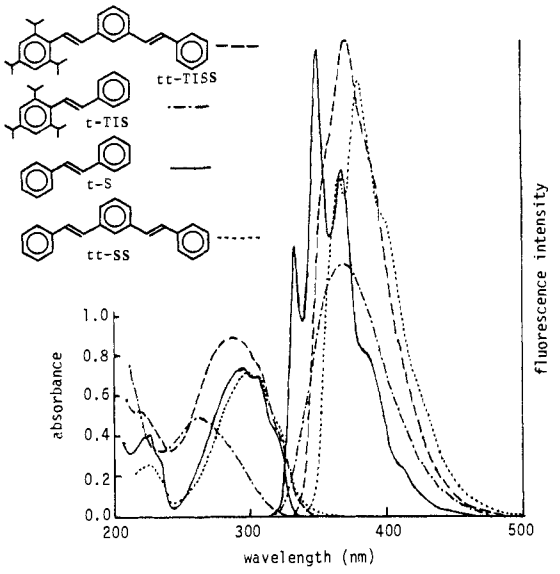


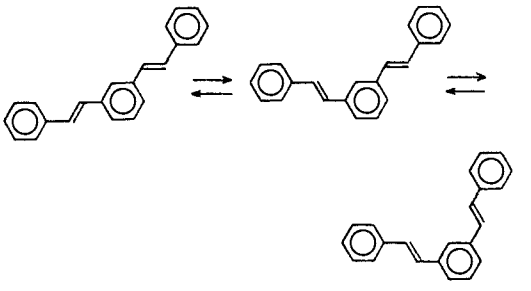
Figure 3. Absorption (at room temperature) and fluorescence spectra (at 77 K) for *tt*-TISS, *tt*-SS, *t*-TIS, and *t*-S in methylcyclohexane: *tt*-TISS, 2.3×10^{-5} M (---); *tt*-SS, 1.5×10^{-5} M (···); *t*-TIS, 2.9×10^{-5} M (·-·); *t*-S, 2.9×10^{-5} M (—).

jugation. For the same reason the absorption maxima of *t*-S and *tt*-SS are nearly at the same position, with the ϵ value of the latter about twice as large as that of the former. The absorption spectrum of *tt*-TISS indicates that, although the incident light (313 nm) is absorbed mainly by the unsubstituted stilbene side of *tt*-TISS, it is the 2,4,6-triisopropyl-substituted side that isomerizes upon direct excitation. Remember that $\Phi(\text{tt} \rightarrow \text{tc})^{\text{direct}} = 0.34$ and $\Phi(\text{tt} \rightarrow \text{ct})^{\text{direct}} = 0.026$ (Table II). A similar situation holds for the direct photoisomerization of *tc*-TISS and *ct*-SS.

A large fluorescence Stokes shift for *t*-TIS ($\lambda_{max} = 262$, $\lambda_{max}^{fl} = 369$ nm) compared with that for *t*-S ($\lambda_{max} = 294$, $\lambda_{max}^{fl} = 350$ nm) suggests a large change in geometry upon excitation of *t*-TIS. The *t*-TIS molecule in its ground state is expected to be severely twisted because of the steric hindrance caused by 2,4,6-triisopropyl substitution.[25] Upon light absorption followed by vibrational relaxation, the molecule will take a much more planar geometry. For ortho-substituted stilbenes such a geometry change (relaxation) in the excited state is believed to occur on the ps time scale.[26]

The fluorescence spectrum of *tt*-SS is quite different in both maximum wavelength and structure from that of *t*-S, contrary to their analogous absorption spectra (Figure 3). Thus, an intramolecular electronic interaction between the cross-conjugated styryl groups of *m*-styrylstilbenes seems to be much more significant in the excited singlet state than in the ground state. This conclusion may be paraphrased to state that the two styryl groups of *m*-styrylstilbenes are not independent in the excited state and intramolecular energy migration (redistribution of the excitation) is very rapid.[1a]

When the temperature is decreased from room temperature to 77 K, the fluorescence intensity increased in all cases measured (Φ_f for *t*-S = 0.04 at 20 °C and 0.95 at 77 K[27]), and the emission maxima moved with all except *t*-S (Table VI). The finding that *tt*-TISS underwent a large blue shift from 381 to 370 nm and *tt*-SS, on the other hand, a red shift from 376 to 380 nm is not surprising. As shown in eq 3, *tt*-SS is known to exist in solution as an equilibrium mixture of three rotamers.[28] The fluorescence spectra of *tt*-SS and *tt*-TISS will depend on distributions of such rotamers, which are potentially temperature dependent.



(3)

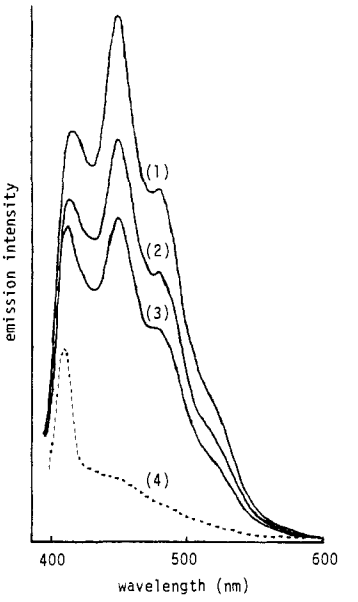


Figure 4. Quenching of benzophenone (BP) phosphorescence by *t*-TIS or *t*-S as quencher (Q) in degassed benzene at room temperature: [BP] $= 2.05 \times 10^{-3}$ M, $\lambda_{exc} = 365$ nm. (1) [Q] = 0. M. (2) [*t*-TIS] = 3.01×10^{-5} M. (3) [*t*-S] = 2.89×10^{-5} M. (4) Residual emission after air saturation: identical spectra were obtained from the each solution (1)-(3).

Table VII. Singlet Energy (E_S) and Triplet Energy (E_T) for Stilbene (S) and 2,4,6-Triisopropylstilbene (TIS)

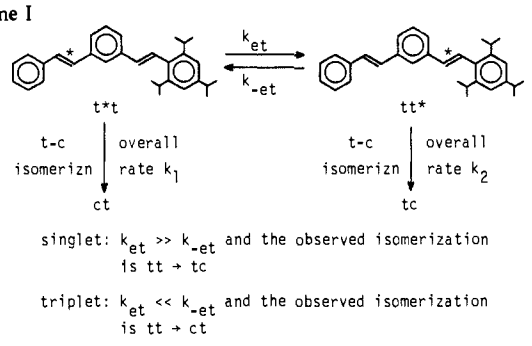
	E_S, kcal/mol		E_T, kcal/mol		
compd	abs end[a]	λ_{max}^{fl} at 77 K[b]	$S_0 \rightarrow T_1$ abs	phos	energy transfer
t-S	85.6[c]	81.7	50[d]	49[e]	48.6[f]
c-S	85.6[g]	65.0	57[h]		48.3[f]
t-TIS	87.4	77.5			*i*
c-TIS	91.1	75.8			*i*

[a] From the absorption end (the wavelength at which the absorption coefficient is 1% of ϵ_{max}). [b] From the fluorescence maximum (Table VI). [c] 85.5 and 85.1 kcal/mol from 0-0 $S_0 \rightarrow S_1$ and 0-0 $S_1 \rightarrow S_0$ bands, respectively.[29a] [d] Reference 29b-d. [e] Reference 29e. [f] Reference 30. [g] 86.1 kcal/mol from 0-0 $S_0 \rightarrow S_1$ band.[29a] [h] Reference 29c. [i] E_T of *t*-TIS and *c*-TIS may be estimated to be near 53 and 55 kcal/mol, respectively, from the values of Φ^{sens} (Table III).

BP Phosphorescence Quenching. Quenching of BP phosphorescence in degassed benzene at room temperature by *tt*-TISS, *tt*-TMSS, *tt*-SS, *t*-TIS, *t*-TMS, and *t*-S afforded $k_q\tau$ values of 17000, 27000, 33000, 12000, 19000, and 27000 M^{-1}, respectively. Typical quenching data are shown in Figure 4. The $k_q\tau$ values were calculated on the basis of the phosphorescence intensity at 480 nm (difference from the air-saturated solution), and two runs agreed within the experimental error (±16%). On the basis of reported triplet lifetime of BP ($\tau = 6.9$ s[31]), the triplet quenching

(25) (a) Bromberg, A.; Muszkat, K. A. *Tetrahedron* **1972**, *28*, 1265. (b) Suzuki, H. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 406.
(26) Bush, T. E.; Scott, G. W. *J. Phys. Chem.* **1981**, *85*, 144.
(27) Saltiel, J.; Marinari, A.; Chang, D.; Mitchener, J. C.; Megarity, E. D. *J. Am. Chem. Soc.* **1979**, *101*, 2982.
(28) Castel, N.; Fischer, E. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1969.
(29) (a) Dyck, R. H.; McClure, D. S. *J. Chem. Phys.* **1962**, *36*, 2326. (b) Ikeyama, T.; Azumi, T. *J. Phys. Chem.* **1985**, *89*, 5332. (c) Evans, D. F. *J. Chem. Soc.* **1957**, 1351. (d) Alder, L.; Gloyna, D.; Wegener, W.; Pragst, F.; Henning, H.-G. *Chem. Phys. Lett.* **1979**, *64*, 503. (e) Saltiel, J.; Khalil, G.; Schanze, K. *Ibid.* **1980**, *70*, 233.
(30) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152.

Scheme I



rate was estimated to be 2.5×10^9, 3.9×10^9, 4.8×10^9, 1.7×10^9, 2.8×10^9, and 3.9×10^9 M^{-1} s^{-1}, respectively.[32] While this result suggests an existence of appreciable steric hindrance to the triplet energy transfer (e.g., the k_q ratio for *t*-S and *t*-TIS is 2.3 and that for *tt*-SS and *tt*-TISS is 2.0), the effect is not sufficiently large to explain the high regioselectivity (95%) observed for the BP-sensitized isomerization of *tt*-TISS (Table IV).

Excitation Energies for S and TIS. Table VII summarizes the excitation energies for *t*-S, *c*-S, *t*-TIS, and *c*-TIS. The energies for the absorption end and the fluorescence maximum (from Table VI) are listed for each compound. The triplet energies of *t*- and *c*-S are taken from the literature. Those of *t*- and *c*-TIS are unknown, but they may be estimated to be ca. 53 and ca. 55 kcal/mol, respectively, judging from sensitized photoisomerization efficiencies with sensitizers of different triplet energies (benzophenone, benzil, and pyrene; Table III).

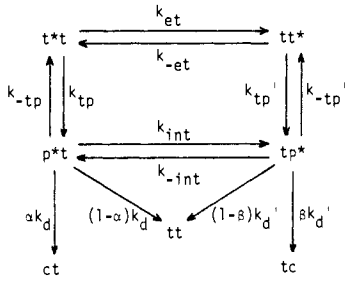
The fluorescence energies of stilbenes and styrenes are usually lowered by ortho alkyl substitution.[21,26,34] The relative λ_{max}^{fl} energies for *t*-S and *t*-TIS (Table VII) agree with this general rule, but those for *c*-S and *c*-TIS are unexpected. The phosphorescence energies of benzophenone[3a,35] and methyl benzoate[36] are increased by ortho alkyl substitution, while the reverse is the case for benzonitrile.[36] Unfortunately, the phosphorescence of *t*-TIS was unobservable. The weak phosphorescence of *t*-S was observable (578 nm) in methylcyclohexane in the presence of ethyl iodide at 77 K, as was previously reported.[29e] However, the phosphorescence of *t*-TIS was undetectable under similar conditions (solvent: methylcyclohexane or ether–pentane–ethanol, 5:5:2).

The above data indicate that the influence of molecular distortion on the excitation energies (E_S and E_T) is very subtle. Furthermore, for distorted molecules the values of E_S and E_T are known to be strongly dependent on their estimation method (Table VII).[30,37] In this paper, however, we did not fully examine these points.

Discussion

Reflection on Highly Regioselective Photoisomerization of Unsymmetrical *m*-Styrylstilbenes. The photokinetics of bichromophoric compounds may be understood in terms of a general scheme dealing with intramolecular energy migration processes (rate constants k_{et} and k_{-et}) and specific reactions of each chromophore (rate constants k_1 and k_2).[38] The situation is illustrated

Scheme II



in Scheme I, where *tt*-TISS is assumed to be bichromophoric, as in the case of TIBB (eq 1).[3a] Of course, Scheme I is oversimplified. According to detailed mechanistic studies on the photoisomerization of stilbene,[39] the isomerization of *tt*-TISS should be interpreted by a much more complex mechanism described in Scheme II. Similar schemes can be written for the other *m*-styrylstilbenes. The symbol p denotes a perpendicular excited species of each stilbene moiety. The interconversion p*t ⇄ tp* may occur in the triplet manifold, since this kind of process has precedence in 1,3-diene triplet chemistry.[40,41]

The results described above for trans–cis photoisomerization of *m*-styrylstilbenes are definitely not sufficient for a detailed mechanistic discussion. The presence of the three rotamers (eq 3)[28] and of the forbidden S_1 state[43] makes the excited-state chemistry of *tt*-SS even more complex than that of *t*-S. In this connection, it is interesting to note that the photoisomerization regioselectivities observed here for unsymmetrical *m*-styrylstilbenes (see Table II or IV) are superficially consistent with the simple energy sink concept (the k_{et}/k_{-et} value).

Thus, as summarized in Table VII, the E_S and E_T values of S and TIS are dependent on their determination methods. However, if the energies calculated from the fluorescence maxima are chosen as the measure of E_S, they can qualitatively accommodate the singlet regioselective isomerizations summarized in Table IV. Similarly, if the energies estimated from the energy-transfer studies are chosen as the measure of E_T, they can qualitatively accommodate the triplet regioselective isomerizations summarized in the same table.

Consider, for example, *tt*-TISS in Scheme I. While E_S (from λ_{max}^{fl}) of *t*-TIS is lower than that of *t*-S, E_T (from energy transfer) of *t*-TIS is higher than that of *t*-S (Table VII). This fact suggests that the singlet excitation resides mainly at the triisopropyl-substituted styryl side ($k_{et}/k_{-et} \gg 1$) and the triplet excitation at the unsubstituted styryl side ($k_{et}/k_{-et} \ll 1$). As a result, the relative value of k_{et} and k_{-et} is consistent with the observed photoisomerization selectivity (tt → tc in the singlet and tt → ct in the triplet manifold from Table IV). Consideration of the more sophisticated mechanism (Scheme II) seems to be unnecessary at the present stage.

Similar explanations based on the energy sink concept are successful for the other *m*-styrylstilbenes (cf. Tables IV and VII). However, in the cases of *ct*-TISS, *cc*-TISS, and *ct*-SS, where the molecule has the unsubstituted *cis*-styryl moiety, the c → t isomerization rate may also be important. In these cases both the low excitation energies of *c*-S and the extremely rapid c →

(31) Wolf, M. W.; Brown, R. E.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 526.
(32) The k_q value for *t*-S based on transient absorption measurements is 6×10^9 M^{-1} s^{-1}.[33]
(33) Görner, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1981**, *85*, 1835.
(34) Lyons, A.; Turro, N. J. *J. Am. Chem. Soc.* **1978**, *100*, 3177.
(35) Wagner, P. J.; Giri, B. P.; Scaiano, J. C.; Ward, D. L.; Gabe, E.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 5483.
(36) Arnold, D. R.; Bolton, J. R.; Palmer, G. E.; Prabhu, K. V. *Can. J. Chem.* **1977**, *55*, 2728.
(37) (a) Kira, A.; Thomas, J. K. *J. Phys. Chem.* **1974**, *78*, 196. (b) Gorman, A. A.; Hamblett, I.; Irvine, M.; Raby, P.; Standen, M. C.; Yeates, S. *J. Am. Chem. Soc.* **1985**, *107*, 4404.
(38) (a) Morrison, H. *Org. Photochem.* **1979**, *4*, 143. (b) Zimmerman, H. E.; Jian-Hua, X.; King, R. K.; Canfield, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 7724.
(39) Saltiel, J.; Charlton, J. L. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1981; Vol. 3, p 25.
(40) Saltiel, J.; Rousseau, A. D.; Sykes, A. *J. Am. Chem. Soc.* **1972**, *94*, 5903.
(41) In fact, a reviewer has suggested that the interconversion p*t ⇄ tp* is more likely to occur than the intramolecular energy migration t*t ⇄ tt* in the case of the triplets, considering potential energy curves for twisting in the stilbene triplet.[42] Therefore, he prefers, rather than the energy-migration processes (k_{et} and k_{-et}), the interconversion of perpendicular excited species (k_{int} and k_{-int}) in order to account for the triplet quantum yields of *m*-styrylstilbenes. This problem is very crucial for olefin photochemistry. At this stage we can only discuss our results superficially.
(42) (a) Saltiel, J.; Marchand, G. R.; Kirkon-Kaminska, E.; Smothers, W. K.; Mueller, W. B.; Charlton, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 3144. (b) Saltiel, J.; Ganapathy, S.; Werking, C. *J. Phys. Chem.* **1987**, *91*, 2755.
(43) Meier, H.; Zertani, R.; Noller, K.; Oelkrug, D.; Krabichler, G. *Chem. Ber.* **1986**, *119*, 1716.

t isomerization rate of *c*-S ($\sim 10^{12}$ s^{-1} [44]) are probably relevant for the observed regioselectivity.

The above discussion is based on the premise that the excited state of *m*-styrylstilbenes can be approximated by the intramolecular energy migration between the localized chromophores. The rate for the intramolecular energy migration (k_{et} and k_{-et}) will be very rapid, since transient intermediates involved in the photoisomerizations of *t*-S, *c*-S, and *tt*-SS are very short-lived: $^1t^*$, 10^{-10} s; $^1p^*$, 10^{-9} s; $^3p^*$, 10^{-7} s; $^1c^*$, 10^{-12} s; $^1tt^*$, 10^{-8} s.[39,43,44] As aforementioned, the comparison of the absorption and fluorescence spectra of *tt*-SS and *t*-S (Figure 3) suggests the presence of a strong interchromophoric interaction in the excited state of *tt*-SS, i.e., a rapid intramolecular energy migration.[1a]

One-Way Photoisomerization. One-way cis-to-trans photoisomerization is known to occur for particular ethylenes bearing a low-triplet-energy aromatic group, e.g., anthrylethylenes, fluoranthenylethylenes, and chrysenylethylenes.[45] The reaction occurs from the triplet state upon direct or sensitized irradiation, and the quantum yields are much greater than unity. These one-way isomerizations were interpreted in terms of a hypothetical triplet energy surface, where the energy minimum is at a transoid geometry rather than near a perpendicular one.

We have found that the c → t photoisomerization of *cc*-SS is also one-way: the reverse isomerizations (ct → cc and tt → cc) do not take place (Tables I and II). This reaction, however, differs from the previous cases in several points. For example, *cc*-SS does not carry a low-triplet-energy aromatic group, and its isomerization quantum yield does not exceed unity ($\Phi^{direct} = 0.21$ and $\Phi^{sens} = 0.80$, from Table II). In our case, the reverse ct → cc isomerization must have been inhibited by the effect of two factors: the low excited-state energy and the fast c → t isomerization rate of the *cis*-stilbene moiety. We believe that postulation of an unusual energy surface is unnecessary in the present case.

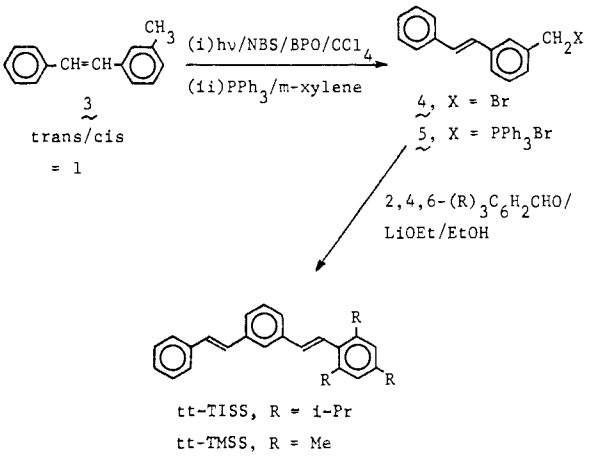
Reflection on One-Photon Two-Double-Bond Isomerizations. Two-double-bond isomerization as a result of absorption of one photon was observed to occur for some conjugated polyene triplets.[40,46] Recently, even a sixfold c → t photoisomerization has been reported for *all-cis*-[2.2.2.2.2.2]orthoparacyclophene triplet.[47] Triplet-sensitized one-photon two-double-bond isomerizations of *cc*-TISS, *cc*-TMSS, and *cc*-SS leading to the corresponding *tt*-isomers (Table II) contrast with the previously published examples, since the two olefinic double bonds are cross-conjugated. Therefore, the present two-double-bond isomerization reactions might not be rationalized by a similar mechanism. In short, twofold photoisomerization of cross-conjugated double bonds does occur in a special case.

Conclusion. The regioselectivity in direct and benzophenone-(BP-) sensitized trans–cis photoisomerizations of *m*-styrylstilbenes like TISS can be understood superficially by the energy sink concept. The rate of the intramolecular energy migration seems to be very rapid, probably owing to strong electronic interaction between the component chromophores in the excited state.

Experimental Section

All melting points were determined on a Yanagimoto micro melting point apparatus, and the values are uncorrected. ^1H NMR spectra were measured on a Varian T-60 or a JEOL GX-400 spectrometer with $CDCl_3$ as the solvent and Me_4Si as the internal standard. IR, UV, emission, and mass spectra were recorded with Jasco IRA-1, Shimadzu UV-240, Shimadzu RF-500, and JEOL JMS-DX 300 spectrometers, respectively. Elemental analyses were carried out at Microanalytical Center of Kyoto University. Thin-layer chromatography was done on a Merck TLC plastic sheet precoated with silica gel 60 F_{254} (for analytical purposes) or on a Merck Kieselgel 60 PF_{254} (for preparative purposes). Column chromatography was carried out on silica gel (Wakogel C-200). HPLC analyses were performed with a Jasco Twinkle or a Shimadzu LC-5A chromatograph equipped with a UV detector (set at 254 nm) by using a silica gel column [Finesil 5, 4.6 mm (o.d.) × 250 mm] and hexane–ethyl acetate (1200–2600:1, v/v, mL/min) as the eluent. All irradiations were done with a 400-W high-pressure mercury lamp.

Scheme III



All solvents used for quantitative experiments were of spectral grade. The trans,trans isomers of 2,4,6-triisopropyl-3′-styrylstilbene (*tt*-TISS) and 2,4,6-trimethyl-3′-styrylstilbene (*tt*-TMSS) were prepared as outlined in Scheme III. The isomer with the trans,cis configuration (*tc*-TMSS) was obtained as a byproduct of this reaction sequence, but the isolation of *tc*-TISS was not attempted.

3-Methylstilbene (3). A solution of lithium ethoxide [prepared by dissolving 1.36 g (0.196 mol) of lithium in 80 mL of absolute ethanol] was aded to a stirred solution of (3-methylbenzyl)triphenylphosphonium bromide (40 g, 0.089 mol) in 150 mL of absolute ethanol. To the resultant yellow-red solution was added 11.32 g (0.11 mol) of benzaldehyde, and the mixture was stirred at room temperature overnight. After removal of the solvent under reduced pressure, the residue was worked up with 200 mL of water and then extracted with 200 mL of benzene. The benzene extract was dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography, using 5:1 v/v hexane–benzene as the eluent. A pale yellow oil (14.6 g, 84%) was obtained and was assigned as a 1:1 mixture of cis- and trans-3-methylstilbene[48] from NMR: NMR (60 MHz) δ 6.92 (s, trans CH=CH), 6.43 (s, cis CH=CH), 2.34 (s, trans CH_3), 2.19 (s, cis CH_3).

(3-Styrylbenzyl)triphenylphosphonium Bromide (5). To a solution of 7.76 g (0.04 mol) of **3** (a 1:1 mixture of cis and trans isomers) in 80 mL of CCl_4 were added 14.24 g (0.08 mol) of *N*-bromosuccinimide and 17.8 mg of benzoyl peroxide. The mixture was irradiated (through Pyrex) for 6 h under refluxing the solution in a water bath. The reaction mixture was cooled to room temperature, filtered to remove the precipitate, and rotary evaporated under reduced pressure to give 14.05 g of a yellow residue containing *trans*-3-(bromomethyl)stilbene (**4**). A small portion of this residue was separated with preparative TLC (hexane) to afford a purified 4: NMR (60 MHz) δ 7.5–7.1 (9H, m, aromatic), 6.98 (2 H, s, trans CH=CH) and 4.42 (2 H, s, CH_2Br). The residue obtained above was dissolved in 150 mL of *m*-xylene, and 10.0 g (0.038 mol) of triphenylphosphine was added. The solution was stirred for 12 h at 100 °C. The resultant pale yellow precipitate was washed with ether and recrystallized from ethanol to give 6.4 g (30% from **3**) of the phosphonium salt **5**: mp 286–288 °C (lit.[49] mp 260 °C); NMR (60 MHz) δ 7.8–6.8 (24 H, m, aromatic), 6.71 (2 H, s, trans CH=CH) and 5.25 (2 H, d, J = 15 Hz, CH_2P); IR (Nujol) 960 cm^{-1} (trans CH=CH).

***trans,trans*-2,4,6-Triisopropyl-3′-styrylstilbene (*tt*-TISS).** To a solution of the phosphonium salt **5** (4.0 g, 7.5 mmol) in 55 mL of absolute ethanol was added a solution of lithium ethoxide prepared by dissolving 0.38 g (0.054 mol) of lithium in 25 mL of absolute ethanol. To the resultant reddish yellow solution was added 2.0 g (8.6 mmol) of 2,4,6-triisopropylbenzaldehyde,[50] and the mixture was stirred at room temperature overnight. The reaction mixture was worked up with water, extracted with benzene, and purified by column chromatography. Recrystallization from ethanol afforded 1.27 g (42%) of *tt*-TISS as colorless needles: mp 154.0–155.2 °C; NMR (400 MHz) δ 7.60–6.49 (15 H, m,

(44) (a) Sumitani, M.; Nakashima, N.; Yoshihara, K. *Chem. Phys. Lett.* **1979**, *68*, 255. (b) Doany, F. E.; Hochstrasser, R. M.; Greene, B. I.; Millard, R. R. *Ibid.* **1985**, *118*, 1.

(45) (a) Arai, T.; Karatzu, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1983**, *24*, 2873. (b) Karatzu, T.; Arai, T.; Sakuragi, H.; Tokumaru, K. *Chem. Phys. Lett.* **1985**, *115*, 9. (c) Arai, T.; Kuriyama, Y.; Karatzu, T.; Sakuragi, H.; Tokumaru, K.; Oishi, S. *J. Photochem.* **1987**, *36*, 125.

(46) Liu, R. S. H.; Butt, Y. *J. Am. Chem. Soc.* **1971**, *93*, 1532.

(47) Sundahl, M.; Wennerstrom, O.; Sandros, K.; Norinder, U. *Tetrahedron Lett.* **1986**, *27*, 1063.

(48) Friedrich, K.; Mirbach, H. *Chem. Ber.* **1959**, *92*, 2751.

(49) Friedrich, K.; Henning, H.-G. *Chem. Ber.* **1959**, *92*, 2756.

(50) Fuson, R. C.; Horning, E. C.; Rowland, S. P.; Ward, M. L. In *Organic Syntheses*; Wiley: New York, **1955**; Collect. Vol. III, p 549.

aromatic and olefinic), 3.29 (2 H, sep, J = 6.9 Hz, ortho C*H*Me$_2$), 2.91 (1 H, sep, J = 6.9 Hz, para C*H*Me$_2$), 1.28 (6 H, d, J = 7.0 Hz, para CH*Me*$_2$), 1.22 (12 H, d, J = 7.0 Hz, ortho CH*Me*$_2$); IR (Nujol) 965 (trans CH=CH), 788, 680 cm^{-1}; MS m/e (rel intens) 408 (M$^+$, 100), 393 (103), 215 (26). Anal. Calcd for $C_{31}H_{36}$: C, 91.12; H, 8.88. Found: C, 90.82; H, 8.92.

Other Geometrical Isomers of TISS. The combined photolysates, which were obtained from external irradiation (Pyrex) of *tt*-TISS (ca. 0.01 M hexane solution) for 2–11 h at 0 °C under bubbling nitrogen, were rotary evaporated to give 158 mg of the residue. The mixture was separated with repeated column chromatography by using hexane as the eluent. The four isomeric TISS were eluted in the order cc, tc, ct, and tt. The cc, tc, and ct isomers were isolated as the colorless viscous material in yields of 6.1 mg (3.9% on the basis of *tt*-TISS employed), 13.0 mg (8.2%), and 8.1 mg (5.1%), respectively. *tc*-TISS: NMR (400 MHz) δ 7.39–6.66 (15 H, m, aromatic and olefinic), 3.17 (2 H, sep, J = 6.9 Hz, ortho C*H*Me$_2$), 2.94 (1 H, sep, J = 6.9 Hz, para C*H*Me$_2$), 1.28 (6 H, d, J = 7.0 Hz, para CH*Me*$_2$), 1.16 and 0.99 (each signal is 6 H, d, J = 6.8 Hz, ortho CH*Me*$_2$); IR (neat) 1210, 950 (trans CH=CH), 785, 745, 670 cm^{-1}; MS m/e (rel intens) 408 (M$^+$, 100), 393 (84), 215 (28). *ct*-TISS: NMR (400 MHz) δ 7.38–6.33 (15 H, m, aromatic and olefinic), 3.18 (2 H, sep, J = 6.9 Hz, ortho C*H*Me$_2$), 2.89 (1 H, sep, J = 6.9 Hz, para C*H*Me$_2$), 1.27 (6 H, d, J = 7.0 Hz, para CH*Me*$_2$), 1.17 (12 H, d, J = 6.8 Hz, ortho CH*Me*$_2$); IR (neat) 960 (trans CH=CH), 870, 780, 675 cm^{-1}; MS m/e (rel intens) 408 (M$^+$, 100), 393 (93), 215 (35). *cc*-TISS: NMR (400 MHz) δ 7.18–6.37 (15 H, m, aromatic and olefinic), 3.13 (2 H, sep, J = 6.8 Hz, ortho C*H*Me$_2$), 2.91 (1 H, sep, J = 6.8 Hz, para C*H*Me$_2$), 1.27 (6 H, d, J = 6.8 Hz, para CH*Me*$_2$), 1.14 and 0.97 (each signal is 6 H, J = 6.8 Hz, ortho CH*Me*$_2$); IR (neat) 1085, 1015, 865, 780, 665 cm^{-1}; MS m/e (rel intens) 408 (M$^+$, 100), 393 (92), 215 (32).

Cis Isomer of 3-[2-[2-(2-Propenyl)-4,6-diisopropylphenyl]ethyl]stilbene (1). A solution of 76.1 mg (0.186 mmol) of *tt*-TISS in hexane (20 mL) was externally irradiated for 8.5 h through a Pyrex filter under bubbling nitrogen. HPLC analyses (1200:1 v/v hexane–ethyl acetate) of the reaction mixture showed one major peak at 10.3 min. Small peaks for the cc (7.4 min), tc (8.6 min), ct (9.4 min), and tt isomers (11.0 min) and for many other byproducts (11.7, 12.3, 26.0, 31.0, 38.4, and 40.5 min) were also observed. The peaks for other than those of the geometrical isomers were invisible at the early stage of the irradiation (<1 h) or under the conditions where the quantum yield measurements were carried out (vide infra).

After evaporation of the solvent under reduced pressure, the residue was subjected to preparative TLC (6:1 v/v hexane–ethyl acetate as the solvent). A colorless solid (34.4 mg, 45%) was isolated and assigned as the title compound **1** from the spectral data. **1**: mp 147–179 °C (not recrystallized); NMR (400 MHz) δ 7.29–7.05 (10 H, m) and 6.79 (1 H, d, J = 1.8 Hz) for aromatic protons, 6.62 and 6.59 (2 H, AB q, J = 12.5 Hz, cis CH=CH), 5.13 (1 H, m, C=C*H*$_2$, J_{gem} = 2.2 Hz and $J_{allylic}$ = 1.5 Hz from decoupling irradiated at δ 2.03), 4.83 (1 H, m, C=C*H*$_2$, J_{gem} = 2.3 Hz and $J_{allylic}$ = 0.9 Hz from decoupling irradiated at δ 2.03), 3.16 (1 H, sep, J = 6.8 Hz, ortho C*H*Me$_2$), 2.85 (1 H, sep, J = 7.0 Hz, para C*H*Me$_2$), 2.79–2.60 (4 H, AA'BB' m, CH$_2$CH$_2$), 2.03 (3 H, br s, =C—CH$_3$), 1.25 (12 H, d, J = 7.0 Hz, CH*Me*$_2$); UV (hexane) λ 275 (ϵ 11 000) nm; MS m/e (rel intens) 408 (M$^+$, 61), 215 (100); HRMS calcd for $C_{31}H_{36}$ 408.2816, found 408.2811.

***trans*,*trans*-2,4,6-Trimethyl-3′-styrylstilbene (*tt*-TMSS).** This compound was prepared by the same procedure as that described for the preparation of *tt*-TISS, from the phosphonium salt **5** and 2,4,6-trimethylbenzaldehyde.[50] Colorless crystals of *tt*-TMSS were obtained in a 23% yield: mp 141.0–143.0 °C from hexane; NMR (400 MHz) δ 7.60–6.59 (15 H, m, aromatic and olefinic) [7.15 (2 H, s, trans CH$_h$=CH$_i$), 7.14 and 6.62 (2 H, AB q, J = 16.4 Hz, trans CH$_b$=CH$_c$), 6.92 (2 H, s, H$_a$)], 2.36 (6 H, s, ortho CH$_3$), 2.29 (3 H, s, para CH$_3$). Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.39; H, 7.41.

A mother liquor from the recrystallization of *tt*-TMSS was subjected to preparative TLC (10:1 v/v hexane–benzene) to furnish a 3.2% yield of the trans,cis isomer *tc*-TMSS as a colorless solid: mp 93.9–96.2 °C (not recrystallized); NMR (400 MHz) δ 7.43–6.55 (15 H, m, aromatic and olefinic) [6.92 (2 H, s, H$_a$), 6.93 and 6.70 (2 H, AB q, J = 16.3 Hz, trans CH$_h$=CH$_i$), 6.64 and 6.57 (2 H, AB q, J = 12.2 Hz, cis CH$_b$=CH$_c$)], 2.34 (3 H, s, para CH$_3$), 2.15 (6 H, s, ortho CH$_3$).

Other Geometrical Isomers of TMSS. A solution containing 99 mg (0.31 mmol) of *tt*-TMSS and 909 mg (5.0 mmol) of benzophenone in benzene (50 mL) was irradiated through Pyrex for 0.5 h. During the irradiation a slow stream of nitrogen gas was passed through the solution. After rotary evaporation under reduced pressure, the residue was separated with preparative TLC (10:1 v/v hexane–benzene) followed by repeated column chromatography (hexane). The four isomeric TMSS were eluted in the order cc, tc, ct, and tt. The ct and cc isomers were isolated as the colorless glassy substance in yields of 9.3 mg (9.4%) and 8.8 mg (8.9%), respectively. *ct*-TMSS: NMR (400 MHz) δ 7.40–6.44 (15 H, m, aromatic and olefinic) [6.88 (2 H, s, H$_a$), 6.88 and 6.47 (2 H, AB q, J = 16.6 Hz, trans CH$_b$=CH$_c$), 6.65 and 6.61 (2 H, AB q, J = 12.2 Hz, cis CH$_h$=CH$_i$)], 2.28 (9 H, s, CH$_3$). *cc*-TMSS: NMR (400 MHz) δ 7.20–6.43 (15 H, m, aromatic and olefinic) [6.81 (2 H, s, H$_a$), 6.51 and 6.46 (2 H, AB q, J = 12.2 Hz, cis CH=CH), 6.51 and 6.46 (2 H, AB q, J = 12.1 Hz, cis CH=CH)], 2.28 (3 H, s, para CH$_3$), 2.07 (6 H, s, ortho CH$_3$).

3-Styrylstilbene (SS) and *cis*-2-Styrylphenanthrene (2). The three isomeric 3-styrylstilbenes (*tt*-, *ct*-, *cc*-SS) were prepared according to the published method.[20d,51] *ct*-SS: NMR (400 MHz) δ 7.47–7.12 (14 H, m), 7.01 and 6.92 (2 H, AB q, J = 16.4 Hz, trans CH=CH), 6.65 and 6.61 (2 H, AB q, J = 12.2 Hz, cis CH=CH). *cc*-SS: NMR (400 MHz) δ 7.23–7.15 (11 H, m), 7.06 (3 H, finely split), 6.55 and 6.50 (4 H, AB q, J = 12.3 Hz, cis CH=CH).

A solution containing 140 mg (0.50 mmol) of *tt*-SS and 1.002 g (5.5 mmol) of benzophenone in 250 mL of hexane was irradiated through Pyrex for 10 min under bubbling nitrogen. After rotary evaporation, the residue was separated with repeated column chromatography (hexane). Phenanthrene **2**, *ct*-SS, and *tt*-SS were eluted sequentially, and 1.7 mg (1.2% on the basis of *tt*-SS employed) of **2** (a viscous oil) and 10.8 mg (7.7%) of *ct*-SS were obtained. **2**: NMR (400 MHz) δ 8.61 (1 H, d, J = 7.7 Hz), 8.50 (1 H, d, J = 8.7 Hz), 7.87 (1 H, d, J = 7.9 Hz), 7.78 (1 H, s), 7.70 (1 H, d, J = 8.9 Hz), 7.65–7.52 (4 H, m), 7.32–7.21 (5 H, m), 6.81 and 6.72 (2 H, AB q, J = 12.3 Hz, cis CH=CH); UV (hexane) λ 245 nm (ϵ 30 400), 268 (37 000), 277 (38 900), 291 (29 300), 305 (16 100); MS m/e (rel intens) 280 (M$^+$, 100); HRMS calcd for $C_{22}H_{16}$ 280.1252, found 280.1247.

Formation of **2** was observable (by HPLC) neither from direct irradiation under similar conditions nor from irradiation where the quantum yield measurements were done (vide infra).

***trans*- and *cis*-2,4,6-Triisopropylstilbene (*t*- and *c*-TIS).** The trans isomer *t*-TIS was prepared by the Grignard reaction of 2,4,6-triisopropylbenzaldehyde with benzylmagnesium chloride, followed by dehydration, as described in the literature:[52] mp 83–86 °C (lit.[52] mp 82.5–83.5 °C); NMR (60 MHz) δ 7.5–7.0 (5 H, m) and 7.02 (2 H, s) for aromatic protons, 7.19 and 6.49 (2 H, AB q, J = 16 Hz, trans CH=CH), 3.60–2.50 (3 H, two sep, J = 7 Hz, C*H*Me$_2$), 1.28 (6 H, d, J = 7 Hz, para CH*Me*$_2$), 1.20 (12 H, d, J = 7 Hz, ortho CH*Me*$_2$); IR (Nujol) 978 cm^{-1} (trans CH=CH).

c-TIS was obtained from irradiation of *t*-TIS. A solution of 447 mg (1.46 mmol) of *t*-TIS in hexane (650 mL) was internally irradiated through Pyrex for 3 h under bubbling nitrogen. After rotary evaporation, the mixture was separated by preparative TLC (hexane) to give 389 mg of *c*-TIS. Distillation in vacuo provided a colorless oil: bp 92–94 °C (0.1 mmHg); NMR (400 MHz) δ 7.11–7.07 (3 H, m), 7.01 (2 H, s), 6.99–6.96 (2 H, m), 6.64 and 6.63 (2 H, AB q, J = 12.5 Hz, cis CH=CH), 3.14 (2 H, sep, J = 6.9 Hz, ortho C*H*Me$_2$), 2.92 (1 H, sep, J = 6.9 Hz, para C*H*Me$_2$), 1.28 (6 H, d, J = 7.0 Hz, para CH*Me*$_2$), 1.14 and 0.96 (each signal is 6 H, d, J = 6.8 Hz, ortho CH*Me*$_2$); IR (neat) 884 cm^{-1}. Anal. Calcd for $C_{23}H_{30}$: C, 90.13; H, 9.87. Found: C, 90.41; H, 9.94.

***trans*- and *cis*-2,4,6-Trimethylstilbene (*t*- and *c*-TMS).** The title compounds were prepared by the Wittig reaction from 2,4,6-trimethylbenzaldehyde and benzyltriphenylphosphonium chloride according to a similar procedure as described for **3**. *t*-TMS: mp 49–50 °C from hexane (lit.[52] mp 55–56 °C); NMR (60 MHz) δ 7.4–7.0 (5 H, m) and 6.75 (2 H, s) for aromatic protons, 6.93 and 6.37 (2 H, AB q, J = 16 Hz, trans CH=CH), 2.30 (6 H, s, ortho CH$_3$), 2.25 (3 H, s, para CH$_3$); MS m/e (rel intens) 222 (M$^+$, 100), 207 (77), 192 (32). *c*-TMS: mp 73–74 °C from hexane; NMR (60 MHz) δ 6.9–7.2 (5 H, m) and 6.80 (2 H, s) for aromatic protons, 6.51 (2 H, finely split s, CH=CH), 2.30 (3 H, s, para CH$_3$), 2.09 (6 H, s, ortho CH$_3$); MS m/e (rel intens) 222 (M$^+$, 100), 207 (75), 192 (29).

Determination of Quasi-Photostationary-State Compositions. A solution containing *tt*-TISS, *tt*-TMSS, *tt*-SS, or *t*-TIS [(2–10) × 10^{-3} M] (and benzophenone (0.1 M)) in hexane (5 mL) was irradiated through Pyrex under bubbling nitrogen at 0 °C. The progress of the isomerization was followed by HPLC analyses until the quasi-photostationary state was achieved. Further irradiation led to considerable side reactions, except in the case of TIS. Irradiation of *cc*-TISS, *ct*-SS, *cc*-SS, and *c*-TIS gave similar photostationary-state compositions.

Determination of Quantum Yields. Samples containing (3–10) × 10^{-3} M of the pure isomeric styrylstilbene or stilbene (and 0.1 M of benzophenone) in hexane were placed in 17 × 120 mm Pyrex tubes. They were degassed by four freeze–thaw cycles below 10^{-2} mmHg and were irra-

(51) Nakaya, T.; Imoto, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1547.
(52) Fuson, R. C.; Denton, J. J.; Best, C. E. *J. Org. Chem.* **1943**, *8*, 64.

diated on a merry-go-round apparatus at 25 °C. Direct irradiations were carried out through a K_2CO_3 (1.3%)-K_2CrO_4 (0.13%) filter solution (mainly 313 nm). Benzophenone-sensitized irradiations were done through a phenanthrene solution (5 g/L) in methanol (>350 nm) or through a glass filter (Riko U-360, mainly 366 nm). The reaction mixtures were analyzed by HPLC, using naphthalene or *m*-terphenyl as the internal standard. A small amount of isomeric olefin impurities involved in the starting material was carefully checked by HPLC: the purities of the *tt*- and *t*-isomers were >99.99% and those of the other isomers were >99.4%. When necessary, corrections were made in the calculation of the quantum yields. In all cases the reaction was stopped at a small conversion (<4%). Two parallel runs for quantum yield measurements agreed within experimental error (±5%). The trans → cis isomerization of *t*-S was used for actinometry ($\Phi^{direct} = \Phi^{sens} = 0.50$[39]).

Intramolecular End-to-End Reactions of Photoactive Terminal Groups Linked by Polymethylene Chains

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Abstract: Intramolecular end-to-end reactions of a pair of photoactive terminal groups, dibenz[*b,f*]azepine (DBA) chromophores, linked by a series of polymethylene chains (DBA-$CO(CH_2)_nCO$-DBA, n = 2-30) were studied by two different approaches. One approach is to measure the intramolecular deactivation rate constants of the excited triplet state of terminal DBA groups by the nanosecond laser photolysis and the other is to measure the intramolecular photocyclization rates of these bichromophoric compounds by the quantitative product analysis with GPC. The excited triplet state of the DBA group is the intermediate of the reaction. The intramolecular deactivation rate constant, k^{intra}, of each compound showed a pronounced chain length dependence, while the intermolecular deactivation rate constant, k^{inter}, was independent of its chain length within the range n = 2-30. The first peak of k^{intra} appeared at the chain length n = 4, and the second peak appeared at n = 18. On the other hand, intramolecular cyclization products were obtained above n = 14, and the quantum yield of the reaction showed the maximum at n = 26 ($\Phi_d^{intra} = 0.34$). This chain length is slightly longer than that for k^{intra} at the second peak. This chain length is interpreted in terms of the ring-closure probability that becomes maximum for a pair of terminal bonds being oriented in directions opposite to each other (anti configuration).

Photoirradiation of bichromophoric compounds undergoes either intra- or intermolecular reactions. The intramolecular reaction gives macrocyclic ring-closure products,[1] while the intermolecular reaction leads to photopolymerization.[2] When intramolecular reactions are compared with the corresponding bimolecular reactions, the rates of the latter are dependent on the concentration of reactants, while those of the former are not, since the effective concentration for the reaction is kept constant by the function of a molecular chain linking two reactants. Therefore, the high reaction yield of intramolecular ring-closure product can be maintained even in highly diluted conditions.

A lot of intramolecular ring-closure reactions have been studied up to now. Intramolecular ring-closure reactions can roughly be classified into two types by the reactivity of the terminal reactants: activation-controlled reaction and diffusion-controlled one. The former occurs only after many collisions of both terminal reactants. In this case, conformational distribution of a molecular chain linking a pair of terminal reactants is kept in equilibrium during the reaction. Therefore, the reaction rate is directly proportional to the ring-closure probability of a molecular chain. On the other hand, the latter occurs immediately when two reactants happen to collide, since the activation energy of the terminal reactants is sufficiently low. Therefore, the reaction rate is proportional to the frequency of collision of terminal reactants.

In the present work, intra- and intermolecular photochemical reactivities are examined by using a series of polymethylene chains having the dibenz[*b,f*]azepine (DBA) group as a pair of terminal groups as shown in Figure 1. Compounds shown in Figure 1 are denoted by DC-n (n = 2-30), each numeral representing the number of methylene units for each polymethylene chain. This reaction system belongs to the activation-controlled one in the classification of the terminal reactivity as mentioned above, since the terminal reactant, DBA, shows a smaller rate constant (3.0×10^7 M^{-1} s^{-1} for 5-valeryl-DBA in dichloromethane at 25 °C)[3] compared with the diffusion rate constant in fluid solutions ($\approx 10^{10}$ M^{-1} s^{-1}). Therefore, the intramolecular reaction rate obtained for a series of bichromophoric compounds in this system will reflect the ring-closure probability of a polymethylene chain.

In the examination on the function of a molecular chain in an intramolecular ring-closure reaction, it is very important to take into consideration the direction of a molecular chain at the terminal position where a pair of terminal groups approach to react with each other. Boens and his co-workers carried out the intramolecular cycloaddition of polymethylene-bis(2-anthroates).[4] They examined chain length dependence of syn head-to-head and syn head-to-tail cyclomer formations and showed that the differences of the terminal structures, i.e., head-to-head or head-to-tail, bring different chain length dependence of the cyclization quantum yields: the head-to-tail cyclomer needs longer chain length, compared with the head-to-head one. As for the present reaction system, when a pair of terminal groups form a cyclobutane ring, there are two types of configurations: syn- and anti-type cyclo-

(1) (a) Galli, C.; Illuminati, G.; Mandolini, L. *J. Am. Chem. Soc.* **1973**, *95*, 8374. (b) De Schryver, F. C.; Put, J.; Leenders, L.; Loos, H. *Ibid.* **1974**, *96*, 6994. (c) Winnik, M. A.; Basu, S. N.; Lee, C. K.; Sanders, D. S. *Ibid.* **1976**, *98*, 2928. (d) Breslow, R.; Rothbard, J.; Herman, F.; Rodriguez, M. L. *Ibid.* **1978**, *100*, 1213. (e) Yamamoto, M.; Goshiki, K.; Kanaya, T.; Nishijima, Y. *Chem. Phys. Lett.* **1978**, *56*, 333. (f) Imanishi, Y. *Macromol. Rev.* **1979**, *14*, 1. (g) Winnik, M. A.; Redpath, T.; Richards, D. H. *Macromolecules* **1980**, *13*, 328. (h) Horie, K.; Schnabel, W.; Mita, I.; Ushiki, H. *Ibid.* **1981**, *14*, 1422. (i) Kanaya, T.; Goshiki, K.; Yamamoto, M.; Nishijima, Y. *J. Am. Chem. Soc.* **1982**, *104*, 3580. (j) De Schryver, F. C.; Demeyer, K.; Toppet, S. *Macromolecules* **1983**, *16*, 89. (k) Srirskaya, P.; Danhelka, J.; Redpath, A. E. C.; Winnik, M. A. *Polymer* **1983**, *24*, 319.

(2) (a) De Schryver, F. C.; Boens, N.; Smets, G. *J. Am. Chem. Soc.* **1974**, *96*, 6463. (b) Boens, N.; De Schryver, F. C.; Smets, G. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 201. (c) Ashikaga, K.; Ito, S.; Yamamoto, M.; Nishijima, Y. *Polym. J.* **1987**, *19*, 727.

(3) Ashikaga, K.; Ito, S.; Yamamoto, M.; Nishijima, Y. *J. Photochem.* **1987**, *38*, 321.

(4) Boens, N.; De Brackeleire, M.; Huybrehts, J.; De Schryver, F. C. *Z. Phys. Chem., N.F.* **1976**, *101*, S417.

0002-7863/88/1510-0198$01.50/0