Bull. Chem. Soc. Jpn., ***64***, *1601—1606 (1991)*

Mechanism of Cis–Trans Isomerization of Fluoranthenylethylenes on Direct Irradiation

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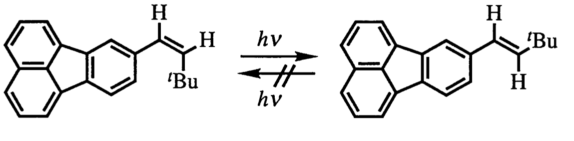
(Received November 19, 1990)

On direct irradiation 8-styrylfluoranthene (SF) and 8-(3,3-dimethyl-1-butenyl)fluoranthene (BF) underwent two-way and one-way isomerizations, respectively, in the triplet manifold after intersystem crossing of the initially produced singlet excited state.

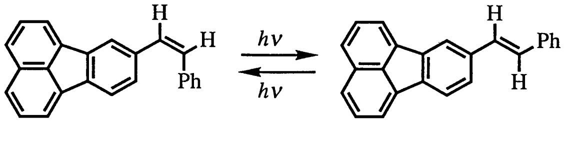
Recently, we have shown that in the triplet sensitized isomerization of olefins the introduction of an anthracene nucleus results in the cis→trans one-way isomerization, no matter which of an alkyl or an aryl group may be substituted on the other ethylenic carbon.[1–3] This is very much contrasted with the mutual two-way isomerization between the cis and trans isomers,[4,5] as well investigated for stilbenes.

Furthermore, we have reported that the olefins substituted by a pyrene[6] or a fluoranthene nucleus[7] whose triplet excitation energy, 48 or 54 kcal mol^{-1},[8] is slightly higher than that of anthracene, 42 kcal mol^{-1},[8] exhibit intermediate behavior between the two-way and one-way isomerizations on triplet sensitization. When a *t*-butyl group is substituted on the other ethylenic carbon, the one-way isomerization occurs with a quantum chain process. On the contrary, when a phenyl group is attached, the two-way isomerization involving a similar quantum chain process takes place.

The direct excitation of olefins also results in their isomerization; however, the mechanism, particularly the spin multiplicity in which the isomerization actually proceeds, depends on the olefins. Stilbene isomerizes in the singlet excited state before intersystem crossing on direct excitation,[9,10] whereas the anthrylethylenes undergo cis→trans one-way isomerization with a quantum chain process on the triplet manifold after intersystem crossing.[1–3] For the olefins exhibiting the intermediate behavior between the two-way and one-way isomerizations, we have recently shown that the direct excitation of the pyrenylethylene with a *t*-butyl group or a phenyl group on the other ethylenic carbon led to the isomerization in the triplet manifold in the same way as the triplet sensitization.[11]



cis-BF *trans*-BF



cis-SF *trans*-SF

These results prompted us to examine whether direct excitation of the fluoranthenylethylenes, whose excitation energies are higher than those of the pyrenylethylenes, brings about the isomerization in the singlet manifold as observed in stilbenes or in the triplet manifold as demonstrated in the anthryl- and pyrenylethylenes.

Experimental

Proton (^{1}H) NMR spectra were recorded on a JEOL JMN-MH-100 spectrometer. Ultraviolet absorption spectra (UV) were taken on a Hitachi 200-20 and a JASCO 660 spectrophotometer. Fluorescence spectra were measured on a Hitachi F-4000 and a Hitachi MPF-4 fluorescence spectrofluorometer. Fluorescence lifetimes were measured using a single photon counting apparatus, Horiba NAES 1100.

Materials. Solvent benzene for photochemical measurements was distilled over calcium hydride. Biacetyl was purified by distillation.

8-Styrylfluoranthene (SF). 8-(Hydroxymethyl)fluoranthene prepared by reducing methyl 8-fluoranthenecarboxylate[12] with lithium aluminum hydride in boiling ether[13] was converted to 8-(bromomethyl)fluoranthene by treating with phosphorus tribromide in the presence of pyridine in chloroform at 0 °C.[13]

8-(Bromomethyl)fluoranthene was refluxed with triphenylphosphine in xylene to give (8-fluoranthenylmethyl) triphenylphosphonium bromide.

The Wittig reaction of benzaldehyde with the ylide prepared from (8-fluoranthenylmethyl)triphenylphosphonium bromide with sodium ethoxide in ethanol gave a mixture of *cis*- and *trans*-8-styrylfluoranthene (SF). Column chromatography on silica gel eluting with hexane and benzene (4 : 1) followed by crystallization from hexane afforded *cis*- and *trans*-SF.

cis-SF: Mp 100—101 °C; UV (benzene) 304 nm (log ε 4.56), 372 (4.09); ^{1}H NMR (CDCl$_3$, 100 MHz) δ=6.63 (d, 1H, J=12.2 Hz, C=CH), 6.69 (d, 1H, J=12.2 Hz, C=CH), 7.2—7.9 (m, 14H, ArH). Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30%. Found: C, 94.64; H, 5.29%.

trans-SF: Mp 131—133 °C; UV (benzene) 322 nm (log ε 4.59), 372 (4.10); ^{1}H NMR (CDCl$_3$, 100 MHz) δ=7.2—7.9 (m, 16H). Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30%. Found: C, 94.58; H, 5.25%.

8-(3,3-Dimethyl-1-butenyl)fluoranthene (BF). A mixture of *cis*- and *trans*-BF was prepared by the Wittig reaction of 2,2-dimethylpropanal with the ylide prepared from (8-fluoranthenylmethyl)triphenylphosphonium bromide with butyllithium in ether. The pure cis and trans isomers were separated by column chromatography on silica gel eluting with petroleum ether.

cis-BF: UV (benzene) 302 nm (log ε 4.65), 330 (3.91).

trans-BF: UV (benzene) 294 nm (log ε 4.56), 327 (3.82), 349 (3.90), 365 (4.95). ^{1}H NMR (CDCl$_3$, 100 MHz) δ=1.06 (s, 9H, C(CH$_3$)$_3$), 5.77 (d, 1H, J=15 Hz, C=CH), 6.65 (d, 1H, J=15 Hz, C=CH), 7.62—8.08 (m, 14H, ArH). Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09%. Found: C, 92.61; H, 7.15%.

Steady State Irradiation. Irradiation of benzene solutions containing *cis*- or *trans*-SF was performed with 436-nm light from a 400-W high-pressure mercury lamp through a filter solution ($CuSO_4 \cdot 5H_2O + NaNO_2$). Similarly, benzene solutions of *cis*- and *trans*-BF were irradiated with 313-nm light isolated from a 400-W high-pressure mercury lamp through an aqueous potassium chromate solution filter and a Toshiba UV-D36B glass filter. For measurements of isomerization quantum yields the sample solutions containing the cis or trans isomer (≥98%, checked by HPLC) were deaerated by bubbling with argon, and irradiated so that the conversions of the isomer were within 20%. The concentrations of the cis and trans isomers in the irradiated samples were determined by HPLC (Waters 600 Multisolvent Delivery System) equipped with an LC spectrophotometer (Waters 490 Programmable Multiwavelength Detector).

The light intensity was measured by a potassium tris(oxalato)ferrate(III) chemical actinometer.

Laser Flash Photolysis. Direct excitation of SF with 351-nm light was performed with a XeF excimer laser (Lambda Physik EMG-101, 10-ns fwhm). Direct excitation at 308 and 337 nm, and biacetyl sensitization with 425-nm light of BF were performed with a XeCl excimer laser (Lambda Physik EMG-101, 10-ns fwhm), a nitrogen laser (National Research Group Inc., 5-ns fwhm), and an excimer laser-pumped dye laser (Lambda Physik FL-3002, Stilbene 3), respectively.

The monitoring beam obtained from a xenon lamp was oriented perpendicularly to the exciting laser beam, passed through a sample cell and a grating monochromator (JASCO CT-25C), and detected with a photomultiplier (Hamamatsu Photonix R928, R446, or R212). The amplified signal was recorded as the time profile of a transmittance change on a storage oscilloscope (Iwatsu TS-8123) and transferred to a personal computer where it was analyzed.

Results

Absorption and Fluorescence Spectra. Figure 1 depicts the absorption and fluorescence spectra of cis and trans isomers of BF and SF. The cis and trans isomers exhibit different fluorescence spectra with different lifetimes from each other. The singlet excitation energies corresponding to the maximum wavelengths of fluorescence spectra ($\lambda_{\max}^{\mathrm{fl}}$) are estimated as 60 kcal mol^{-1} for both *cis*- and *trans*-SF, and 63 and 62 kcal mol^{-1} for *cis*- and *trans*-BF, respectively (Table 1). Because of the broad fluorescence band for every fluoranthenylethylene the energy of the 0–0 transition cannot be determined precisely. When the 0–0 band is assumed to correspond to the crossing point of the absorption and fluorescence spectra, the energies of the 0–0 transition are estimated as 67 and 65 kcal mol^{-1} for *cis*- and *trans*-SF, respectively, and 70 and 69 kcal mol^{-1} for *cis*- and *trans*-BF, respectively (Table 1).

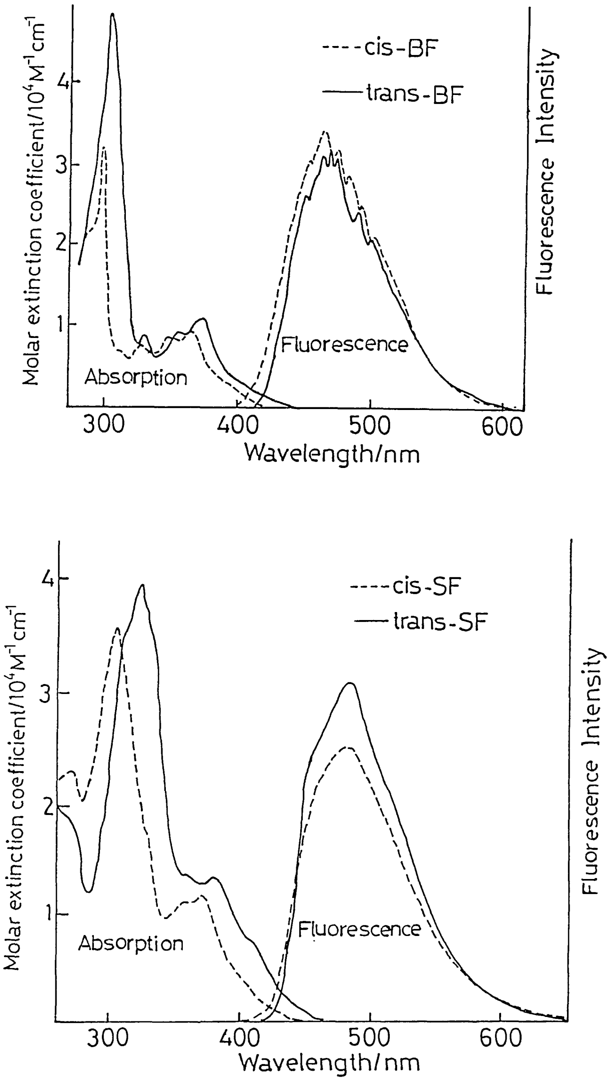


Fig. 1. Absorption and fluorescence spectra of BF and SF in benzene.

In Fig. 1, the differences in energy between the absorption and fluorescence spectra (the Stokes shifts, here defined as the difference in wavelength between the longest absorption maximum and the emission maximum) are calculated as 6000 and 5600 cm^{-1} for *cis*- and *trans*-SF, respectively, and as 5600 and 5200 cm^{-1} for *cis*- and *trans*-BF, respectively. These results indicate that the photoexcitation causes a pronounced change in their structure from the ground states, as reported for the parent hydrocarbon, fluoranthene.[14]

The fluorescence quantum yields (Φ_f) were determined in benzene as 0.40 and 0.48 for *cis*- and *trans*-SF, respectively, and 0.16 and 0.19 for *cis*- and *trans*-BF, respectively, by using anthracene (Φ_f=0.27)[8] (for SF) or

Table 1. Physical Data for the Singlet Excited State of Fluoranthene, BF, and SF

Compound	$\lambda^{\mathrm{fl}}_{\mathrm{max}}$/nm ($E$/kcal mol^{-1})	$\lambda_{0\text{-}0}$$^{a)}$/nm ($E_S$/kcal mol^{-1})	E_T/kcal mol^{-1}	τ_S/ns	Φ_f
Fluoranthene	463 (62)	405 (71)	54	43.7	0.30$^{b)}$
cis-BF	457 (63)	410 (70)	52	28.3	0.16
trans-BF	465 (62)	415 (69)	49	19.4	0.19
cis-SF	480 (60)	430 (67)	46	12.4	0.40
trans-SF	480 (60)	440 (65)	44	9.7	0.48

a) See text. b) In hexane; Ref. 8.

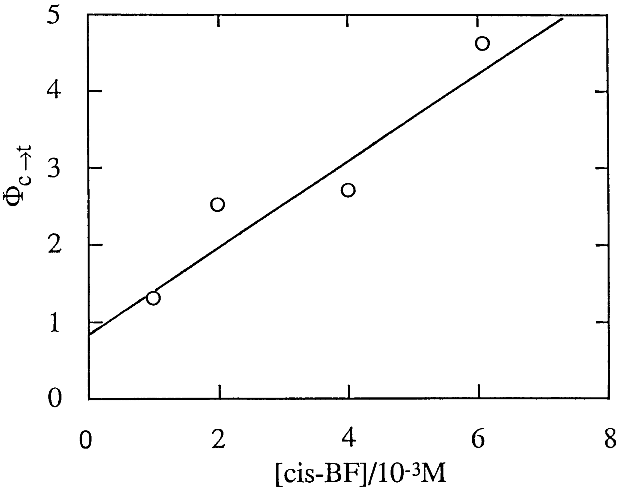


Fig. 2. Plot of the quantum yields for cis→trans isomerization of BF on direct irradiation in benzene.

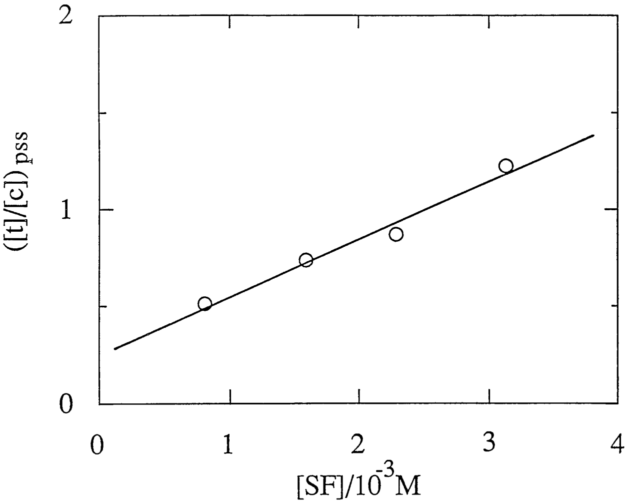


Fig. 3. Plot of the photostationary state isomer ratios against the total SF concentration on direct irradiation in benzene.

fluoranthene (Φ_f=0.30 in hexane)[14] (for BF) as a standard. The singlet lifetimes measured in benzene by the single photon counting method (SPC) are 12.4, 9.7, 28.3, and 19.4 ns for *cis*-SF, *trans*-SF, *cis*-BF, and *trans*-BF, respectively. The fluorescence quantum yields and lifetimes of the BF and SF isomers are summarized in Table 1.

Isomerization Quantum Yields and Photostationary State Isomer Ratio. On direct excitation as well as on triplet sensitized irradiation,[7b)] BF underwent cis→trans one-way isomerization. Figure 2 illustrates a concentration dependence of the quantum yield ($\Phi_{c\to t}$) for cis→trans isomerization on direct irradiation. This figure indicates that $\Phi_{c\to t}$ increases with increasing *cis*-BF concentration, attaining nearly 5 at [*cis*-BF]=6×10^{-3} M (1M=1 mol dm^{-3}). On biacetyl sensitization, $\Phi_{c\to t}$ also increased with increasing [*cis*-BF] up to nearly 20 at [*cis*-BF]= 3×10^{-3} M.

The photostationary state isomer composition, ([t]/[c])$_{\mathrm{pss}}$, for SF was determined on irradiation with a 436-nm line to be 0.51 at the total olefin concentration of 9×10^{-4}M. The ([t]/[c])$_{\mathrm{pss}}$ value increased with increasing olefin concentration to attain 0.94 at [SF]=2.3×10^{-3} M (Fig. 3). The quantum yields of cis-trans isomerization, $\Phi_{c\to t}$ and $\Phi_{t\to c}$ were determined on 436-nm excitation as 0.22 and 0.029, respectively, on starting with pure *cis*- and *trans*-SF at [SF]= 2.3×10^{-3}M.

The ([t]/[c])$_{\mathrm{pss}}$ value is expressed by the product of the ratios of isomerization quantum yields and of the extinction coefficients ($\varepsilon_c/\varepsilon_t$) at the irradiation wavelength as described by Eq. 1.

$$([t]/[c])_{\mathrm{pss}}=(\varepsilon_c/\varepsilon_t)(\Phi_{c\to t}/\Phi_{t\to c}) \quad (1)$$

The extinction coefficients at 436 nm were determined as 310 and 2500 for *cis*- and *trans*-SF. Thus, at an olefin concentration of 2.3×10^{-3}M the ([t]/[c])$_{\mathrm{pss}}$ value is calculated from Eq. 1 as 0.94 [=(310/2500)×(0.22/0.029)], which is in good agreement with the observed value.

Laser Flash Photolysis Studies. The transient absorption spectra were observed on 308- or 337-nm laser excitation of *cis*- and *trans*-BF (4×10^{-4} M) in benzene. Both isomers exhibited the same spectra having two bands at 400—480 and 550—650 nm with the same lifetime (τ_T=25 μs) as measured at the peak wavelengths.

The spectra and lifetimes were essestially identical with those observed on triplet sensitized excitation.[7a] Under similar conditions fluoranthene exhibited its T–T absorption at 400—440 nm (τ_T=30 μs). The transient absorption spectra of SF were effectively quenched by azulene (E_T=39.8 kcal mol^{-1});[15] the quenching rate constant was determined as 3.6×10^{-9} M^{-1} s^{-1} on excitation of *cis*-BF.

On excitation of *cis*- and *trans*-SF (6×10^{-5}M) with 351-nm laser pulses in benzene, both isomers exhibited the same transient absorption spectra with a sharp intense and a broad weak band around 490 and 600 nm, respectively. The spectra decayed with a lifetime of 500 ns under deaerated conditions. The spectral properties are identical with those observed on camphorquinone-sensitized laser excitation.[7b] From these results the observed transient spectra can be reasonably assigned to the trans triplets in both cases.

Discussion

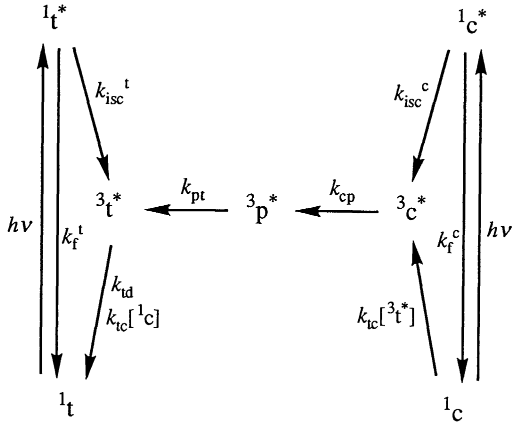
Isomerization Mechanism of BF and SF on Direct Excitation. The results of stationary irradiation and flash photolysis indicate that the triplet mechanism describes the cis→trans one-way isomerization of BF on direct irradiation. Thus, the cis triplet (^{3}c*) produced by intersystem crossing of the cis excited singlet (^{1}c*) undergoes twisting around the double bond to give the trans triplet (^{3}t*), which subsequently undergoes unimolecular deactivation to the trans isomer or energy transfer to the cis isomer to regenerate ^{3}c* leading to a quantum chain process (Scheme 1). According to this mechanism, the quantum yield ($\Phi^{\mathrm{dir}}_{\mathrm{c\to t}}$) for cis→trans isomerization is expressed by Eq. 2.

$$\Phi^{\mathrm{dir}}_{\mathrm{c\to t}} = \Phi_{\mathrm{isc}}(1 + k_{\mathrm{tc}}\tau_{\mathrm{T}}[\textit{cis}\text{-BF}]) \qquad (2)$$

where Φ_{isc}, k_{tc}, and τ_{T} denote the quantum yield for intersystem crossing of *cis*-BF, the rate constant for energy transfer from ^{3}t* to *cis*-BF, and the lifetime of the trans triplet of BF.

Figure 2 gives a slope, $\Phi_{\mathrm{isc}}k_{\mathrm{tc}}\tau_{\mathrm{T}}$, of 600 M^{-1}, an intercept, Φ_{isc}, of 0.83, and therefore, $k_{\mathrm{tc}}\tau_{\mathrm{T}}$ of 720 M^{-1}. The obtained value for Φ_{isc}, 0.83, is very close to $1-\Phi_{\mathrm{f}}=1-0.16=0.84$, showing that the singlet excited state of *cis*-BF decays through either fluorescence emission or intersystem crossing to ^{3}c*. Dividing the obtained $k_{\mathrm{tc}}\tau_{\mathrm{T}}$ values by τ_{T} (=25 μs, determined by laser flash photolysis) affords k_{tc} of 2.9×10^7 M^{-1} s^{-1}.

In the excited singlet state, the energy transfer from ^{1}t* to ^{1}c leading to the quantum chain process could not compete with the deactivation of ^{1}t* with $k_{\mathrm{td}}(=1/\tau_{\mathrm{S}})=5\times10^7$ s^{-1}; the energy transfer via the resonance mechanism could not operate because of an insufficient overlap of the *trans*-SF emission and *cis*-SF absorption (Fig. 1), and the energy transfer via the exchange mechanism might be much slower ($\ll10^{10}$ M^{-1} s^{-1}) than diffusion-controlled since this process is nearly 1 kcal mol^{-1} endothermic on the basis of the fluorescence data. Thus, the pseudo-first-order energy transfer rate may be $\ll10^7$ s^{-1} in the concentration range of ca. 10^{-3} M. A mechanism involving a ground state complex can be also ruled out since there was no evidence for the formation of such a complex in either absorption or fluorescence spectra for various concentrations of *trans*-BF.



Scheme 1.

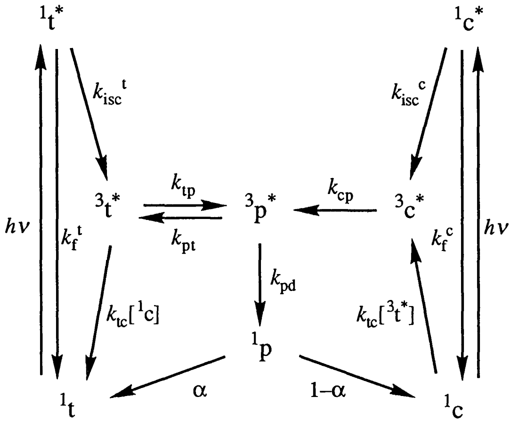
As mentioned above, k_{tc} is determined to be 2.9×10^7 M^{-1} s^{-1}. The following equation is established for endothermic energy transfer:[16]

$$k_{\mathrm{tc}} = A\exp(-E_{\mathrm{a}}/RT), \qquad (3)$$

where

$$-E_{\mathrm{a}} = \Delta E_{\mathrm{T}} = E_{\mathrm{T}}(\textit{trans}\text{-BF}) - E_{\mathrm{T}}(\textit{cis}\text{-BF}) \qquad (4)$$

On substituting $k_{\mathrm{tc}}=2.9\times10^7$ M^{-1} s^{-1} into this equation and assuming $k_{\mathrm{tc}}=5\times10^9$ M^{-1} s^{-1} at $\Delta E_{\mathrm{T}}=0$,[16] the energy transfer from ^{3}t* to *cis*-BF is estimated to be endothermic by 3 kcal mol^{-1}. Therefore, the triplet energy of *cis*-BF is nearly 3 kcal mol^{-1} higher than that of *trans*-BF.



Scheme 2.

Contrary to BF, SF undergoes two-way isomerization on direct irradiation similarly to the previously reported triplet sensitization.[7b)] *cis*-SF exhibited the fluorescence spectrum with a different lifetime and different spectral properties from those of *trans*-SF. Moreover, the T–T absorption spectrum was also observed on direct excitation of *cis*-SF. The photostationary state isomer composition $([\mathrm{t}]/[\mathrm{c}])_{\mathrm{pss}}$ increased with increasing total olefin concentration. These results clearly indicate that the isomerization on direct excitation proceeds through the triplet manifold as shown in Scheme 2.

Potential Energy Surface of Fluoranthenylethylenes. The excited singlet states of fluoranthenylethylenes emit fluorescence or undergo intersystem crossing with decay rate constants of $1/\tau_{\mathrm{S}}=8.1\times10^{7}\,\mathrm{s}^{-1}$ for *cis*-SF and $3.5\times10^{7}\,\mathrm{s}^{-1}$ for BF, but the isomerization cannot be detected in the singlet manifold. Therefore, the latter process might be slower than 1/100 of $1/\tau_{\mathrm{S}}$, $10^{6}\,\mathrm{s}^{-1}$. If we assume a frequency factor A of 10^{11}—$10^{12}\,\mathrm{s}^{-1}$ for twisting around the double bond as reported for some triplet olefins,[2b,17)] the activation barrier for isomerization might be higher than 7 kcal mol^{-1} in the singlet manifold. Thus, the potential energy surfaces of SF are depicted in Fig. 4a taking into account the previously reported triplet energy surface.[7b)]

In Fig. 4a, the direct excitation of *cis*- and *trans*-SF produces the respective singlet excited states which emit fluorescence or undergo intersystem crossing to produce the triplet states, which are deactivated to the ground state from either the perpendicular or trans triplet state, resulting in the photostationary mixture of cis and trans isomers.

On direct irradiation, BF undergoes one-way isomerization in the triplet manifold after intersystem crossing, and its potential energy surfaces is similarly drawn in Fig. 4b.

As mentioned above, on direct irradiation the two-way isomerizing olefins such as stilbene usually undergo isomerization in the singlet manifold, while the one-way isomerizing olefins undergo isomerization in the triplet manifold. The fluoranthenylethylenes employed also isomerize in the triplet manifold irrespective of the substituent on the other ethylenic carbon, *t*-butyl or phenyl, therefore behaving similarly to the anthryl- and pyrenylethylenes.

On the triplet energy surface of olefins, the introduction of an aromatic group with a low triplet energy lowers the energy of ^{3}t* and ^{3}c* to put them, instead of ^{3}p*, at the energy minima. A similar situation may happen on the singlet energy surface. On substitution of an aryl group on the terminal carbon of styrene, those with low singlet excitation energies like 8-fluoranthenyl (80 kcal mol^{-1})[8)] make both ^{1}c* and ^{1}t* fluorescent and apt to intersystem cross to the triplet state with considerable efficiencies (Table 1), whereas those with high singlet energies like phenyl (110 kcal mol^{-1})[8)] and 2-naphthyl (92 kcal mol^{-1})[8)] do not make ^{1}c* fluorescent but lead it to isomerize in the singlet manifold before intersystem crossing.[8)] These results indicate that the substitution of the aromatic group with a low singlet energy sufficiently stabilizes ^{1}c*

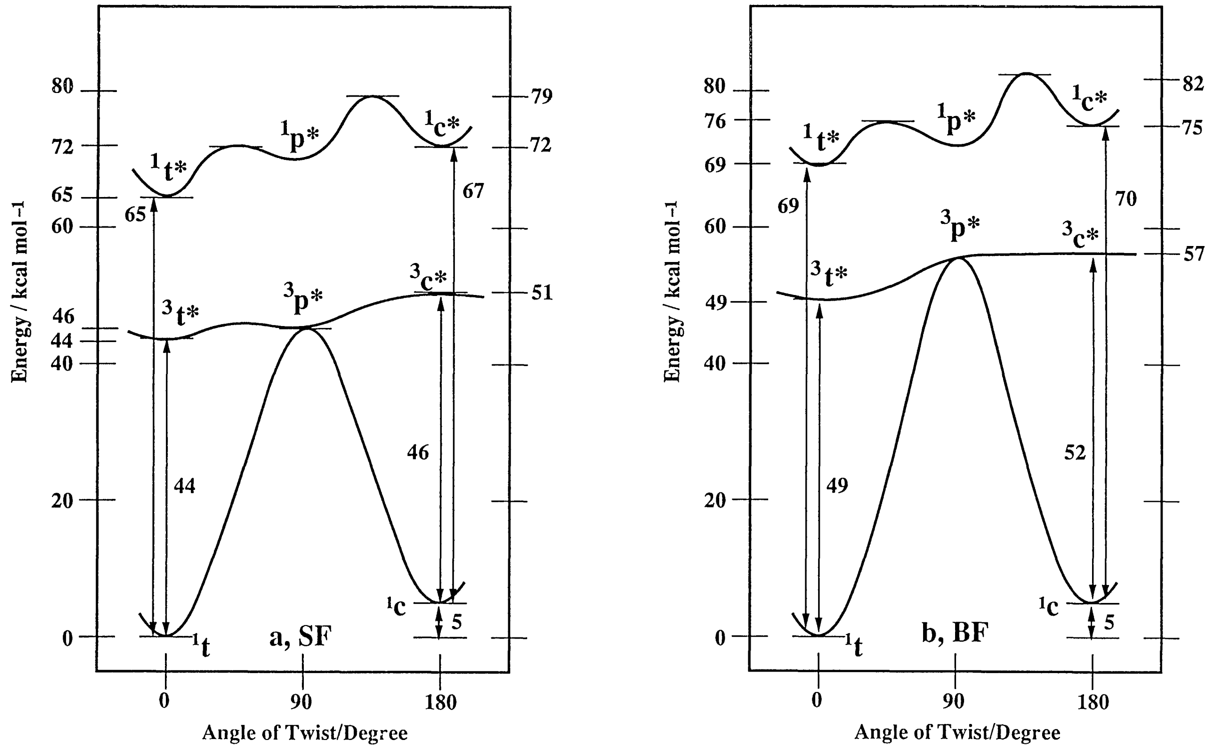


Fig. 4. Potential energy surfaces of cis–trans isomerization of SF (a) and BF (b).

to reside at an energy minimum and to have a sufficient lifetime to emit fluorescence. This situation may reflect the presence of a considerable energy barrier for isomerization in the singlet manifold. Therefore, the isomerization takes place in the triplet state after intersystem crossing. This is contrasted to the effect of substitution of the aromatic group with higher energies as observed in stilbene, where $^1c^*$ is not so stabilized as to fluoresce practically and isomerizes facilely on the singlet energy surface. Therefore, the singlet and triplet excitation energies of the aromatic group on the double bond control the course of isomerization, (1) the spin multiplicity in which the isomerization takes place on direct excitation, and (2) the mode of isomerization, two-way or one-way, in the triplet state.

The authors thank to the Ministry of Education, Science and Culture for partial support of this work by Grant-in-Aid for Special Project Research Nos. 61123001, 62113001, and 63104001 (K. T.) and by Grant-in-Aid for Scientific Research Nos. 61740242, 01740255 (T. A.), and 02453019 (K. T.). Thanks are also due to University of Tsukuba for partial support by the President's Special Grant for Education and Research, 1990 (K. T.).

References

1) a) T. Arai, T. Karatsu, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **24**, 2873 (1983); b) T. Karatsu, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **115**, 9 (1985); c) H. Hamaguchi, M. Tasumi, T. Karatsu, T Arai, and K. Tokumaru, *J. Am. Chem. Soc.*, **108**, 1698 (1986).

2) a) T. Arai, T. Karatsu, M. Tsuchiya, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **149**, 161 (1988); b) T. Karatsu, M. Tsuchiya, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **169**, 36 (1990).

3) T. Arai, T. Karatsu, H. Misawa, Y. Kuriyama, H. Okamoto, T. Hiresaki, H. Furuuchi, H. Zeng, H. Sakuragi, and K. Tokumaru, *Pure Appl. Chem.*, **60**, 989 (1988), and references cited therein.

4) a) J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, in "Organic Photochemistry," ed by O. L. Chapman, Marcel Dekker, New York (1973), Vol. 3, p. 1; b) J. Saltiel and J. L. Charlton, in "Rearrangement in Ground and Excited States," ed by P. de Mayo, Academic Press, New York (1980), Vol. 3, p. 25.

5) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. B. Bradshaw, D. O. Cowan, R. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

6) a)T. Arai, H. Okamoto, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **157**, 46 (1989); b) H. Okamoto, T. Arai, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **63**, 2881 (1990).

7) a) T. Arai, Y. Kuriyama, T. Karatsu, H. Sakuragi, K. Tokumaru, and S. Oishi, *J. Photochem.*, **36**, 125 (1987); b) H. Furuuchi, T. Arai, Y. Kuriyama, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **162**, 211 (1989).

8) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York (1973), p. 5.

9) J. Saltiel, A. Marinari, D. W.-L. Chang, J. C. Mitchener, and E. D. Megarity, *J. Am. Chem. Soc.*, **101**, 2983 (1979).

10) M. Sumitani and K. Yoshihara, *J. Chem. Phys.*, **76**, 738 (1982).

11) H. Okamoto, T. Arai, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **64**, 216 (1991).

12) a) J. v. Braun and G. Manz, *Justus Liebigs Ann. Chem.*, **496**, 170 (1932); b) N. Campbell and W. W. Easton, *J. Chem. Soc.*, **1949**, 340; c) T. Sasaki, K. Kanematsu, and T. Hiramatsu, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1213.

13) S. Akiyama, S. Misumi, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, **35**, 1826 (1962).

14) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York (1971), p. 390.

15) A. A. Gorman, I. Hamblett, M. Irvine, P. Raby, M. C. Standen, and S. Yeates, *J. Am. Chem. Soc.*, **107**, 4404 (1985).

16) W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

17) H. Misawa, T. Karatsu, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **146**, 405 (1988).