November, 1991] Bull. Chem. Soc. Jpn., 64, 3355—3362 (1991)

Triplet Intermediates in Cis-Trans Photoisomerization of 3-Chrysenylethylenes

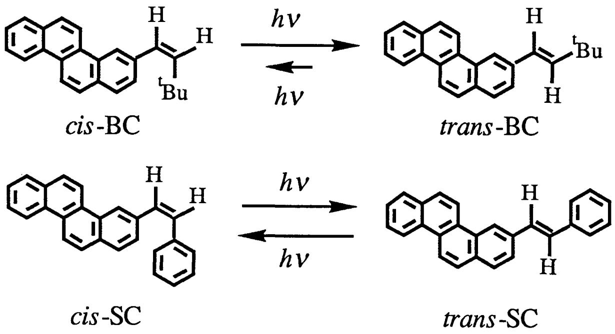
Takashi Karatsu,*,† Tatsuro Hiresaki, Tatsuo Arai, Hirochika Sakuragi,
Katsumi Tokumaru,* and Jakob Wirz††
Department of Chemistry, The University of Tsukuba, Tsukuba, Ibaraki 305
† College of Arts and Sciences, Chiba University, Yayoi-cho, Chiba 260
†† Institut für Physikalische-Chemie der Universität Basel,
Klingelbergstrasse 80, CH-4056 Basel, Switzerland
(Received June 24, 1991)

The effect of substitution of 3-chrysenyl group (Ar) on unsaturated double bonds in their triplet sensitized isomerization was investigated for Ar–CH=CH–R, R=^{t}Bu (BC) and Ph (SC) by means of stationary irradiations, laser flash photolyses, and MO calculations. Both olefins undergo mutual isomerization between their cis- and trans-isomers. However, BC has a unique triplet energy surface with two decay funnels at the planar trans (^{3}t*) and twisted (^{3}p*) conformations, which are in equilibrium with each other; ^{3}t* undergoes either unimolecular decay to the ground-state trans isomer or triplet energy transfer to the cis isomer (quantum chain process) and ^{3}p* decays to the ground state to give the cis and trans isomers. $T_n \leftarrow T_1$ absorptions observed for BC and SC are mainly attributed to ^{3}t* and ^{3}p*, respectively, on the basis of semiempirical MO calculations. The populations at ^{3}t* and ^{3}p* are estimated.

Recently, we demonstrated that the mode of photoisomerization, one-way (solely from cis to trans) or two-way (mutually between cis and trans) of aromatic olefins, Ar–CH=CH–R, in the triplet state is governed by the nature of substituents on the double bond, and proposed that the triplet energy of an aromatic group (Ar) and the conjugative property of substituent R (aryl or alkyl) play important roles in determining the mode of their isomerization by affecting the relative location of the trans and twisted triplets on their energy surface.[1–4] The lower the triplet energy of Ar, the more stabilized the trans triplet (^{3}t*) compared to the perpendicularly twisted triplet (^{3}p*) tending to result in one-way isomerization. However, a phenyl group on the β-ethylenic carbon (R=Ph) stabilizes of ^{3}p*, which favors two-way isomerization.[2–4] 2-Anthrylethylenes[5,6] and stilbenes[7,8] are extreme cases undergoing the one-way and two-way isomerizations, respectively.

Substitution of 1-pyrenyl[3] (triplet energy; E_T= 48 kcal mol^{-1}) and 8-fluoranthenyl[4] (52 kcal mol^{-1}) as Ar whose triplet energies are slightly or moderately higher than that of anthracene (42 kcal mol^{-1}) on an ethylenic carbon led to new mode of isomerization when R=Ph. These results in intermediate behavior between typical one-way and two-way isomerizations, whereas, with R=^{t}Bu, one-way isomerization takes place.[3] In the intermediate mode, the triplet states have two minima at ^{3}t* and ^{3}p* in equilibrium, and the deactivation takes place from ^{3}t* and from ^{3}p*.

These findings have led us to investigate the effect of substitution of 3-chrysenyl group on an unsaturated bond, Ar–CH=CH–R, as Ar whose triplet energy (57 kcal mol^{-1}) is slightly lower than that of naphthalene (61 kcal mol^{-1}),[9] with R=^{t}Bu, 3-(3,3-dimethyl-1-butenyl)chrysene (BC), and R=Ph, 3-styrylchrysene (SC).



Experimental

Materials. Sensitizers (thioxanthone, benzophenone, 1- and 2-acetylnaphthalene, anthraquinone, benzil, 9-fluorenone, and biacetyl) were purified by crystallization or distillation. Solvent benzene was distilled over calcium hydride before use.

1-(Bromomethyl)naphthalene. Refluxing a mixture of 1-methylnaphthalene (25.0 g, 0.176 mol) and *N*-bromosuccinimide (30.0 g, 0.169 mol) in CCl$_4$ in the presence of dibenzoyl peroxide gave 1-(bromomethyl)naphthalene (37.5 g, 96%).[10] ^{1}H NMR (CDCl$_3$) δ=4.64 (s, 2H, CH$_2$Br), 7.2—8.2 (m, 7H, ArH).

(1-Naphthylmethyl)triphenylphosphonium Bromide. 1-(Bromomethyl)naphthalene (37.5 g, 0.17 mol) was treated with triphenylphosphine (46.0 g, 0.18 mol) in refluxing toluene to give (1-naphthylmethyl)triphenylphosphonium bromide (69.5 g, 85%).

1-(*p*-Methylstyryl)naphthalene. 1-(*p*-Methylstyryl)-naphthalene was synthesized in a similar manners with those reported for 2-styrylnaphthalene.[11] *p*-Methylbenzaldehyde (25.0 g, 0.21 mol) was allowed to react with (1-naphthylmethyl)triphenylphosphonium bromide (38 g, 0.08 mol) in the presence of sodium ethoxide (39.0 g, 0.58 mol) in absolute ethanol under dry nitrogen to give 1-(*p*-methylstyryl)naphthalene (11.9 g, 62%).

3-Methylchrysene. 3-Methylchrysene was prepared by photochemical cyclization of 1-(*p*-methylstyryl)naphthalene. The procedures were essentially the same as those described for chrysene in the literature.[12] 1-(*p*-Methylstyryl)naphthalene (2.5 g, 0.01 mol) was irradiated by 400 W HPML (3 h) in cyclohexane (1 dm^3) in the presence of iodine (0.13 g, 0.5 mmol) under oxygen atmosphere to give 3-methylchrysene (1.97 g, 79%); mp 171—172 °C; ^{1}H NMR (CDCl$_3$) δ=2.68 (s, 3H, CH$_3$), 7.39—8.03 (m, 7H, ArH), 8.57—8.79 (m, 4H, ArH).

3-(Bromomethyl)chrysene. 3-(Bromomethyl)chrysene was prepared by bromination of 3-methylchrysene (5.8 g, 24 mmol) with *N*-bromosuccinimide (4.3 g, 24 mmol) in carbon tetrachloride in the presence of dibenzoyl peroxide. 3-(Bromomethyl)chrysene was purified by crystallization from benzene (3.4 g, 44%); mp 176—177 °C; ^{1}H NMR (CDCl$_3$) δ=4.81 (s, 2H, CH$_2$), 7.57—8.07 (m, 7H, ArH), 8.61—8.85 (m, 4H, ArH).

(3-Chrysenylmethyl)triphenylphosphonium Bromide. 3-(Bromomethyl)chrysene (3.4 g, 11 mmol) was treated with triphenylphosphine (3.2 g, 12 mmol) in refluxing toluene to give (3-chrysenylmethyl)triphenylphosphonium bromide (5.0 g, 82%).

3-(3,3-Dimethyl-1-butenyl)chrysene (BC). (3-Chrysenylmethyl)triphenylphosphonium bromide (5.0 g, 8.6 mmol) was suspended in absolute ether (200 ml) with mechanical stirring under dry nitrogen. To this solution was gradually added a solution of butyllithium in hexane (15%, 15 ml). The stirring was continued for 30 min, and then a solution of 2,2-dimethylpropanal in ether (70%, 20 ml) was added to this solution. The reaction mixture was refluxed gently for 30 min. The precipitate was filtered off and the filtrate was washed with water. After drying of extract with anhydrous sodium sulfate, evaporation of the solvent gave an isomeric mixture of 3-(3,3-dimethyl-1-butenyl)chrysene (1.4 g, 54%). The cis isomer was separated by column chromatography (SiO$_2$) with petroleum ether (bp<69 °C) and the trans isomer was obtained by irradiating a benzene solution of the isomeric mixture with a tungsten-halogen lamp in the presence of iodine under argon.

cis-BC: Mp 166—167 °C; ^{1}H NMR (CDCl$_3$) δ=1.06 (s, 9H, CMe$_3$), 5.82 (d, 1H, J=12 Hz, C=CH), 6.71 (d, 1H, J=12 Hz, C=CH), 7.40—8.05 (m, 7H, ArH), 8.60—8.86 (m, 4H, ArH); UV (cyclohexane) λ_{max} 228 nm (ε 20200), 264 (53100), 273 (86800), 298 (13100), 310.5 (13500), 324.5 (13200), 347 (680), 365 (530). Calcd for C$_{24}$H$_{22}$: C, 92.85; H, 7.14%. Found: C, 92.74; H, 7.12%.

trans-BC: Mp 158—159 °C; ^{1}H NMR (CDCl$_3$) δ=1.22 (s, 9H, CMe$_3$), 6.56 (d, 1H, J=16 Hz, C=CH), 6.60 (d, 1H, J=16 Hz, C=CH), 7.50—8.07 (m, 7H, ArH), 8.58—8.81 (m, 4H, ArH); UV (cyclohexane) λ_{max} 237 nm (ε 28900), 274 (87500), 283 (79600), 304.5 (16800), 317.5 (23100), 332 (23000), 354 (1100), 374 (730). Calcd for C$_{24}$H$_{22}$: C, 92.85; H, 7.14%. Found: C, 92.81; H, 7.31%.

3-Styrylchrysene (SC). Benzaldehyde (0.55 g, 5.2 mmol) was allowed to react with (3-chrysenylmethyl)triphenylphosphonium bromide (1.2 g, 2.1 mmol) in the presence of sodium ethoxide (1.4 g, 20.6 mmol) in absolute ethanol under dry nitrogen to give 3-styrylchrysene (0.66 g, 70%). The cis and trans isomers were separated by column chromatography (SiO$_2$) with benzene:hexane (=1:9) mixture, then purified by crystallization from benzene.

cis-SC: Mp 176—177 °C; ^{1}H NMR (CDCl$_3$) δ=6.80 (d, 1H, J=12 Hz, C=CH), 6.85 (d, 1H, J=12 Hz, C=CH), 7.05—8.04 (m, 7H, ArH), 8.32—8.83 (m, 4H, ArH); UV (benzene) λ_{max} 326 nm (ε 21600), 335 (21700). Calcd for C$_{26}$H$_{18}$: C, 94.55; H, 5.45%. Found: C, 94.83; H, 5.58%.

trans-SC: Mp 225—227.5 °C; ^{1}H NMR (CDCl$_3$) δ=7.30—8.08 (m, 14H, C=CH and ArH), 8.60—8.83 (m, 4H, ArH); UV (benzene) λ_{max} 294 nm (ε 47000), 306 (45000), 327 (31000), 341 (42000), 355 (35000), 380 (4500). Calcd for C$_{26}$H$_{18}$: C, 94.55; H, 5.45%. Found: C, 94.64; H, 5.63%.

Stationary Irradiation. Photostationary isomer ratios were measured in degassed benzene solutions (three freeze-pump-thaw cycles) in the presence of a desired concentration of a sensitizer in a 1-cm diameter quartz tube. The irradiation was performed with 366- and 405-nm light isolated through a Toshiba UV-D36B and an L-39 glass filter, respectively, from a 400-W high-pressure mercury lamp. The light intensity was determined using potassium tris(oxalato)ferrate(III) actinometry,[13] and the concentrations of olefins in the reaction mixtures were determined by GLPC or HPLC analysis.

Phosphorescence Measurement. Phosphorescence spectra were measured at 77 K in deaerated 3-methylpentane or EPA (ether:isopentane:ethanol=5:5:2) on Hitachi F-4000 or F-4010 spectrofluorimeter equipped with phosphorescence accessories.

Laser Flash Photolyses. Laser flash photolyses were performed by using an excimer laser (Lambda Physik EMG101, XeCl, 308 nm, 150±7 mJ, 10-ns fwhm) or an excimer laser-pumped dye laser (Lambda Physik FL-3002, 425 nm, 3.5±0.3 mJ, Stilbene 3) and a pulsed xenon arc (Wacom KXL-151, 150 W) as a monitoring light source.[4] Sample solutions (benzene or carbon tetrachloride) were deaerated by three freeze-pump-thaw cycles or argon purging.

Calculation. Oscillator strengths and transition energies of $T_n \leftarrow T_1$ absorptions of chrysene and 3-chrysenylethylenes and $D_n \leftarrow D_1$ absorptions of 3-chrysenylmethyl radicals were calculated by the semiempirical PPP-SCF-SCI method.[14]

Results

Isomerization Behavior on Stationary Irradiation. On triplet sensitization both BC and SC underwent two-way isomerization mutually between their cis- and trans-isomers.

However, in the isomerization of BC sensitized with anthraquinone (1×10^{-2} mol dm^{-3}) in deaerated benzene as Fig. 1 (plot a) shows, the photostationary state isomer ratios ([t]/[c])$_s$ increased linearly with increasing concentration of *cis*-BC in (2.5—10.0)×10^{-3} mol dm^{-3}. As Table 1 indicates, the composition of the trans isomer at the photostationary state [(% trans)$_s$] ([BC]=1.0×10^{-3} mol dm^{-3}) was increased with lowering of the triplet energy of the sensitizers employed.

Moreover, (%trans)$_s$ decreased with increase of the concentration of the sensitizers. Thus, on 9-fluorenone sensitization, (%trans)$_s$ decreased from 8.2% at 5×10^{-3} mol dm^{-3} to negligible amounts at higher than 5×10^{-2} mol dm^{-3}, indicating that the isomerization proceeds almost one-way at 5×10^{-2} mol dm^{-3} of the sensitizer.

Addition of azulene in the range of (3.3—13)×10^{-4} mol dm^{-3} linearly increased ([t]/[c])$_s$ as illustrated in Fig. 1 (plot b) on anthraquinone (1×10^{-2} mol dm^{-3}) sensitization.

Table 1. The Effect of Triplet Sensitizers on the Composition of the trans Isomer at the Photostationary State (%trans)$_s$ of BC (1.0×10^{-3} mol dm^{-3}) in Benzene

Sensitizer	E_T/kcal mol^{-1} [a]	Concn/mol dm^{-3}	λ_{ex}/nm [b]	(%trans)$_s$
Benzophenone	69	0.01	366	62
Anthraquinone	62	0.01	405	75
1-Acetylnaphthalene	56	0.07	366	74
Benzil	53	0.05	405	93
9-Fluorenone	52	0.05	405	>99

a) Ref. 15. b) Wavelengths of light used for irradiation.

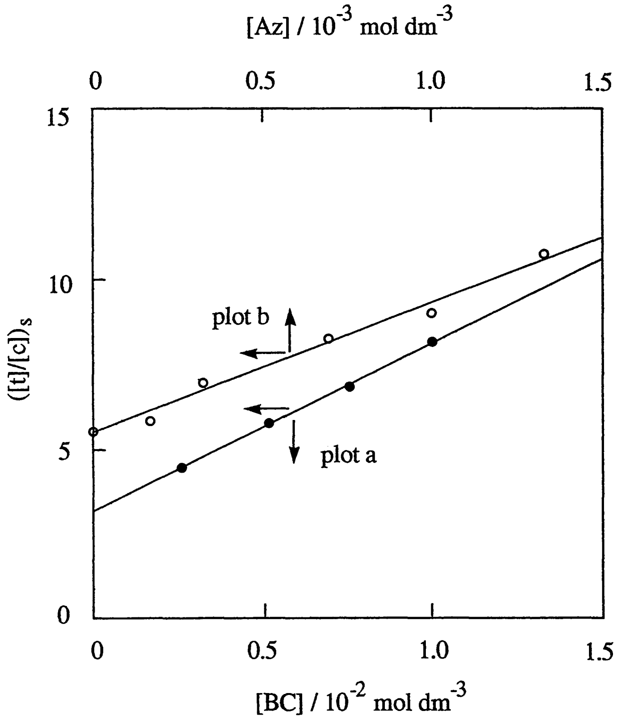


Fig. 1. Plots of the photostationary state isomer ratios against concentration of BC (plot a; closed circles) or azulene (plot b; open circles).

On the other hand, in the isomerization of SC ([t]/[c])$_s$ was not changed at all with its concentration in $(0.8—3.3)\times10^{-4}$ mol dm^{-3}, however, (%trans)$_s$ was varied among the sensitizers; 37.0 and 29.4% on sensitization with biacetyl (E_T=56.3 kcal mol^{-1},[15] 0.1 mol dm^{-3}) and benzil (0.14 mol dm^{-3}), respectively.

Phosphorescence Spectra.

cis-BC, *trans*-BC, and *trans*-SC exhibited phosphorescence in 3-methylpentane and EPA (ether:isopentane: ethanol=5:5:2) at 77 K. However, *cis*-SC did not phosphoresce at all.

As Fig. 2 illustrates, *trans*- (Fig. 2a) and *cis*-BC (Fig. 2b) exhibited different spectra. However, as depicted in Fig. 2b, the spectrum of *cis*-BC was changed very rapidly during the measurement; the weak band at 500 nm decreased and the strong bands at 515 and 560 nm increased in intensity for each scanning of the spectrum,

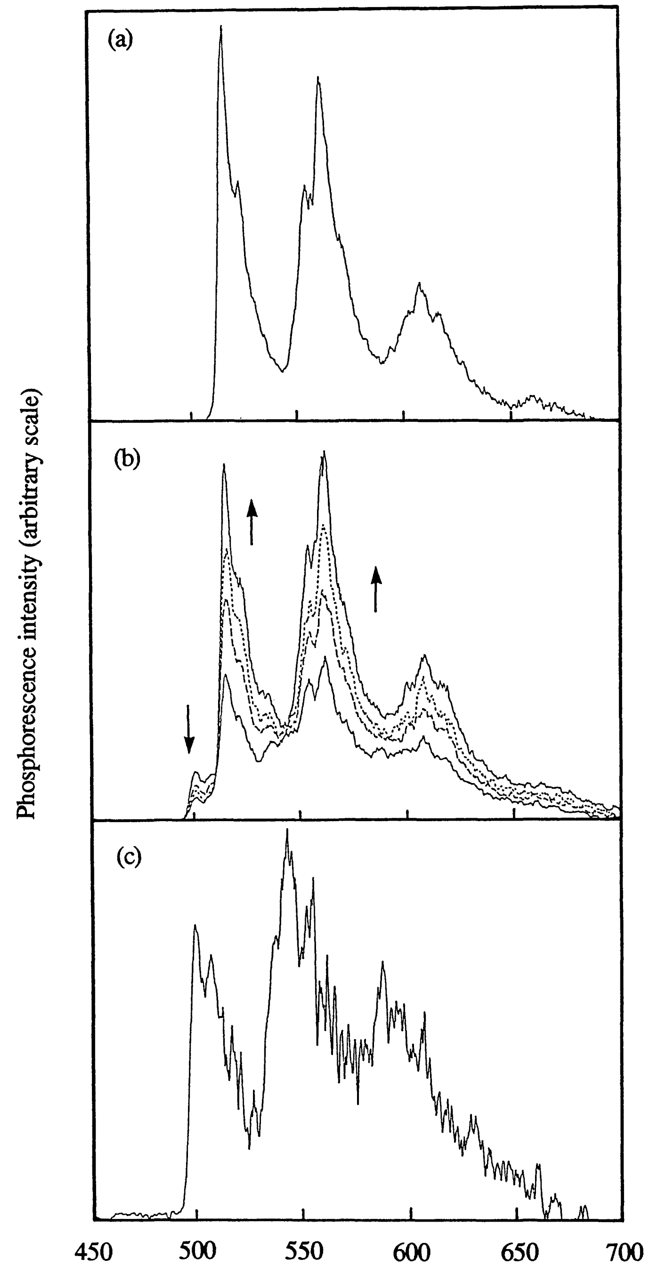


Fig. 2. Phosphorescence spectra obtained on excitation of *trans*-BC (a) and *cis*-BC (b) in 3-methylpentane at 77 K, and a difference spectra (c, subtracted a from b). Solid lines indicate the first and the 4th scans, and dashed and dotted lines indicate the second and the third scans, respectively (see text).

and finally, the spectrum became identical with that of *trans*-BC.

Therefore, the observed phosphorescence spectrum of *cis*-BC is reasonably assigned to a mixture of the cis and trans isomers. The phosphorescence spectrum due to *cis*-BC is obtained by the subtracting the spectrum of the trans isomer from that of the mixture multiplied by an adequate factor (Fig. 2-c). The lifetime measurement was unsuccesful and also it is not clear whether the emission comes from adiabatic isomerization on the triplet energy surface or re-excitation of the trans isomer after diabatic isomerization through $^3p^*$. However it should be noted that the isomerization of BC takes place even in rigid media at 77 K in spite of the presence of two relatively large substituents on both of it's ethylenic carbons. This is a property of it's T_1 potential energy surface.

The phosphorescence excitation spectrum showed the same behavior. The excitation spectrum of *trans*-BC was identical with its absorption spectrum irrespective of the monitoring wavelength either 515 or 560 nm (Fig. 3). On the other hand, the excitation spectrum of *cis*-BC was also identical, when monitored at 500 nm (Fig. 3), but not identical, when monitored at 515 nm, with its absorption spectrum, and the spectral profile was changed during

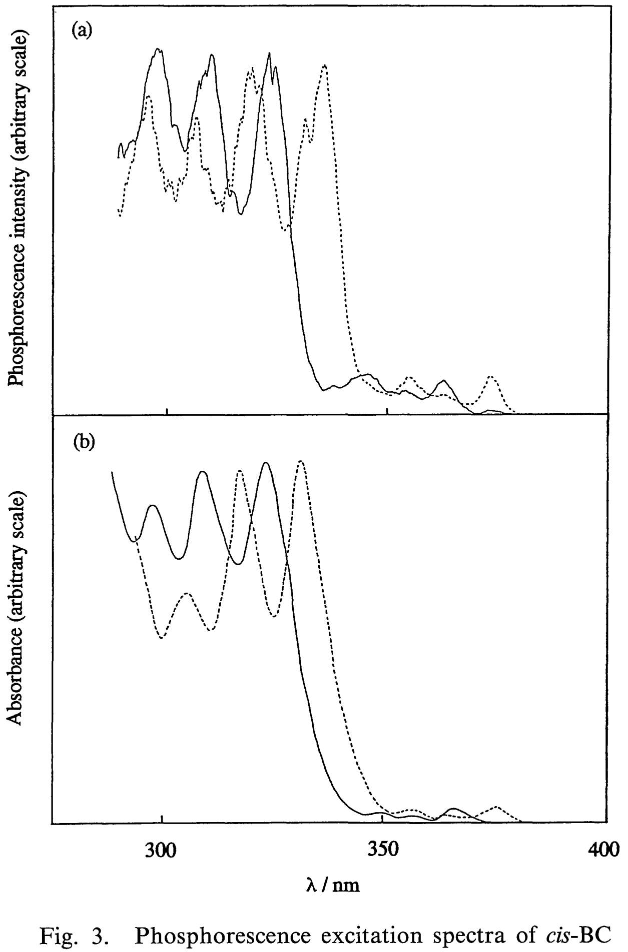


Fig. 3. Phosphorescence excitation spectra of *cis*-BC monitored at 500 nm (—) and *trans*-BC monitored at 520 nm (⋯⋯) in EPA at 77 K (a), and absorption spectra of *cis*-BC (—) and *trans*-BC (⋯⋯) in benzene at ambient temperature (b).

Table 2. Phosphorescence Spectral Data of Chrysenyl Compounds in 3-Methylpentane and EPA (indicated in parentheses) at 77 K

Compound	0,0 Band/nm	E_T/kcal mol^{-1}	Lifetime/s
Chrysene	498 (497)	57.4 (57.5)	2.6
trans-BC	516 (515)	55.4 (55.5)	1.5
cis-BC	500 (500)	57.2 (57.2)	—
trans-SC	521	54.9	2.0
cis-SC	—	—	—

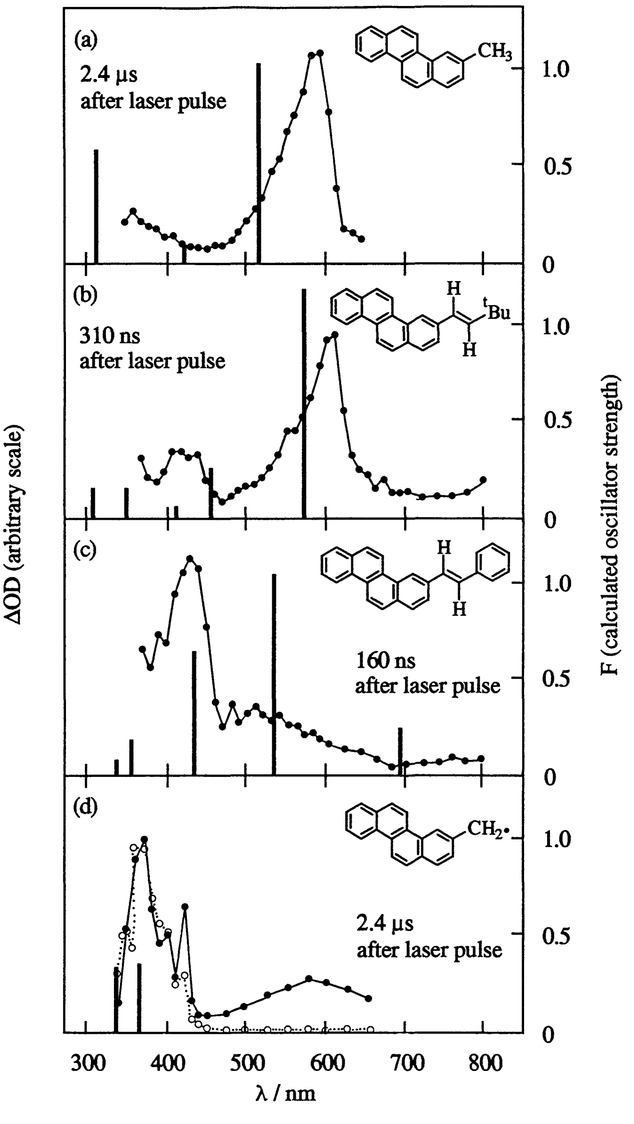


Fig. 4. $T_n \leftarrow T_1$ and $D_n \leftarrow D_1$ absorption spectra and calculated oscillator strengths (see text) of 3-methylchrysene (a), 3-(3,3-dimethyl-1-butenyl)chrysene (b), 3-styrylchrysene (c), and 3-chrysenylmethyl radical (d). Solid line was measured in deaerated benzene and dotted line was measured in deaerated CCl_4. The calculation was made for 3-vinylchrysene instead of BC.

measurement.

Table 2 summarizes the triplet energies of *trans*- and *cis*-BC, *trans*-SC along with chrysene estimated from the 0-0 band of their phosphorescence spectra.

Transient Absorption Spectra. Figure 4 depicts transient absorption spectra of the triplet state of BC, SC and related species. *trans*-BC exhibited two major $T_n \leftarrow T_1$ absorption bands around 430 and 580 nm, and *trans*-SC a strong band at 430 nm and a weak broad band around 500 nm in deaerated benzene (Fig. 4b and 4c) on sensitized excitation with biacetyl or thioxanthone (as a triplet sensitizer) with 425-nm laser pulses. The decay profiles of their absorption bands were essentially independent of wavelength and single-exponential with lifetimes of 810 ns for *trans*-BC and of 210 ns for *trans*-SC. On excitation under similar conditions *cis*-BC and *cis*-SC also exhibited almost the same absorptions with the same lifetimes as the corresponding trans isomers.

3-Methylchrysene showed almost identical $T_n \leftarrow T_1$ absorption around 580 nm with 17 μs lifetime under similar conditions (Fig. 4a) as chrysene[16] (the lifetime was determined to be 30 μs). 3-Chrysenylmethyl radical,[17] a model of the triplet olefins with a twisted conformation, generated by photolysis of 3-(bromomethyl)chrysene with 308-nm laser pulses, showed an absorption around 360 nm (Fig. 4d).

The oscillator strengths and transition energies of $T_n \leftarrow T_1$ or $D_n \leftarrow D_1$ absorptions were calculated for chrysene, 3-vinylchrysene, *trans*-SC and 3-chrysenylmethyl radicals by the semiempirical PPP-SCF-SCI method,[14] and are included in Fig. 4 as bar indications. The length of the bars indicates the relative oscillator strength.

Estimation of Extinction Coefficients of $T_n \leftarrow T_1$ Absorption for $^3t^*$ and $^3p^*$. The molar extinction coefficients (ε_T) of $T_n \leftarrow T_1$ absorption of $^3t^*$ and $^3p^*$ were determined by comparison with that of anthracene triplets (ε_T=46000 dm^3 mol^{-1} cm^{-1} at 430 nm).[18] The triplet states of the chrysenylethylenes were produced by energy transfer from thioxanthone triplets in deaerated benzene. The sensitizer was irradiated at a fixed concentration with laser pulses of a constant intensity with changing concentration of the substrates, anthracene and the chrysene derivatives to measure the optical densities (ΔOD) of their resulting triplet states. The ΔOD values increased with increasing concentration of the substrate and attained a plateau at higher concentrations. By assuming the energy transfer efficiency to be unity, ε_T value of the triplet 3-methylchrysene was determined to be 20000 dm^3 mol^{-1} cm^{-1} at 580 nm. The $T_n \leftarrow T_1$ absorption of BC exhibited ε_T=2900 and 10000 dm^3 mol^{-1} cm^{-1} at 430 and 580 nm, respectively, and that of SC showed ε_T=5900 and 1300 dm^3 mol^{-1} cm^{-1} at 430 and 580 nm, respectively.

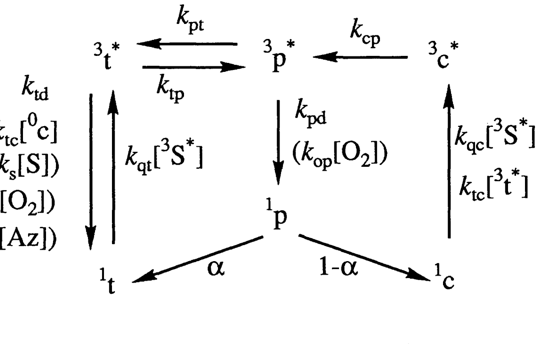
Quenching Rate Constants of Olefin Triplets by Azulene and Oxygen. The $T_n \leftarrow T_1$ absorptions of BC and SC were efficiently quenched in benzene by azulene and oxygen without change of spectral profiles. The decay rate constant, k_d (=$1/\tau_T$) value increased linearly with increasing concentration of azulene or oxygen, and the slope gave a quenching rate constant by azulene (k_{az}^{obsd}) or oxygen (k_{ox}^{obsd}). The k_{az}^{obsd} values were obtained as 9.5×10^9, 6.8×10^9, and 3.5×10^9 mol^{-1} dm^3 s^{-1} for chrysene, BC, and SC, respectively. The k_{ox}^{obsd} values were 2.0×10^9, 3.5×10^9, and 5.6×10^9 mol^{-1} dm^3 s^{-1} for chrysene, BC, and SC, respectively.

Discussion

On anthraquinone sensitization of BC, the observed increase of the photostationary isomer ratio, $([t]/[c])_s$, linearly with BC concentration (Fig. 1) and with lowering of the triplet energies of the sensitizer employed indicates the following two things. The first, trans ($^3t^*$) and twisted triplets ($^3p^*$) are in equilibrium ($K_{tp}=k_{tp}/k_{pt}$), and the second, $^3t^*$ has a sufficient lifetime to transfer its triplet energy to the cis isomer leading to quantum chain process and $^3p^*$ decays to the ground state to give the cis and trans isomers (Scheme 1). Therefore, BC undergoes a mutual isomerization between the cis and trans isomers accompanied by quantum chain isomerization from cis to trans isomers.

In contrast to BC, the lack of concentration effects of the olefin and triplet sensitizer on $([t]/[c])_s$ for the SC isomerization indicates that SC undergoes typical two-way isomerization with a single-decay funnel at $^3p^*$.

In the transient absorption, the band around 580 nm observed for BC can be assigned to the planar trans triplet, $^3t^*$, and those around 430 nm (strong in SC and weak in BC) to $^3p^*$ by comparison with $T_n \leftarrow T_1$ absorptions of the model compounds and based on MO calculations. First, the band around 580 nm is very close in wavelength to the $T_n \leftarrow T_1$ absorptions of chrysene and 3-methylchrysene, and the other band at 430 nm to the absorption of 3-chrysenylmethyl radicals. The long tail observed for SC at longer wavelengths is likely to be due to $^3t^*$ in equilibrium with $^3p^*$. Second the observed absorption wavelengths for BC fit well with the calculated values. For SC, however, the observed spectrum around 500 nm did not fit well with the calculated result for $^3t^*$, and can be ascribed to $^3p^*$. The



Scheme 1. Photoisomerization scheme of BC and SC.

absorption band of $^3p^*$ is at longer wavelengths ($\lambda_{max} \approx 430$ nm) than that of 3-chrysenylmethyl radicals ($\lambda_{max} \approx 360$ nm) and this might imply some kind of interaction between the two chromophores of twisted "1,2-biradicals".

Furthermore when one assumes that the planar triplets ($^3t^*$) of the olefins have the same ε_T values as the 3-methylchrysene triplets at the peak wavelength, the observed ΔOD values of these olefin triplets at 580 nm are to be obtained when $^3t^*$ is populated in 50% among the triplet state of BC and in 7% for SC. Accordingly, the population of $^3p^*$ is to be 50% for BC and 93% for SC in triplet state. Based on these populations, ε_T at 430 nm for $^3p^*$ is estimated as 5800 and 6300 for BC and SC, respectively, and these values are in excellent agreement with each other. This is quite reasonable, because $^3p^*$'s of BC and SC may have similar twisted structures.

The observed apparent quenching rate constants of the triplet states with azulene, k_{az}^{obsd}, and by oxygen, k_{ox}^{obsd}, enable one to estimate K_{tp}. The k_{az}^{obsd} and k_{ox}^{obsd} values are related with K_{tp} as expressed by Eqs. 1 and 2,[9] where k_{ot} and k_{op} are the rate constants for quenching of $^3t^*$ and $^3p^*$ by oxygen, respectively.

$$k_{az}^{obsd} = \frac{k_{az}}{1+K_{tp}}, \tag{1}$$

$$k_{ox}^{obsd} = \frac{k_{ot}+k_{op}K_{tp}}{1+K_{tp}}. \tag{2}$$

When we assume that k_{az} for $^3t^*$ of BC and SC are the same as that for chrysene, 9.5×10^9 mol^{-1} dm^3 s^{-1}, K_{tp} is estimated as 0.39 ($^3t^*$ 72%) for BC and 1.7 ($^3t^*$ 37%) for SC from Eq. 1. Likewise, reasonable assumption of $k_{ot}=2 \times 10^9$ as for chrysene and $k_{op}=9 \times 10^9$ dm^3 mol^{-1} s^{-1} as for stilbene $^3p^*$,[8] affords K_{tp} as 0.23 ($^3t^*$ 81%) and 0.83 ($^3t^*$ 55%) for BC and SC, respectively. The population of $^3t^*$ is estimated here from the quenching rate constants are slightly higher than those estimated from the extinction coefficients ($^3t^*$ 50% for BC and 7% for SC). The difference in K_{tp} between the methods of estimation may be attributed to difficulty in assumption of the quenching rate constants, k_{az}, k_{op}, k_{ot}, and ε. However, for the convenience of the subsequent discussion, one could assume the average population of $^3t^*$ as 68% and 33% for BC and SC, respectively.

Triplet energy of $^3t^*$ is estimated for BC and SC from the population of $^3t^*$ and $^3p^*$ by using an equation $\Delta G=-RT \ln([^3p^*]/[^3t^*])$. $^3t^*$ of BC is 0.5 kcal mol^{-1} lower in energy than $^3p^*$ for BC ($[^3p^*]/[^3t^*]=32\%/68\%=0.47$) and $^3t^*$ of SC is 0.4 kcal mol^{-1} higher in energy than $^3p^*$ ($[^3p^*]/[^3t^*]=67\%/33\%=2.0$). These results together with the results of phosphorescence (Table 2) enable us to propose the potential energy surfaces along the twisting of the double bond for BC and SC as depicted in Fig. 5.

According to Scheme 1, the change of $([t]/[c])_s$ with [*cis*-BC] (plot a in Fig. 1) is expressed by Eq. 3,[2] the slope (5.3×10^2 mol^{-1} dm^3) corresponds to $k_{tc}/(1-\alpha)K_{tp}k_{pd}$ and the intercept denotes $([t]/[c])_s$ value (population of 74.8% of the trans isomer) when quantum chain process does

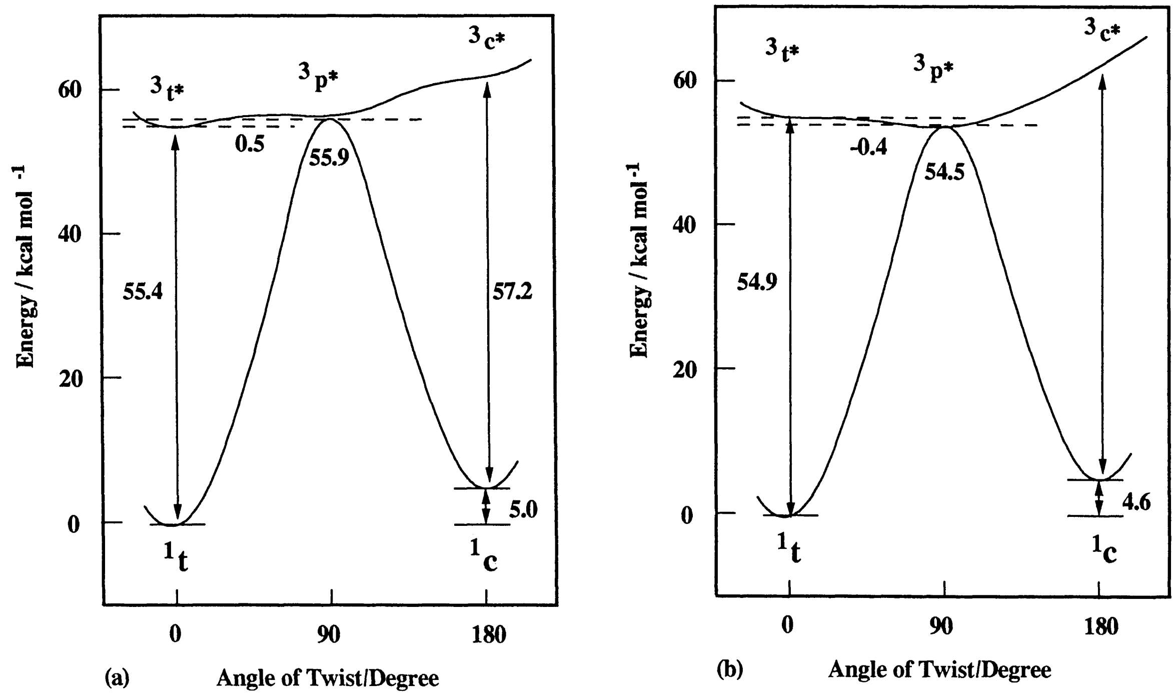


Fig. 5. Estimated potential energy surfaces for BC (a) and SC (b) plotted against rotational angle around the C–C double bond.

not participate at all.

$$([\mathrm{t}]/[\mathrm{c}])_\mathrm{s} = \frac{\alpha K_\mathrm{tp}k_\mathrm{pd} + k_\mathrm{td} + k_\mathrm{tc}[\mathit{cis}\text{-BC}]}{(1-\alpha)K_\mathrm{tp}k_\mathrm{pd}}, \quad (3)$$

where we assume that the equilibrium between ^{3}t* and ^{3}p* is accomplished, that is $k_\mathrm{tp} \gg k_\mathrm{td}$, $k_\mathrm{tc}[\mathit{cis}\text{-BC}]$ and $k_\mathrm{pt} \gg k_\mathrm{pd}$.

The observed triplet lifetime of BC is expressed by Eq. 4.

$$\tau_\mathrm{T} = \frac{1 + K_\mathrm{tp}}{K_\mathrm{tp}k_\mathrm{pd} + k_\mathrm{td}}. \quad (4)$$

The rate constant for deactivation of the trans triplets, k_td, can be reasonably assumed to be similar to that for 3-methylchrysene ($3.3\times10^4\ \mathrm{s}^{-1}$). Substitution of the observed values for $K_\mathrm{tp}(=0.67)$ and $\tau_\mathrm{T}(=810\ \mathrm{ns})$ into Eq. 4 gives k_pd as $3.0\times10^6\ \mathrm{s}^{-1}$. This is lower than the deactivation rate constant reported for stilbene ($2\times10^7\ \mathrm{s}^{-1}$).[8)]

Furthermore, Eq. 3 and Fig. 1 (plot a) give two important results. The intercept corresponds to $([\mathrm{t}]/[\mathrm{c}])_\mathrm{s}=\alpha/(1-\alpha)$ when [BC]=0, since $k_\mathrm{td}/(1-\alpha)K_\mathrm{tp}k_\mathrm{pd}$ is negligible, therefore, the observed value, $[([\mathrm{t}]/[\mathrm{c}])_\mathrm{s}=3]$ gives α as 0.75. The slope, $k_\mathrm{tc}/(1-\alpha)K_\mathrm{tp}\ k_\mathrm{pd}$, ($5.3\times10^2\ \mathrm{mol^{-1}\,dm^3}$) combined with K_tp and k_pd gives a rate constant, k_tc, for the energy transfer from ^{3}t* to cis isomer (quantum chain process) as $k_\mathrm{tc}=2.7\times10^8\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$. According to the triplet energies of *trans*- and *cis*-BC determined by their phosphorescence, 55.4 and 57.2 kcal mol^{-1}, the energy transfer from ^{3}t* to *cis*-BC is 1.8 kcal mol^{-1} endothermic. The above value for k_tc is in good agreement with a value ($2.5\times10^8\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$) estimated for 1.8 kcal mol^{-1} endothermic energy transfer from the following well-accepted equation:[19)]

$$k_\mathrm{tc} = A\exp(-E_\mathrm{a}/RT), \quad (5)$$

where, $A=5\times10^9\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$, and $-E_\mathrm{a}=\Delta E_\mathrm{T}=E_\mathrm{T}$(*trans*-BC)$-E_\mathrm{T}$(*cis*-BC)=1.8 kcal mol^{-1} (Table 2).

In the presence of azulene, $([\mathrm{t}]/[\mathrm{c}])_\mathrm{s}$ is expressed by Eq. 6,[3)]

$$([\mathrm{t}]/[\mathrm{c}])_\mathrm{s} = \frac{\alpha K_\mathrm{tp}k_\mathrm{pd} + k_\mathrm{td} + k_\mathrm{tc}[\mathit{cis}\text{-BC}] + k_\mathrm{az}[\mathrm{Az}]}{(1-\alpha)K_\mathrm{tp}k_\mathrm{pd}}, \quad (6)$$

where k_az is quenching rate constant of ^{3}t* by azulene. The slope of plot b in Fig. 1, $k_\mathrm{az}/(1-\alpha)K_\mathrm{tp}k_\mathrm{pd}$, $3.8\times10^3\ \mathrm{mol^{-1}\,dm^3}$, combined with α, K_tp, and k_pd values gives k_az as $1.9\times10^9\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$. This value is quite reasonable since energy transfer from triplet state of *trans*-BC (E_T=55.4 kcal mol^{-1}, Table 2) to azulene (39.8 kcal mol^{-1})[20)] is exothermic.

The $([\mathrm{t}]/[\mathrm{c}])_\mathrm{s}$ values for BC depends on the triplet energy (Table 1) and concentration of the sensitizers, and the isomerization is seemingly almost one-way on sensitization with high concentration of 9-fluorenone, 0.05 mol dm^{-3}. This fact is attributed to an equilibrium between ^{3}t* and the triplet state of the sensitizer employed (S),

$$^3\mathrm{S}^* + {}^1\mathrm{t} \rightleftarrows \mathrm{S} + {}^3\mathrm{t}^*, \quad (7)$$

because of their small difference in triplet energy. Therefore, $([\mathrm{t}]/[\mathrm{c}])_\mathrm{s}$ is expressed by Eq. 8, where k_s denotes the rate constant for the energy transfer from ^{3}t* to S, as previously reported for the isomerization of 2-(3,3-dimethyl-1-butenyl)naphthalene (BN) using sensitizers of low triplet energy.[21)]

$$([\mathrm{t}]/[\mathrm{c}])_\mathrm{s} = \frac{\alpha K_\mathrm{tp}k_\mathrm{pd} + k_\mathrm{td} + k_\mathrm{tc}[\mathit{cis}\text{-BC}] + k_\mathrm{s}[\mathrm{S}]}{(1-\alpha)K_\mathrm{tp}k_\mathrm{pd}}. \quad (8)$$

From the above arguments, triplet and ground state potential energy surfaces for BC and SC are proposed as depicted in Fig. 5.

For BC (Fig. 5-a), the triplet energies of ^{3}t* and ^{3}c* were estimated to be 55.4 and 57.2 kcal mol^{-1}, respectively, from their 0-0 bands of phosphorescence spectra. The triplet energy of ^{3}p* was estimated relatively to ^{3}t* using an equation $\Delta G=-RT\ \ln([^3\mathrm{p}^*]/[^3\mathrm{t}^*])$ based on the population of ^{3}t* and ^{3}p* ($[^3\mathrm{p}^*]/[^3\mathrm{t}^*]=0.47$) obtained from ε_T and quenching rate constant by azulene, thus ^{3}t* of BC is 0.5 kcal mol^{-1} lower in energy than ^{3}p*. Ground state energy difference between cis and trans isomers due to steric hindrance is estimated as 5 kcal mol^{-1}, the same as 2-(3,3-dimethyl-1-butenyl)anthracene.[22)]

For SC (Fig. 5-b), the triplet energies of ^{3}t* (54.9 kcal mol^{-1}) and ^{3}p* (0.4 kcal mol^{-1} lower in energy than ^{3}t*, $[^3\mathrm{p}^*]/[^3\mathrm{t}^*]=2.0$) are estimated similarly as for BC. However, the triplet energy of ^{3}c* is supposed not to be lower than that for ^{3}t*, 54.9 kcal mol^{-1}, and not higher than that of chrysene, 57.4 kcal mol^{-1}, because of its lack of phosphorescence. Ground state energy difference between cis and trans isomers is estimated 4.6 kcal mol^{-1}, the same as reported to stilbene.[7)]

The differences of phtochemical behavior and triplet potential energy surfaces between BC and SC may originate from the stabilization of ^{3}p* of SC due to conjugation with diaryl substituents compared to that of BC.

Conclusion

In the triplet sensitized isomerization of 3-chrysenylethylenes, 3-styrylchrysene (SC) shows the typical two-way mode, whereas 3-(3,3-dimethyl-1-butenyl)chrysene (BC) behaves by intermediate mode with "dual decay funnel". The SC triplet decays only at the twisted geometry. On the other hand, BC triplet decays at both of the twisted and planar trans conformations leading to a quantum chain process from the latter. Therefore in the (3,3-dimethyl-1-butenyl)arene series, Ar–CH=CH–^{t}Bu, BC with 3-chrysenyl group (E_T of chrysene=57 kcal mol^{-1}) is located at a boundary position between typical two-way mode with Ar=2-naphthyl (E_T of naphthalene=60 kcal mol^{-1}) and cis→trans one-way mode with Ar=8-fluoranthenyl (E_T of fluoranthene=53 kcal mol^{-1}) derivative.

The present work contributes to revealing that the mode of photoisomerization of aromatic olefins, Ar–CH=CH–R, in the triplet state is controlled by the relative location of the trans and twisted triplets on the energy surface which is defined by the triplet energy of an aromatic group (Ar) and the nature of substituent R (aryl or alkyl).

The authors thank Dr. Shigero Oishi, Kitasato University, for valuable suggestions regarding the transient absorption measurements. This work was partially supported by Grant-in-Aid for Special Project Research Nos. 61123001, 62113001, and 63104001 (K.T.) and Grant-in-Aid for Scientific Research Nos. 61740242, 01740255 (T.A.), and 02453091 (K.T.) from the Ministry of Education, Science and Culture.

References

1) 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.

2) T. Arai, T. Karatsu, M. Tsuchiya, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **149**, 161 (1988).

3) 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); c) H. Okamoto, T. Arai, H. Sakuragi, K. Tokumaru, and Y. Kawanishi, *Bull. Chem. Soc. Jpn.*, **64**, 216 (1991).

4) 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).

5) T. Arai, T. Karatsu, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **24**, 2873 (1983).

6) T. Karatsu, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **115**, 9 (1985).

7) 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.

8) H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.*, **85**, 1835 (1981).

9) T. Arai, H. Sakuragi, K. Tokumaru, Y. Sakaguchi, J. Nakamura, and H. Hayashi, *Chem. Phys. Lett.*, **98**, 40 (1983).

10) M. Bullpitt, W. Kitching, D. Doddrell, and W. Adcock, *J. Org. Chem.*, **41**, 760 (1976).

11) G. S. Hammond, S. C. Shim, and S. P. Van, *Mol. Photochem.*, **1**, 89 (1969).

12) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964).

13) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York (1973), p. 119.

14) M. Gisin and J. Wirz, *Helv. Chim. Acta*, **66**, 1556 (1983).

15) Ref. 13, p. 3.

16) G. Porter and M. W. Windsor, *Proc. R. Soc. London, Ser. A*, **245**, 233 (1958).

17) a) D. Weir, L. J. Johnston, and J. C. Scaiano, *J. Phys. Chem.*, **92**, 1742 (1988); b) L. J. Johnston and J. C. Scaiano, *J. Am. Chem. Soc.*, **107**, 6368 (1985).

18) R. Bensasson and E. J. Land, *Trans. Faraday Soc.*, **67**, 1904 (1971).

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

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

21) T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Lett.*, **1980**, 1335.

22) T. Karatsu, M. Tsuchiya, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **169**, 36 (1990).