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Effects of Substitution with Positionally Isomeric Anthryl Groups on the One-Way Isomerization

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1- and 9-Anthrylethylenes, AnthCH=CHBu^t (Anth = anthryl) undergo photochemical cis→trans one-way isomerization in a similar way to that of 2-AnthCH=CH-Bu^t on both direct and sensitized irradiation. The adiabatic cis→trans conversion of their triplets proceeds with an activation energy decreasing in the order of 2-, 1-, and 9-AnthCH=CHBu^t, as determined by transient absorption spectroscopy.

Contrary to the well-investigated photochemical isomerization of stilbene and related compounds proceeding mutually between their cis and trans isomers,1) we have shown that the ethylenic linkage substituted with a 2-anthryl group or other aromatic nuclei with a low triplet excitation energy undergoes cis→trans one-way isomerization.2) In the one-way isomerization, the initially resulting cis triplet ($^3c^*$) undergoes twisting around the double bond passing through an energy maximum located at a nearly perpendicular conformation to give the trans triplet ($^3t^*$), which subsequently deactivates to the trans isomer.

Orlandi,3) Momicchioli,4) and their coworkers computed the triplet energy surfaces of anthrylethylenes and showed that the excitation is mostly localized in the anthracene nuclei to stabilize $^3t^*$ and $^3c^*$ and, therefore, the $^3c^* \rightarrow {}^3t^*$ conversion requires a sizable activation energy. Actually, we have shown that the triplet state of 2-AnthCH=CHD isomerizes in benzene with an activation energy (E_a) of 11 kcal mol^{-1} along a symmetrical energy surface5) and, furthermore, $^3c^*$ of 2-AnthCH=CHBu^t (2BA) is converted to $^3t^*$ with E_a of 6.0 kcal mol^{-1} in benzene (frequency factor, log (A/s^{-1}) = 10.7).6)

In the triplet state of anthracene the spin density is highest at the 9-position and decreases at the 1- and the 2-position in this order.7) The problem is how the substitution of a double bond on various positions of the anthracene nucleus affects the shape of the triplet energy surface and accordingly the activation energy of the isomerization. In order to solve this problem we studied the triplet sensitized isomerization of 1-AnthCH=CHBu^t (1BA) and 9-AnthCH=CHBu^t (9BA) and compared their behavior with that of 2BA.2,6)

Direct or benzil-sensitized irradiation of 1BA and 9BA in deaerated benzene8) resulted in similar cis→trans one-way isomerization to that previously reported for 2-BA.2) The quantum yields ($\phi_{c\rightarrow t}$) increased with increasing cis isomer concentration (2.5×10^{-4}–1×10^{-3} mol dm^{-3}) to attain, for example, nearly 6 at [*cis*-1BA] = 10^{-3} mol dm^{-3} on benzil (5.5×10^{-3} mol dm^{-3}) sensitization.

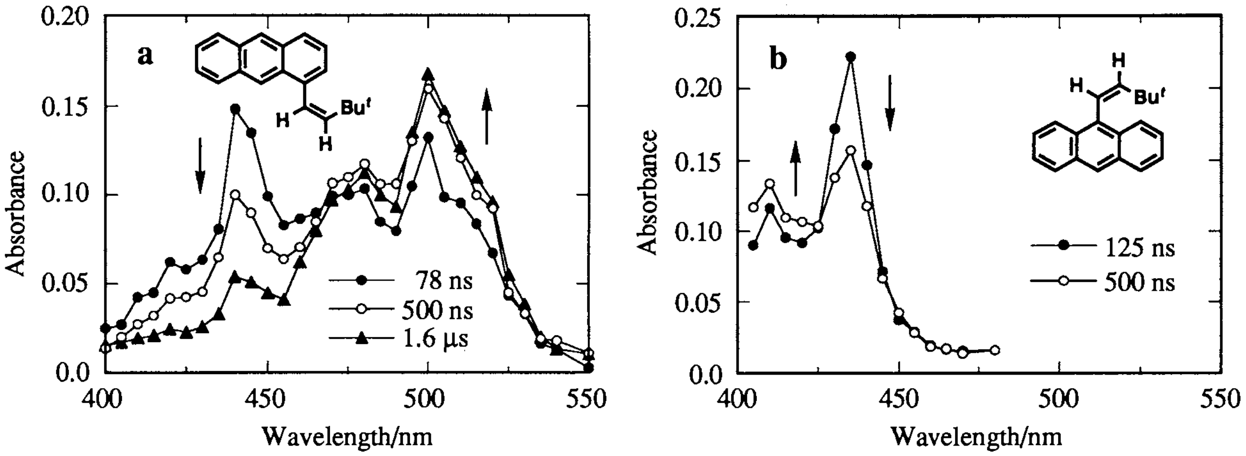

Fig. 1. Transient absorption spectra observed on pulsed laser excitation of *cis*-1BA (1×10^{-4} mol dm^{-3}) at 24 °C (a) and *cis*-9BA (1×10^{-4} mol dm^{-3}) at 25 °C (b) in deaerated toluene.

Table 1. The rate constants (k_r), activation energies (E_a), and frequency factors (A) for $^3c^*\rightarrow{}^3t^*$ conversion of BA's in toluene

Olefin	k_r/s^{-1} (Temp/°C)	E_a/kcal mol^{-1}	log (A/s^{-1})
2BA[a)	2.1×10^6 (23)	6.0	10.7
1BA	2.1×10^6 (24)	4.6	9.7
9BA	2.0×10^6 (25)	3.1	8.6

a) In benzene; Ref. 6.

Pulsed laser excitation of *cis*-1BA (1×10^{-4} mol dm^{-3}) at 308 nm in deaerated toluene[6,9) afforded transient absorption spectra depicted in Fig. 1a. The band at 440 nm observed immediately after excitation decreased in intensity and concurrently another band grew up at 500 nm. By comparing with the spectra observed on excitation of *cis*- and *trans*-1BA at 77 K in EPA the former band is assigned to cis triplets and the latter to trans triplets. Analyses of the time profiles of these absorptions[10) afforded the rate constant for the conversion of $^3c^*$ to $^3t^*$ as 2.1×10^6 s^{-1} at 24 °C. The determination of the rate constants at varying temperatures (2.4–32.8 °C) gave the activation parameters of $E_a = 4.6$ kcal mol^{-1} and log (A/s^{-1}) = 9.7.

Similar irradiation of *cis*-9BA (1×10^{-4} mol dm^{-3}) exhibited transient absorption bands shown in Fig. 1b. The spectral assignment was again based on the low temperature experiments. The decay of $^3c^*$ at 435 nm was accompanied by the rise of $^3t^*$ at 410 nm with a rate constant of 2.0×10^6 s^{-1} at 25 °C. Temperature dependence of the rate constant in a similar temperature range afforded the activation parameters for $^3c^*\rightarrow{}^3t^*$ conversion; $E_a = 3.1$ kcal mol^{-1} and log (A/s^{-1}) = 8.6.

Table 1 lists the rate constants at ambient temperature and the activation parameters for $^3c^*\rightarrow{}^3t^*$ conversion of the three positional BA isomers. The activation energy decreases in the order of 2BA, 1BA, and 9BA, indicating that the energy barrier around $^3p^*$ conformation is affected by the position of anthracene nucleus at which the ethenyl moiety is substituted. This might be due to the spin distribution in the triplet state.

The cis triplets of BA's exhibit the absorption in the narrow wavelength range in 430–450 nm where anthracene triplets also exhibits its T-T absorption as shown in Fig. 1 and previously reported for 2BA.6) This fact indicates that the excitation is mostly localized on the anthracene nucleus in the cis triplets irrespective of the substitutional positions due to their highly twisted conformation from the plane of the ethylenic linkage. Actually, the triplet excitation energies [E_T(cis)] of *cis*-1BA and *cis*-2BA are 42.0 and 42.56) kcal mol^{-1} as determined from their phosphorescence spectra. On the other hand, the energy of ^{3}t* [E_T(trans)] is affected by the substitutional position; the phosphorescence 0-0 bands of *trans*-1BA and *trans* 2BA correspond to 40.7 and 42.5 kcal mol^{-1}, and the triplet energy of *trans*-9BA is estimated as nearly 39.5 kcal mol^{-1} from the S-T absorption of 9- vinylanthracene in CH_2Br_2.11) Thus, the energy decreases in the order of 2BA, 1BA, and 9BA.

Previously, we assumed that the energy difference (ΔE_{tp}) between ^{3}t* and ^{3}p* in 2BA is equivalent with the activation energy, E_a, for triplet isomerization of 2-AnthCH=CHD. Similar studies on 1-AnthCH=CHD and 9-AnthCH=CHD afforded 7.7 and 4.6 kcal mol^{-1}, respectively, as E_a for triplet isomerization.12) From these values the energies of ^{3}p* [E_T(trans)+ΔE_{tp}] above the ground-state trans isomer are reasonably estimated as 53.5, 48.2, and 44.1 kcal mol^{-1} for 2BA, 1BA, and 9BA, respectively. This order of energies for the twisted conformations is supported by theoretical13) and experimental studies14) on stabilization energies of isomeric anthrylmethyl radicals.

The above estimation of triplet energies leads to the triplet energy surfaces of positionally isomeric BA's as depicted in Fig. 2. In Fig. 2, the cis triplets of 2BA, 1BA, and 9BA are located at 47.5, 43.6, and 41.0 kcal mol^{-1}, respectively, above the ground-state trans isomers. For the trans conformers the introduction of an ethenyl group at the 1- and the 9-position stabilizes the triplet state through increased conjugation, though the latter case might involve a twisting of the anthryl group from the olefinic molecular plane; however, the introduction at the 2-position brings about almost no stabilization. For the sterically hindered cis conformers only the ethenyl group introduced at the 9-position is effective in stabilization of the triplet state. Thus, the present positionally isomeric anthrylethylenes undergo one-way isomerization along the highly different triplet energy surfaces.

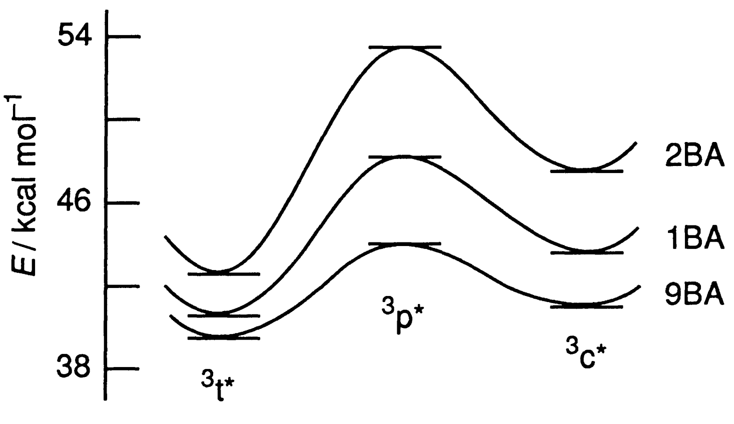

Fig. 2. The estimated triplet energy surfaces for positionally isomeric BA's.

To our knowledge, this is the first paper to report the positional substitution effect of aromatic nuclei on the activation processes in excited-state adiabatic reactions.

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8) Stationary irradiation was performed with a 400-W high-pressure mercury lamp using UV-D36B glass filter (366 nm light; for direct irradiation) or $CuSO_4$ and $NaNO_2$ solution filter (435 nm light; for sensitized excitation).
9) Transient absorption spectra were also measured by using a JASCO laser photolysis system with a Lambda Physik EMG-101 excimer laser (XeCl 150 mJ/pulse, 10-ns fwhm).
10) The rate constant of *cis*-1BA decay at 440 and that of *trans*-BA rise at 500 nm were in good agreement with each other.
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