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Rotational Isomerization of *trans*-2-Styrylanthracene between (s)-*trans* and (s)-*cis* Rotamers in the Excited States. Investigation of Its Sterically Restricted Model Compounds

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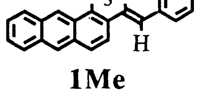
Rotational isomerizm of (s)-*cis* and (s)-*trans* rotamers of *trans*-2-styrylanthracene was investigated by the comparison of the absorption, emission and transient absorption spectra with those of the model compounds. The (s)-*cis* isomer is more stable than the (s)-*trans* on the excited state and (s)-*trans*→(s)-*cis* one-way rotational isomerization takes place on the triplet state with an activation energy of 7.2 kcal mol^{-1}.

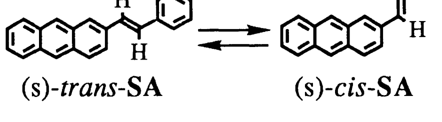
Ethylenes substituted with polycyclic aromatic nuclei often have rotational isomers around the single bond connecting the aryl group and the unsaturated carbon, (s)-*trans*- and (s)-*cis*-rotamers aligning their double bonds along the long and short axis of the aromatic ring, respectively. The rotational isomerization between these rotamers in the excited states is a subject of current interest in the photochemistry of arylethylenes.$^{1,2)}$

trans-2-Anthrylethylenes which do not undergo geometrical isomerization around the double bond$^{2-4)}$ exhibit strong dependence of their fluorescence on excitation wavelength due to the presence of the two rotamers.$^{5-9)}$ *trans*-2-Styrylanthracene (**SA**) have two rotamers, one with shorter λ^{f}_{max}: 412 and 436 nm with a 28.6 ns lifetime (at 20 °C in toluene)$^{9b,10)}$ mostly populated on excitation at 308-394 nm and another with longer λ^{f}_{max}: 423 and 450 nm with a 9.1 ns lifetime (at 20 °C in toluene)$^{9b,10)}$ populated on excitation around 415 nm, and they do not interconvert during their lifetimes in the excited singlet state and decay independently obeying to NEER (non-equilibration of excited rotamers) rule,$^{1,6,8a,9b)}$ though their conformations have not yet been assigned. The above behavior is in contrast to that of 2-vinylanthracene and *trans*-2-(3,3-dimethyl-1-butenyl)anthracene in which a conformer converts to the another in the singlet excited state during their lifetimes.$^{9a,11)}$ Moreover, the T-T absorption of **SA** changes with lowering of temperature, which suggests that the two rotamers show different T-T absorptions and their population is changed with temperature.$^{12,13)}$

In order to assign the conformation of the rotamers of **SA** and examine the possibility of their interconversion in the triplet state, model compounds for (s)-*trans* and (s)-*cis* rotamers with restricted conformations controlled by methyl groups, *trans*-1-methyl- (**1Me**) and *trans*-3-methyl-2-styrylanthracene (**3Me**) respectively, were prepared and their behavior in the ground (S_0), the lowest singlet (S_1) and the lowest triplet (T_1) states were investigated, and the potential energy surfaces between the two rotamers at S_0, S_1 and T_1 states



1Me



(s)-*trans*-**SA** (s)-*cis*-**SA**

3Me

are now depicted as in Fig. 1 based on their fluorescence and T-T absorption behaviors.[14)]

Figure 2 shows fluorescence spectra of **1Me**, **3Me** and **SA** for comparison in argon purged benzene. The excitation wavelength did not affect at all the fluorescence spectra, quantum yields and lifetimes of both **1Me** and **3Me**. Their spectra were unchanged with lowering temperature. **1Me** shows fluorescence spectrum (solid line in Fig. 2a, τ_f: 14 ns) with $\lambda_{max}{}^f$ at 422 and 447 nm, which is similar to that of a rotamer of **SA** with shorter $\lambda_{max}{}^f$ (solid line in Fig. 2b). Fluorescence of **3Me** (dashed line in Fig. 2a, τ_f: 14 ns) with $\lambda_{max}{}^f$ at 433 and 462 nm is similar to that of another rotamer of **SA** with longer $\lambda_{max}{}^f$ (dashed line in Fig. 2b). The above facts strongly suggest that the rotamers with shorter and longer $\lambda_{max}{}^f$ correspond to (s)-*trans* and (s)-*cis* rotamers, respectively.

Regarding to the triplet state of **SA**, Krongauz et al. suggested the presence of two species based on their findings by the conventional microseconds flash photolysis that the T-T absorption spectra in 2-methyltetrahydrofuran (MeTHF) were different between at 153 and 213 K exhibiting the longest $\lambda_{max}{}^{T\text{-}T}$ at 670 and 620 nm, respectively, and the absorption was time-dependent at lower temperatures.[12)] Subsequently, some of the present authors found that on laser flash photolysis of **SA** in EPA the absorption with $\lambda_{max}{}^{T\text{-}T}$ at 670 nm observed at 150 K was converted to that with $\lambda_{max}{}^{T\text{-}T}$ at 620 nm with a time constant of around 10 μs at 200 K and attributed it to the conversion between rotational isomers in the triplet state.[13)]

Figure 3a and 3b illustrates T-T absorption spectra of **SA**, **1Me**, and **3Me** in benzene at ambient temperature. In MeTHF, the absorptions of both **1Me** and **3Me** were unaffected by temperature, however, the absorption of **SA** was much shifted to longer wavelength by lowering temperature to 123 K as shown in Fig. 3c. Fig. 3d shows that at 223 K in MeTHF the initially observed absorption (500 ns after the excitation) around 660 nm was decreased in intensity and disappeared after 5 μs; concurrently absorptions around 620 and 570 nm were increased in intensity. The T-T absorption of **1Me** with $\lambda_{max}{}^{T\text{-}T}$ at 465, 610 and 660 nm (lifetime, τ_T: 14 μs in benzene under

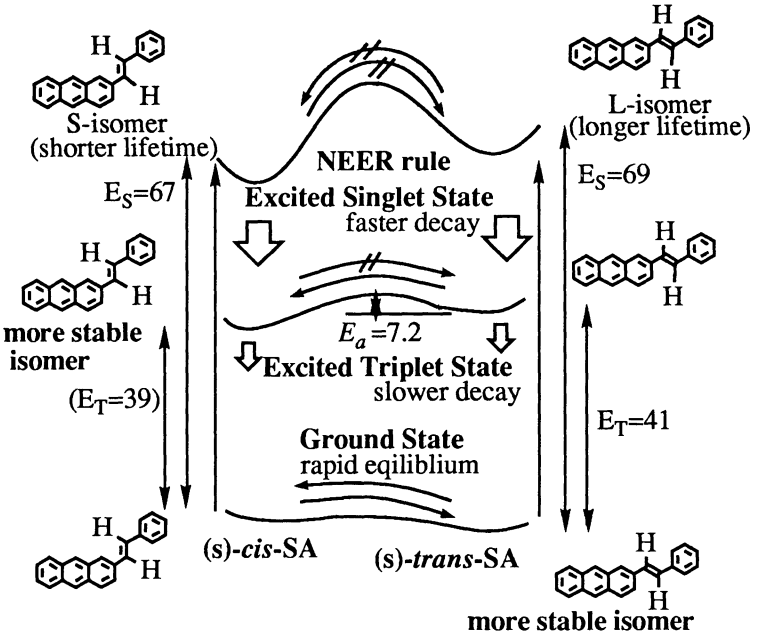


Fig. 1. Potential energy surfaces of rotational isomerization of SA.

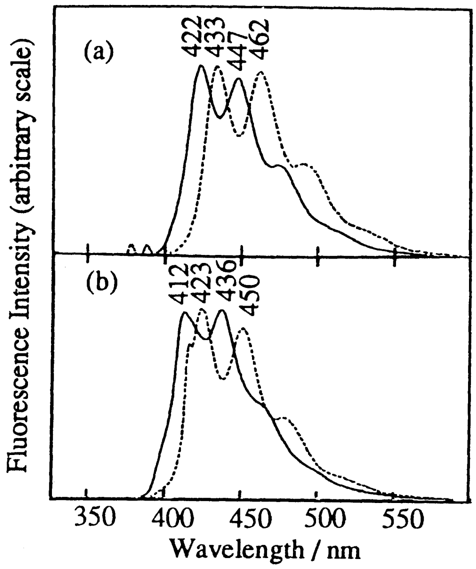


Fig. 2. Fluorescence spectra of **1Me**, **3Me** (a) and **SA** (b), in argon purged benzene. The spectra were measured on excitation at 388 nm (solid line) for **1Me**, at 378 nm (dashed line) for **3Me**, and 308 nm (solid line) and 415 nm (dashed line) for **SA**.

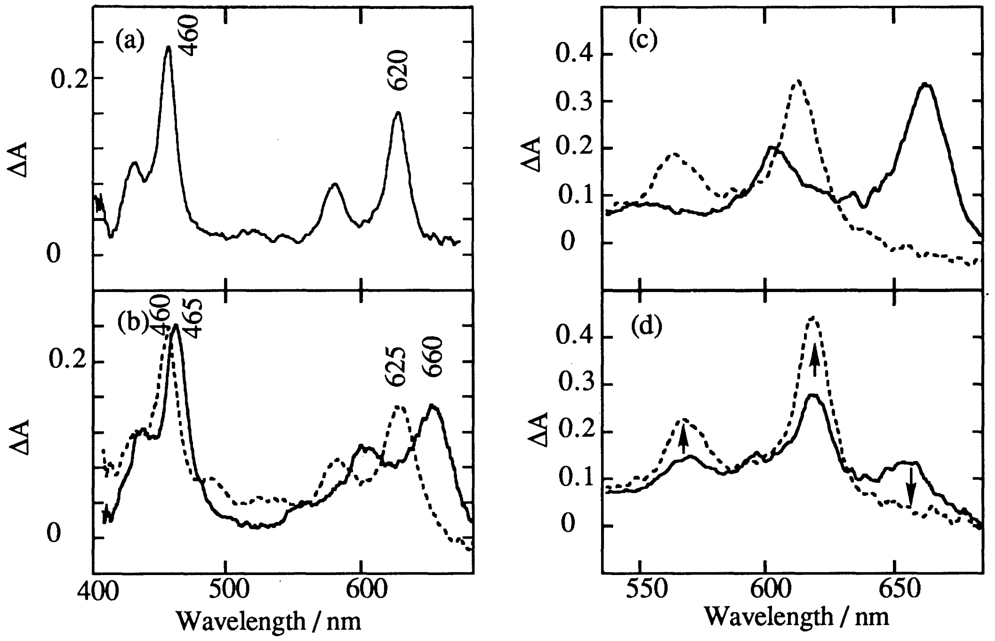


Fig. 3. $T_n \leftarrow T_1$ absorption spectra of **SA**, **1Me**, and **3Me**. (a) **SA**, (b) **1Me** (solid line) and **3Me** (dashed line) 1 μs after laser pulse at ambient temperature in argon purged benzene. (c) **SA** at 123 K (solid line) at 293 K (dashed line) 1 μs after laser pulse, and (d) 500 ns (solid line) and 5 μs (dashed line) after laser pulse at 223 K in degassed 2-methyltetrahydrofuran.

argon) is similar to that of **SA** observed immediately after the excitation at low temperature. On the other hand, the T-T absorption of **3Me** with $\lambda_{max}{}^{T\text{-}T}$ at 460, 580, and 625 nm (τ_T: 18 μs in benzene under argon) is similar to that of **SA** observed at the later period after the excitation at low temperature and also to that of **SA** observed at ambient temperature. The above findings indicate that the time-dependent change of the T-T absorption of **SA** corresponds to the internal rotation of (s)-*trans* to (s)-*cis* rotamers at the triplet state, in sharp contrast to the *trans*-2-styrylnaphthalene which do not undergo rotational isomerization between the rotamers during their short triplet lifetimes.[15)]

The Arrhenius plot of the observed rate constants between 203-243 K in MeTHF affords an activation energy (E_a) and frequency factor (A) as 7.2 kcal mol^{-1} and 2.2×10^{12} s^{-1} (log A=12.4), respectively.[16)] Increase of temperature reduced the absorption at 660 nm for (s)-*trans* rotamer and made the absorption at 620 nm for (s)-*cis* appear immediately after the excitation. It corresponds to the increase of the population of (s)-*cis* rotamer relative to that of (s)-*trans* in the ground state with increasing temperature.

In the phosphorescence spectra in EPA at 77 K, **SA** and **1Me** showed very similar spectra with their 0,0 bands in very close wavelengths (691 nm, triplet excitation energy: E_T=41 kcal mol^{-1} for **SA**[13b)]; 690 nm, E_T=41 kcal mol^{-1} for **1Me**), which are higher in energy than the 0,0 band of **3Me** (736 nm, E_T=39 kcal mol^{-1}). Accordingly, the phosphorescence of **SA** is assigned to its (s)-*trans* rotamer, which is much more populated than (s)-*cis* rotamer in the ground state at 77 K; and its internal rotation to (s)-*cis* is frozen at 77 K. The above assignment agrees well with those made based on the fluorescence at 77 K and T-T absorption at low temperature.

Phosphorescence of (s)-*cis* rotamer of **SA** could not be observed due to its extremely low population at 77 K, however, if it is assumed to be nearly the same as that of **3Me**, the potential energy surfaces of the rotational isomerization of **SA** can be depicted as in Fig. 1. In S_1, NEER rule holds, however in T_1 the rotational isomerization proceeds as (s)-*trans*→(s)-*cis* one-way mode with an activation energy of 7.2 kcal mol^{-1}. The E_T of (s)-*trans* rotamer is 2 kcal mol^{-1} higher than (s)-*cis* rotamer, although, in S_0, (s)-*trans* is more stable than (s)-*cis* rotamer. These results may indicate that the energy difference in S_0 is smaller than or nearly the same as that in T_1, and this was supported by the reported energy difference of the two isomers in S_0 as 1 kcal mol^{-1}.6) This value corresponds to 16% of (s)-cis isomer in equilibrium at 300 K estimated from the Boltzmann distribution.

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16) The E_a value agrees well with 6.4 kcal mol^{-1} calculated by CS-INDO SCI method in Ref. 15b.

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