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Effect of Substituents on the Equilibrium between Trans and Perpendicular Conformers in the Triplet Excited State of Substituted Styrylpyrenes

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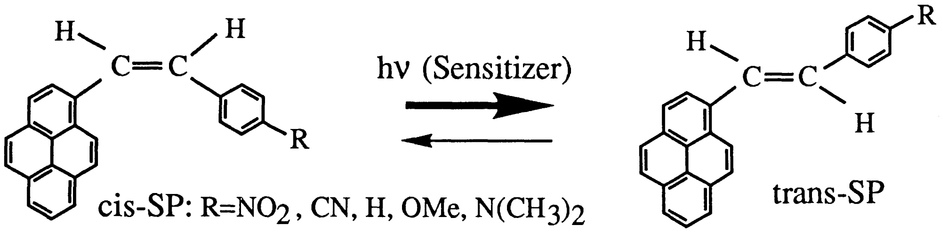
In the equilibrium between trans ($^3t^*$) and perpendicular ($^3p^*$) conformers in the triplet excited state of 1-styrylpyrenes, substitution by electron-accepting groups at the para-position of styryl group more effectively stabilizes $^3t^*$ than $^3p^*$, therefore affording very high composition of their trans isomers at the photostationary state.

Molecules can take different conformations, sometimes being in equilibrium, in the excited states as well as in the ground state.1,2) However, the effect of polar substituents on the equilibrium between the conformers has scarcely been investigated for the excited states in contrast to the extensive works for the ground state.

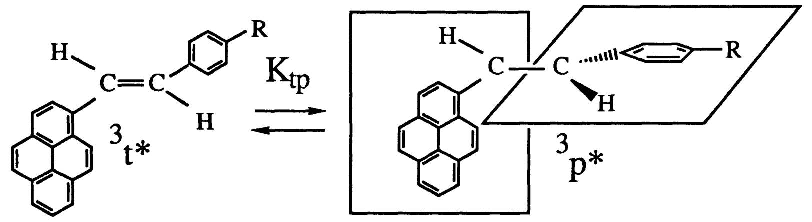
In the course of an investigation on the photochemical isomerization of unsaturated bonds,3,4) we have found that in the triplet excited state of 1-styrylpyrene (SP) two conformers, trans ($^3t^*$) and perpendicular ($^3p^*$) conformers, are in equilibrium;5) $^3t^*$ deactivates solely to trans undergoing typical one-way cis to trans isomerization like $^3t^*$ of 2-anthrylethylenes,3,4) whereas $^3p^*$ deactivates to trans and cis isomers undergoing typical conventional two-way isomerization as $^3p^*$ of stilbene.6,7) The potential energy surface of SP is drawn in Fig. 1 (a).5)

Actually, the photochemical isomerization of SP in the triplet state occurs seemingly in a mutual way between cis and trans isomers as in stilbene, however, giving very much higher composition of trans to cis at the photostationary state. Furthermore, the photostationary isomer ratio $([t]/[s])_s$ and the quantum yields of cis→trans isomerization, $\Phi_{c\rightarrow t}$, increase with total SP concentration and cis-SP concentration, respectively, like in 2-anthrylethylenes.

These findings have prompted us to examine the effect of substituents on the equilibrium between $^3t^*$ and $^3p^*$ conformers in substituted SPs. We now reveal that more electron accepting substituents like CN and NO_2 more effectively stabilize $^3t^*$ than $^3p^*$ therefore enhancing the decay from $^3t^*$ than $^3p^*$ resulting in increase of $([t]/[c])_s$.



cis-SP: R=NO_2, CN, H, OMe, $N(CH_3)_2$



Irradiation of substituted styrylpyrenes, PyCH=CHAr (SP, Py: 1-pyrenyl; Ar: 4-R-C_6H_4, R=NO_2, CN, OMe, and $N(CH_3)_2$) in the presence of benzil (at 436 nm) or camphorquinone (at 480±10 nm) as triplet sensitizers in deaerated benzene at 20 °C resulted in mutual isomerization between their cis and trans isomers. As Fig. 2 shows, $([t]/[c])_s$ increased with total concentration of SPs.[8] Furthermore, $\Phi_{c\rightarrow t}$ increased linearly with the concentration of initial cis-isomers to attain as high as 18 at 4×10^{-3} M (M=mol dm^{-3}) of cis-OMe-SP concentration. These concentration effects on $([t]/[c])_s$ and on $\Phi_{c\rightarrow t}$ indicate that the cis→trans isomerization proceeds through a quantum chain process[3-5] regenerating $^3c^*$ by energy transfer from $^3t^*$ to ^1c (the ground state cis-isomer) as in unsubstituted styrylpyrene (Scheme 1). The slopes and intercepts of Fig. 2 increase in the order of OMe, CN, and NO_2; the unsubstituted SP exhibits very similar concentration dependence to CN-SP.[5] Thus, the values of the intercept are 1.64, 2.17, 2.29, and 3.28 and those of the slope are 2.02×10^4, 2.67×10^4, 2.62×10^4, and 3.40×10^4 M^{-1}, respectively for OMe-, H-, and CN-, and NO_2-SP. These results suggest that, the higher these values, the smaller K_{tp} ($=[^3p^*]/[^3t^*]$), the equilibrium constant between $^3p^*$ and $^3t^*$, therefore leading to more facile deactivation of the triplet state from $^3t^*$. According to Scheme 1, where k's denote the rate constants for the corresponding decay processes, the photostationary state isomer ratio is expressed as Eq. 1.

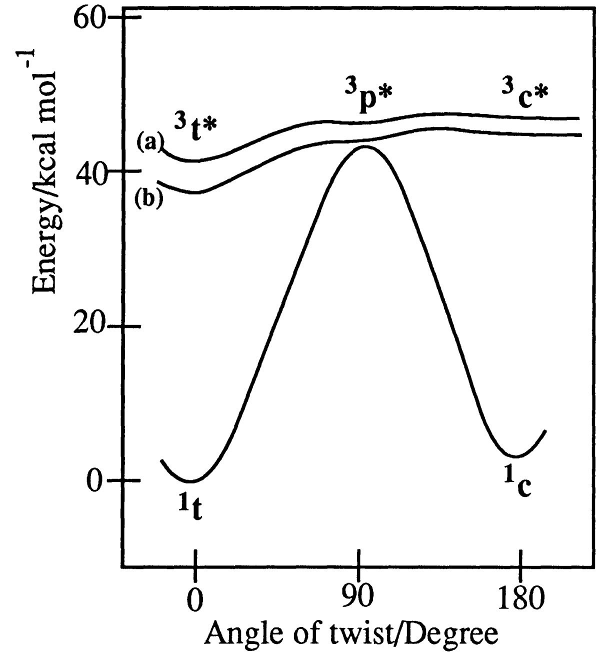


Fig. 1. Potential energy surfaces of isomerization of SP in the triplet state. (a); R=H, (b); R=NO_2.

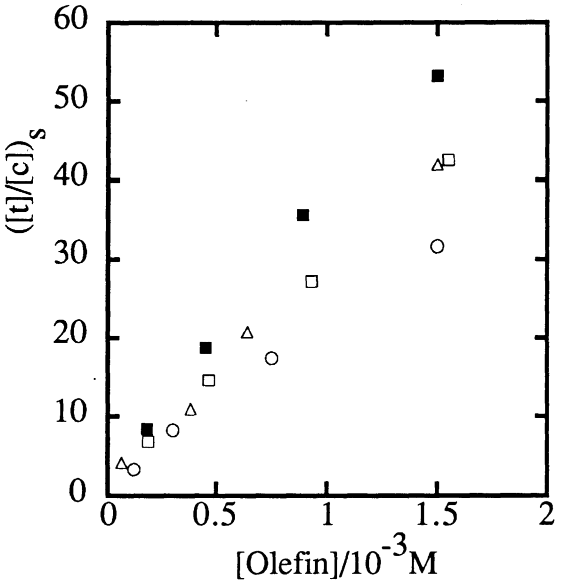
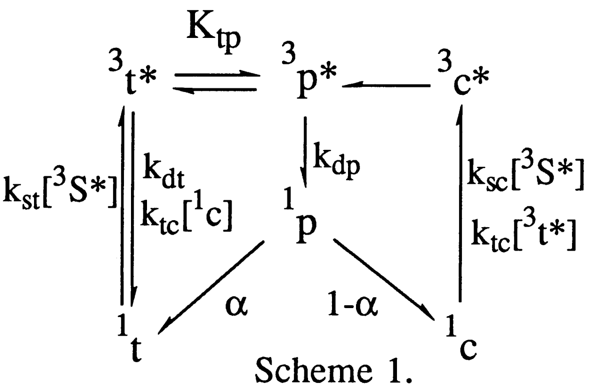


Fig. 2. Effect of SP concentration on $([t]/[c])_s$ for OMe- (○), H- (△), CN- (□), and NO_2-SP (■).



Scheme 1.

S: Sensitizer

$$\left(\frac{[t]}{[c]}\right)_S = \frac{k_{dt} + \alpha K_{tp}k_{dp} + k_{tc}[SP]}{(1-\alpha)K_{tp}k_{dp}} \qquad (1)$$

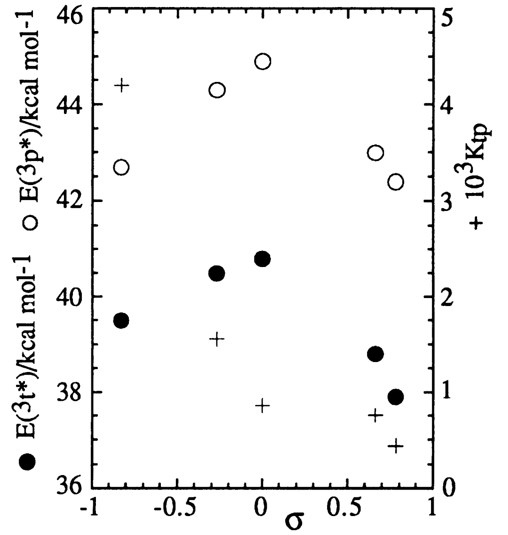


Fig. 3. Substituent effect on the triplet energies of $^3t^*$ and $^3p^*$ and on their equilibrium constant (K_{tp}).

The intercept corresponds to $([t]/[c])_S$ at an infinitely dilute solution resulting from the deactivation of the triplet state from both $^3t^*$ solely giving trans and $^3p^*$ giving trans and cis in a ratio of α and (1-α). Since α is taken as 0.5, the intercept gives the ratio of the fraction of the triplet state deactivating at $^3p^*$ and $^3t^*$ as 1:0.32, 1:0.59, 1:0.65, and 1:1.14 for OMe-, H-, CN-, and NO_2-SP, respectively. Therefore, more electron-accepting substituents favor the decay from $^3t^*$ compared with that from $^3p^*$.

The $^3p^*$ is situated very close to ^1p (perpendicular conformation in the ground state) and much more rapidly deactivates with a rate constant of k_{dp} (2×10^7 s^{-1} [7]) than $^3t^*$, which is situated more than 40 kcal mol^{-1} (1 cal=4.184 J) above ^1t (the ground state trans isomer) and accordingly deactivates with a lower rate constant of k_{dt} (1×10^4 s^{-1} [3-5]). Therefore, the above values of the ratio of the fraction of the triplet state deactivating from $^3p^*$ and $^3t^*$ means that $^3p^*$ is very much less populated than $^3t^*$.

In Eq. 1, the intercept values correspond to $(k_{dt}+\alpha K_{tp}k_{dp})/(1-\alpha)K_{tp}k_{dp}$. Since the values of α, k_{dt}, and k_{dp} can be assumed to be essentially the same among the SPs, K_{tp} at 20 °C and subsequently ΔG_{tp} (Gibbs energy difference between $^3p^*$ and $^3t^*$) are estimated from the observed intercepts. K_{tp} is 1.6×10^{-3}, 8.6×10^{-4}, 7.6×10^{-4}, and 4.4×10^{-4}, and ΔG_{tp} is 3.8, 4.1, 4.2, and 4.5 kcal mol^{-1} for OMe, H, CN, NO_2 substituents, respectively. Similarly, the value of the slope increased from 2×10^4 of OMe-SP to 3.4×10^4 M^{-1} of NO_2-SP, reflecting the decrease of K_{tp} accompanied by reduction of the decay fraction from $^3p^*$ in nearly the same magnitude as observed by the change of intercepts. Thus, the more electron-accepting substituents lower the K_{tp} value, and accordingly, increase ΔG_{tp} enriching one-way mode character.

Laser excitation of SPs directly or in the presence of sensitizers, camphorquinone and benzil, afforded the transient absorption spectra of the triplet states of SPs (T-T absorption spectra). Excitation of either cis- or trans-isomers afforded the same absorption, which decays with nearly 30 μs for all SPs. The T-T absorption maxima shifted to red with introduction of CN or NO_2 group to 540 or 670 nm compared to 520 nm for unsubstituted SP. The lifetime of the triplet states, τ_T, comprising from equilibrating $^3t^*$ and $^3p^*$ ($\tau_T=(1+K_{tp})/(k_{dt}+K_{tp}k_{dp})$) decreased with the increase of temperature (from 4 to 59 °C) in all cases, which indicate that K_{tp} is increased with increasing temperature in accordance with the aforementioned proposition that $^3p^*$ is less stable than $^3t^*$. The temperature effect on the triplet lifetime afforded the enthalpy difference between $^3t^*$ and $^3p^*$ (ΔH_{tp}) to be 3.2, 4.2 and 4.8 kcal mol^{-1}, respectively for $N(CH_3)_2$-, H-, and NO_2-SP; thus, an electron donating substituent reduces the energy difference between $^3t^*$ and $^3p^*$ as described above.

To discuss the actual triplet energy of SPs, because of the lack of their phosphorescence, the energies of $^3t^*$ ($E(^3t^*)$) were estimated from the energy transfer equilibrium between their trans triplets and azulene triplets (E_T=39.8 kcal·mol^{-1}) observed by laser photolysis[5b,9] for $N(CH_3)_2$-, MeO-, H-, CN-, and NO_2-SP as 39.5, 40.5, 40.8, 38.8, and 37.9 kcal mol^{-1}, respectively. Fig. 3 plots the obtained values against the Hammett's sigma constants, together with K_{tp} and the energies of $^3p^*$ ($E(^3p^*)$) calculated by assuming $\Delta G_{tp} \approx E(^3p^*) - E(^3t^*) \approx \Delta H_{tp}$.[10]

The potential energy surface for NO_2-SP is depicted in Fig. 1 (b) as an example of substituted SPs, which illustrates how $^3t^*$ is stabilized by the substitution of electron-accepting NO_2 group.

To our knowledge, this is the first paper to reveal the effect of polar substituents on the conformational equilibrium between $^3t^*$ and $^3p^*$ in the triplet state of unsaturated molecules and on the photostationary state isomer ratios. Although the polar substituents do not alter the mode of isomerization at very low concentration of SPs, trans-isomer composition at the photostationary state is largest in NO_2 substituent at any SP concentration. Furthermore, in 1.5×10^{-3} M, the trans-isomer composition of NO_2-SP attains higher than 98% to exhibit almost one-way like phenomenon.

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10) In Fig. 3, $E(^3p^*)$ (=42.7 kcal mol^{-1}) and K_{tp} (4.2×10^{-3}) for $N(CH_3)_2$-SP group are plotted based on its ΔH_{tp}.

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