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EXCITED STATE MULTIPLICITY INVOLVED IN PHOTOCYCLOADDITION OF POLYMETHYLENE DICINNAMATES AS STUDIED BY QUENCHING EXPERIMENTS

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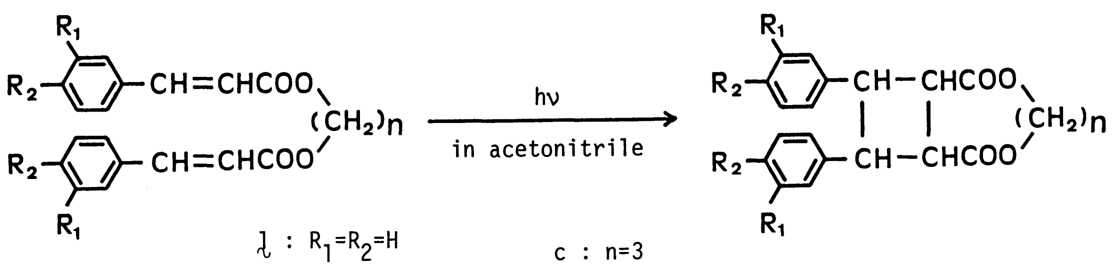
The excited state multiplicity involved in photocycloaddition of polymethylene dicinnamates was studied by quenching experiments using ferrocene, and the ratio of such multiplicities deduced from the Stern-Volmer plots based on a generalized Stern-Volmer expression was shown to vary depending upon the substituent and the methylene chain.

Various experimental works have been reported on the photoreaction of cinnamic acid and its derivatives.[1-11] It was initially considered that the photodimerization of cinnamic derivatives proceeds through the excited singlet state (S_1) on direct irradiation and through the excited triplet state (T_1) on triplet-sensitized irradiation.[1,2]

Recently, however, it has been suggested that the cycloaddition on the direct irradiation involved T_1 state as well as S_1 state and that the two pathways differ in their quantum efficiencies in the photoreaction of solid polyvinylcinnamate and ethyl cinnamate.[8,9]

In previous papers,[10,11] we have reported that the rate of photocyclization of polymethylene dicinnamate was enhanced by the methoxy substitution at the 3-position of benzene ring and the trimethylene chain. These effects were caused by the feasibility of the intramolecular exciplex formation in the S_1 state. We have also shown by the excited state calculation by the CNDO/S-CI method that the rate of exciplex formation and the cyclization are well correlated with π-electron density of the benzene ring and odd electron density of the olefinic carbon in the S_1 state of the cinnamate moiety. These results indicate that the excited state multiplicity involved in these reactions should also be reflected by the substituent.



1 : $R_1=R_2=H$
2 : $R_1=OCH_3$, $R_2=H$
3 : $R_1=H$, $R_2=OCH_3$

c : n=3
d : n=4
e : n=5
f : n=6

In the present paper, we have studied the excited state multiplicity responsible for the intramolecular cycloaddition of polymethylene dicinnamates 1-3, which was determined by quenching experiments using ferrocene.

Figure 1 illustrates the Stern-Volmer plots of the Φ^{0}/Φ values of 1-3 against the ferrocene concentration.[12)] The line-fitting of these plots using a generalized Stern-Volmer expression was made by the Gauss-Newton method. This type of expression has been presented by Turro et al. for the quenching of a reaction which occurs from both singlet and triplet excited states by a quencher which can quench both excited states, and shown in Eq. 1.[13)] According to the standard procedure, an oblique asymptote can be derived and shown in Eq. 2.

It can be seen that many of these plots do not show a straight line, implying that the reactions involve more than one excited state and there seems to be three distinct line features.

In the case of unsubstituted dicinnamates 1c and 1d, the plots approach a horizontal asymptote at higher concentration of the quencher.[14)] This implies that the reaction is occurring from both singlet and triplet states but only triplet state of the reaction are being quenched.

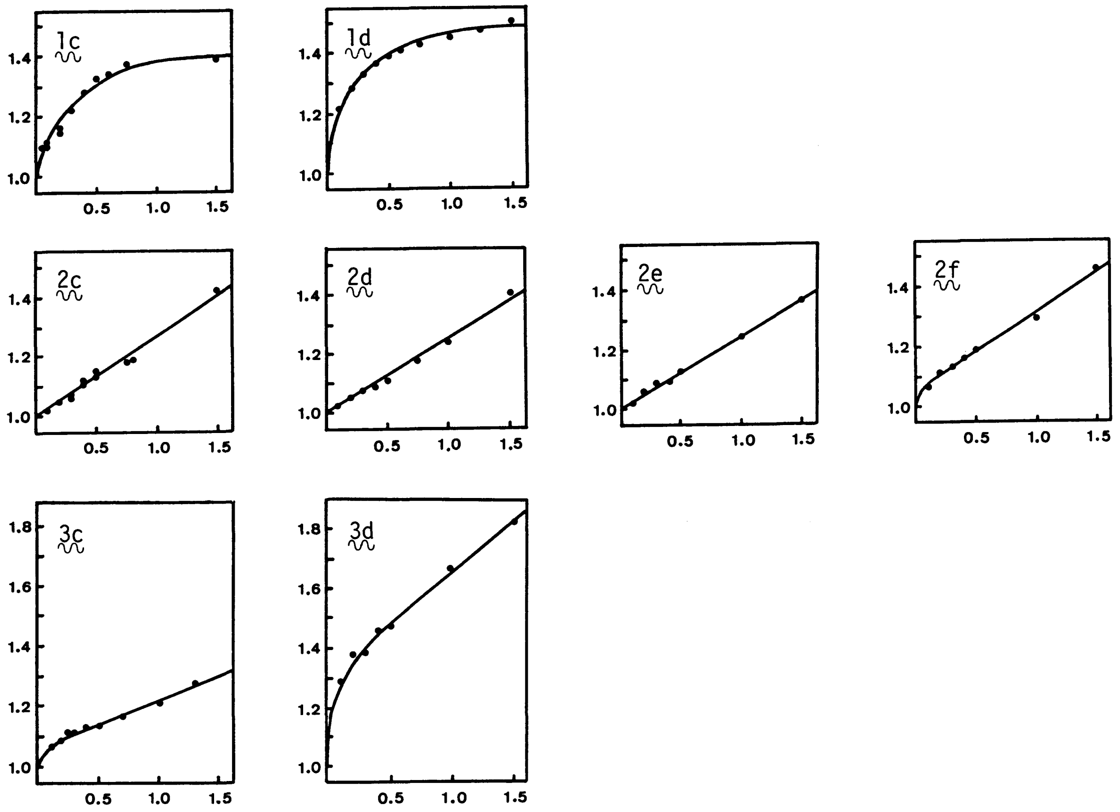


Fig. 1. A Stern-Volmer plot (Φ^{0}/Φ) for the pseudo-dimerization of polymethylene dicinnamates as a function of the ferrocene concentration [FcH] (10^{2} mol dm^{-3}) in acetonitrile.

A generalized Stern-Volmer expression for reactions which involve quenching of more than one excited state of the reactant.

$$\frac{\Phi^0}{\Phi} = \left\{ 1 + k_S\tau_S^0[Q] \right\} \left\{ 1 + k_T\tau_T^0[Q] \right\} \left\{ \frac{1 + \Phi_T^0/\Phi_S^0}{1 + \Phi_T^0/\Phi_S^0 + k_T\tau_T^0[Q]} \right\} \qquad (1)$$

Φ^0 and Φ : Total quantum yield in the absence and presence of quencher

Φ_T^0 and τ_S^0 : Quantum yield from the excited triplet and singlet state

τ_S^0 and τ_T^0 : Lifetime of the excited singlet and triplet state

k_S and k_T : Rate constant for quenching of the excited singlet and triplet state

An oblique asymptote

$$\frac{\Phi^0}{\Phi} = k_S\tau_S^0 \left\{ 1 + \Phi_T^0/\Phi_S^0 \right\} [Q] + 1 + (\Phi_T^0/\Phi_S^0) \left\{ 1 - \frac{k_S\tau_S^0 (1 + \Phi_T^0/\Phi_S^0)}{k_T\tau_T^0} \right\} \qquad (2)$$

In a series of 3-methoxy derivatives **2**, the plots showed a straight line up to the pentamethylene derivatives **2e**, which means that the initial slope is equal to the slope of the oblique asymptote and involves a single excited state.[15)]

In the case of 4-methoxy derivatives **3** and 3-methoxy hexamethylene derivative **2f**, the initial slope is greater than that of the oblique asymptote and asymptotically approach a straight line with a slope lower than that of the initial slope. This indicates that both reaction and quenching occurred from both the singlet and triplet states.

Thus, it is shown that the nature of the excited states involved in these reactions varies with the substituent introduced and the number of the methylene groups.

Since ferrocene quenching of the triplet is much more efficient than that of singlet state ($k_S\tau_S^0 \ll k_T\tau_T^0$) and the reaction proceeds predominantly from the singlet state ($\Phi_T^0 < \Phi_S^0$), the value interpolated at [Q]=0 on the asymptote can be considered to be equal to $1+ \Phi_T^0/\Phi_S^0$. Based on this characteristic of the oblique asymptote, the ratio of quantum yield from the singlet and triplet state was deduced and the results are shown in Table 1.

Table 1. The ratio of pseudo-dimerization from the singlet and triplet

Compounds	Singlet		Triplet
1c	74	:	26
1d	68	:	32
2c	100	:	0
2d	100	:	0
2e	100	:	0
2f	94	:	6
3c	94	:	6
3d	75	:	25

It can be seen that the participation of the excited singlet state is enhanced by the introduction of methoxy substituent and is the highest on trimethylene dicinnamates.[11)] Another interesting feature is that, in a series of 3-methoxy derivatives, the reaction proceeds exclusively from the singlet state even in tetramethylene (n=4) and pentamethylene (n=5) derivatives.

Thus, the present result clearly demonstrates a striking parallelism between the acceleration character of 3-methoxy substituent and/or trimethylene chain[11)] (*vide supra*) and the involvement of the singlet state in the reaction.

It should be mentioned here that a nitro substituent at the benzene ring of cinnamate derivatives is also known to accelerate the photocyclization, but the participation of the excited singlet state is nearly the same as that of unsubtituted cinnamate.[4)] Thus, the substituent effect discussed here should be considered distinct in nature from that of nitro substituent.

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12) The rate of the cyclization was determined by the method similar to those previously reported.[11)]
13) D. J. C. Dalton and N. J. Turro, Mol. Photochem., 2, 133, (1970).
14) Equation 1 simplifies to $\dfrac{\Phi^0}{\Phi} = \left\{ 1 + k_T\tau_T^0[Q] \right\} \left\{ \dfrac{1 + \Phi_T^0/\Phi_S^0}{1 + \Phi_T^0/\Phi_S^0 + k_T\tau_T^0[Q]} \right\}.$
15) Equation 1 simplifies to $\dfrac{\Phi^0}{\Phi} = 1 + k_S\tau_S^0 \left\{ 1 + \Phi_T^0/\Phi_S^0 \right\} [Q].$

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