

Each of the acetonitrile solutions containing the trans-trans dicinnamate derivatives (ca. 2.0×10^{-5} M) was irradiated with a grating monochromator with 2 kW xenon lamp and 3 nm bandwidth (Model CRM-FM, JASCO).⁵ The resulting solution was subjected to electronic spectral measurement at appropriate intervals. The relative efficiencies (ϕ_{rel}) of the photocyclization were illustrated in Figure 1.⁶

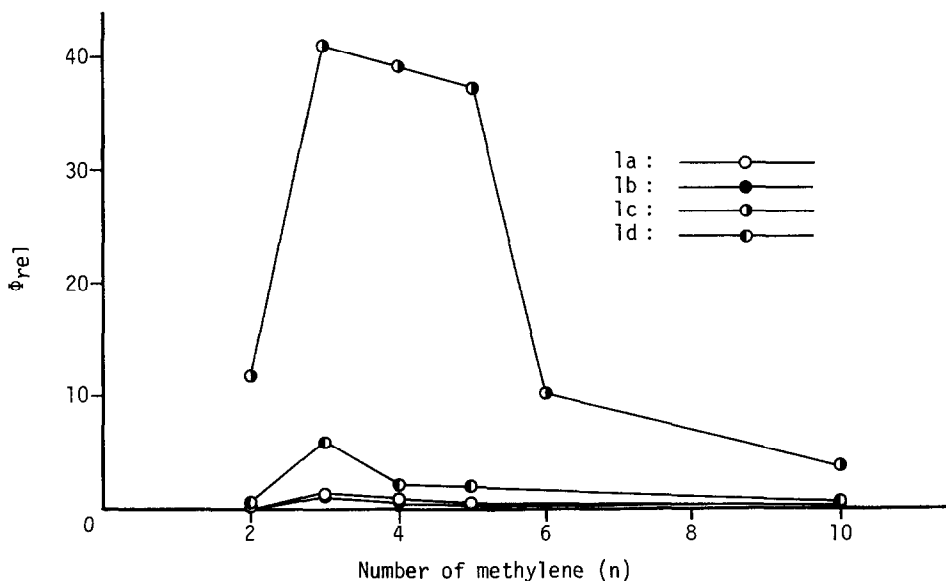


Figure 1. Methoxy substituent effect and methylene chain effect upon photolability toward the intramolecular cycloaddition of n-methylene dicinnamates

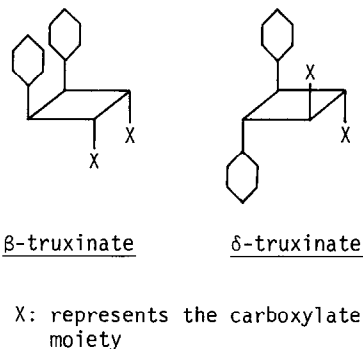
It can be seen that the photocyclization of 3-methoxy derivative $1c$, was exceptionally fast, while 4-methoxy derivative $1b$, is rather slightly slow relative to the unsubstituted one $1a$. Another noticeable point is that trimethylene chain exhibited the greatest topotactic assistance by the immobilization of the two cinnamoyl groups in favor for the photocyclization in all cases examined, and in a series of 3-methoxy derivatives $1c$, the similar rate enhancements were observed even in tetramethylene ($n=4$) and pentamethylene ($n=5$) dicinnamates. The separate experiments on the similarly methoxy-substituted methyl cinnamates demonstrated that the rate of trans-cis isomerizations had of no marked difference from each other. Based on these results, it could be concluded that an introduction of 3-methoxy group largely accelerated the photocyclization to cyclobutane derivatives.

In order to gain further insight into the 3-methoxy substituent effect, we have performed the photolyses of $1c$ in acetonitrile solution (ca. 2×10^{-2} M) in a preparative scale together with those of unsubstituted one $1a$, for comparison. The photoconversions were clean and no polymer formation was observed in

all cases, indicating that the intermolecular crosslinks were negligible.⁷ The stereochemical analyses of the photoproducts were summarized in Table I.

Table I. 3-Methoxy effect and methylene chain concentration effect upon the photoproduct composition

Substrate	n	Product ratio ^{a)}	
		β -truxinate	δ -truxinate
la	2	100	: 0
	3	99	: 1
	4	28	: 72
lc	2	100	: 0
	3	91	: 9
	4	73	: 27



a) determined by the NMR integration of each photolysate

Table I shows that β -truxinate is the major product of trimethylene dicinnamates ($n=3$) in both cases, la and lc . In the case of tetramethylene derivatives ($n=4$), however, the major product is δ -truxinate on the unsubstituted dicinnamate la , whereas the major product was unaltered on the 3-methoxy derivative lc . This can be interpreted as gaining an advantage of the excited state electronic structure for the formation of the transition state with the ground state cinnamoyl residue leading to the β -truxinate such as the formation of intramolecular excimer.

The electronic structures of hydroxy ring-substituted cinnamic acids were also theoretically evaluated by the CNDO/S-CI excited state calculation to assess the nature of the substituent perturbations. Details of the computed spectral and other electronic features will be presented elsewhere. However, the sense of the results pertinent to the present discussion is briefly mentioned here: the CI state of the lowest excited triplet state (T_1) consisted of nearly single HOMO-LUMO transition in all cases, while that of the lowest excited singlet state (S_1) consisted of an admixture of many configurations. 4-Hydroxy substituent enhanced the mixing of HOMO-LUMO excitation and reduced that of NHOMO-LUMO excitation, whereas 3-hydroxy substituent enhanced the mixing of HOMO-LUMO excitation. Also, the HOMO and LUMO are largely polarized to the olefinic double bond. These characteristics of the CI states of S_1 reflects strongly on the odd electron densities of the olefinic double bond. The calculated odd electron densities were listed in Table II together with the relative efficiencies for the photocyclization (ϕ_{rel}). In fact, the observed ϕ_{rel} were considerably well correlated with the odd electron densities at C_α of S_1 states as being indicated by the correlation coefficient (r) of the least square treatment between the odd electron densities (Q_{odd}) and the relative efficiencies of trimethylene derivatives of la-d ($\log \phi_{rel}$).⁸

Table II. Relative efficiencies (ϕ_{rel}) and odd electron densities (Q_{odd}) of olefinic carbons on S_1 of cinnamic derivatives computed by the CNDO/S-CI method

Substrate	ϕ_{rel}	Q_{odd}	
		C_α	C_β
$R_1=R_2=H$	1.00	0.1951	0.1462
$R_1=H, R_2=OH$	0.84	0.1836	0.1118
$R_1=OH, R_2=H$	40.69	0.2405	0.1832
$R_1=R_2=OH$	5.42	0.2162	0.1525
$C_\alpha : r = 0.9873$		$C_\beta : r = 0.8953$	

We are elaborating the further precise nature of alkoxy substituent effect upon the intramolecular photocyclization of dicinnamates and it will be the subject of the forthcoming paper.

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- The irradiation wavelength where the UV absorption of the photoproduct is negligible was selected in each run.
- The relative efficiencies were approximated with $\phi_{rel} = (p \times \epsilon)^{-1}$ where p is the irradiated photon number for the one-half decrease in concentration of the total dicinnamate and ϵ is the molar absorptivity at the irradiating wavelength.
- The isolated yields of the photoproducts were more than 90 % in all cases, and each mass spectrum of the photolysates showed the molecular ion to be the same as the starting dicinnamate.
- Examinations of the similar correlation with the odd electron densities of T_1 state were shown to be poor indicating that T_1 state is of minor importance for the cyclizations of these compounds.

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