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Nature of Substituent Effect of Nitro and Methoxyl Group on Photocycloaddition of Polymethylene Dicinnamates

Masayuki Kuzuya,* Naohisa Yokota, Akihiro Noguchi, and Takachiyo Okuda
Gifu Pharmaceutical University, 6-1, Mitahora-higashi 5-Chome, Gifu 502

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The nature of the nitro substituent effect and topotactic assistance by the polymethylene chain of polymethylene dicinnamates upon the rate of photocyclization and the stereochemistry of photoproducts have been explored, in comparison with the similar effect of a methoxyl substituent; a striking rate enhancement and stereospecificity of the photoproduct were observed on a trimethylene dicinnamate derivative. However, the detailed study of the stereochemical course of the photoproduct has revealed that the dependence of the topotactic assistance of nitro derivatives on the polymethylene chain length largely differs from that of methoxy derivatives. Based on the results of the CNDO/S-CI excited state calculation of the model compounds, it is concluded that the acceleration character of the nitro substituent is mainly due to the odd electron density at the reaction site, i.e. the olefinic double bond; it is not due to the facile exciplex formation on the excited singlet state, unlike that of a methoxyl substituent.

In a previous paper of this series,[1] we have reported the excited state multiplicity responsible for an intramolecular photocycloaddition of polymethylene dicinnamates bearing methoxyl substituent at the benzene ring as studied by quenching experiments. We have shown a striking parallelism between the acceleration character of a 3-methoxyl substituent and the involvement of the excited singlet state in the reaction.

It is also known that a 4-nitro substituent in the benzene ring of cinnamate derivatives accelerates the photocycloaddition, and the participation of the excited singlet state is nearly the same as that of an unsubstituted cinnamate.[2] This indicates that the nature of the substituent effect on the rate of the photocycloaddition should differ from that of a methoxyl substituent.

Accordingly, it is of interest to study how a strong electron-withdrawing nitro substituent exerts an influence upon the photocycloaddition of polymethylene dicinnamates in comparison with that of a methoxyl derivatives.

In the present paper, we report an accelerating action of a nitro substituent and a polymethylene chain effect based upon the electronic structure and the stereochemistry of the photoproducts.

Experimental

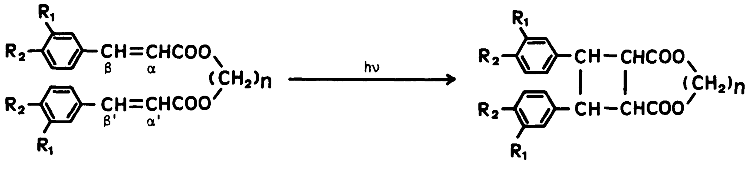
Melting points were determined on a Shibata melting point apparatus and are uncorrected. IR spectra on KBr disks were recorded on a JASCO A-102 spectrometer, ^{1}H NMR spectra in CDCl$_3$ with TMS as internal standard on a Hitachi R-20 (60 MHz) spectrometer, UV spectra in acetonitrile on a Hitachi 323 spectrophotometer, and MS on a JEOL JMS-D300 spectrometer at 70 eV. Elemental analyses were carried out by the Microanalytical Laboratory, Gifu Parmaceutical University.

Materials. Polymethylene bis(nitrocinnamate)s **4b—j** and **5b—j** were prepared in 60—80% yields from α,ω-dibromoalkanes (n=2—6 and 10) and sodium nitrocinnamates according to the reported procedure.[3] The physical and spectral data are shown in Table 1.

UV-Irradiation. Each of the acetonitrile solutions of the di-trans-cinnamate derivatives (1.7×10^{-5} mol dm^{-3}) was irradiated with a grating monochromator (JASCO Model CRM-FM) with 2 kW Xenon lamp and 3 nm bandwidth. The resulting solution was subjected to UV spectral measurement at appropriate intervals.

The quantum efficiencies were determined in a similar manner to that previously reported[4] by the relative efficiencies approximated with the following formula on the basis of ethylene dicinnamates (**1b**).

$$\Phi_{\mathrm{rel}} = (p\times\varepsilon)^{-1}$$



1—5 **11—15**

1, 11: R$_1$=R$_2$=H
2, 12: R$_1$=OCH$_3$, R$_2$=H
3, 13: R$_1$=H, R$_2$=OCH$_3$
4, 14: R$_1$=NO$_2$, R$_2$=H
5, 15: R$_1$=H, R$_2$=NO$_2$

b: n=2
c: n=3
d: n=4
e: n=5
j: n=10

Scheme 1.

Table 1. Physicochemical Properties of Polymethylene Dicinnamates

Compound	Mp θ_m/°C	IR$_{\nu_{c=0}}$	UV$\lambda_{max}(\varepsilon)$	^{1}H NMR (CDCl$_3$) δ (ppm)					Anal		
				-CH$_2$-CH$_2$-CH$_2$-	-O-CH$_2$-	C$_\alpha$-H	C$_\beta$-H	Aromatic	Found (Calcd)		
4b	154.9—156.0	1715	261 (57000)	—	4.47 (s)	6.52 (d, J=16)	7.60 (d, J=16)	7.20—8.33 (m)	C, 58.10 (58.35)	H, 4.02 (3.92)	N, 6.79 (6.81)
4c	111.5—112.9	1710	261 (60000)	1.93—2.33 (quin)	4.23—4.43 (t)	6.45 (d, J=18)	7.59 (d, J=18)	7.26—8.33 (m)	C, 59.11 (59.16)	H, 4.23 (4.25)	N, 6.55 (6.57)
4d	139.8—141.2	1705	261 (64000)	1.66—2.00 (m)	4.10—4.40 (m)	6.45 (d, J=18)	7.59 (d, J=18)	7.20—8.30 (m)	C, 59.79 (60.00)	H, 4.54 (4.58)	N, 6.31 (6.36)
4f	156.1—157.0	1708	261 (60000)	1.41—2.00 (m)	4.00—4.30 (m)	6.46 (d, J=18)	7.60 (d, J=18)	7.18—8.23 (m)	C, 61.39 (61.54)	H, 5.11 (5.13)	N, 6.01 (5.98)
4j	94.5—96.0	1710	261 (55000)	1.21—5.50 (m)	4.07—4.27 (m)	6.46 (d, J=17)	7.63 (d, J=17)	7.17—8.23 (m)	C, 63.99 (64.11)	H, 6.17 (6.15)	N, 5.41 (5.34)
5b	186.0—187.3	1715	301 (42000)	—	4.43 (s)	6.47 (d, J=18)	7.59 (d, J=18)	7.62, 8.31 (d, J=9)	C, 58.05 (58.35)	H, 4.01 (3.92)	N, 6.71 (6.81)
5c	185.5—187.5	1712	301 (44000)	1.60—2.21 (quin)	4.10—4.30 (t)	6.45 (d, J=16)	7.59 (d, J=16)	7.65, 8.12 (d, J=9)	C, 59.08 (59.16)	H, 4.31 (4.25)	N, 6.53 (6.57)
5d[3]	175.1—176.0	1710	302 (43000)	1.60—2.10 (m)	4.12—4.30 (m)	6.45 (d, J=16)	7.59 (d, J=16)	7.65, 8.12 (d, J=9)	C, 59.97 (60.00)	H, 4.54 (4.58)	N, 6.45 (6.36)
5e	118.9—120.0	1709	301 (41000)	1.45—2.00 (m)	4.10—4.30 (m)	6.45 (d, J=16)	7.59 (d, J=16)	7.65, 8.12 (d, J=9)	C, 60.52 (60.79)	H, 4.97 (4.85)	N, 6.45 (6.17)
5f	122.0—123.5	1708	303 (38000)	1.30—1.90 (m)	4.10—4.30 (m)	6.45 (d, J=16)	7.59 (d, J=16)	7.65, 8.12 (d, J=9)	C, 61.31 (61.54)	H, 5.19 (5.13)	N, 6.07 (5.98)
5j	119.0—119.3	1709	302 (38000)	1.10—1.90 (m)	4.10—4.30 (m)	6.45 (d, J=16)	7.59 (d, J=16)	7.65, 8.12 (d, J=9)	C, 63.81 (64.11)	H, 6.13 (6.15)	N, 5.53 (5.34)

Here p is the irradiated photon number for the one-half decrease in concentration of total dicinnamate, which is calculated by an integrator of the grating monochromator used in the UV-irradiation and ε is the molar absorptivity at the irradiating wavelength.

Stereochemical Analysis of Photoproducts. A nitrogen saturated acetonitrile solution containing ca. 2×10^{-5} mol of each dicinnamate derivative was irradiated on a 400 W high pressure mercury lamp (RIKO Model RH 400-10 W) through a Pyrex filter for 10—100 h until the reaction proceeded to 90%. After the solvent was removed, the ^{1}H NMR spectrum of the residue was measured and the stereochemistry of the products was determined as follows: It is known that in the ^{1}H NMR spectrum the protons of *cis*-1,2-benzene rings on cyclobutane ring are shifted upfield owing to mutual shielding.[5] In fact, the aromatic proton signals of β-truxinate produced by the photolysis of **1c** appeared up field by ca. δ 0.36 above that of **1c**. The photolysate of **1d** showed two aromatic signals shifted upfield by δ 0.36 and 0.13 compared with that of **1d** so that the latter can be attributed to δ-truxinate. Based on these facts, the structures of the photoproducts were assigned; several selected ^{1}H NMR spectral features of the aromatic region of trimethylene series are listed in Table 2. Furthermore, in the MS no intermolecular photo-adduct was detected.

Table 2. Aromatic Proton Signals of Photoproduct

Photo-product No.	β-Truxinate		δ-Truxinate	
	$\Delta\delta$	δ	$\Delta\delta$	δ
11c	−0.36,	6.70—7.12 (m)	−0.11,	7.23 (s)
12c	−0.55,	6.30—6.60 (m)	−0.24,	6.61—6.90 (m)
13c	−0.02,	6.73 (d, J=8)	+0.35,	7.10 (d, J=8)
	−0.52,	6.83 (d, J=8)	−0.04,	7.27 (d, J=8)
15c	−0.65,	7.00 (d, J=8)	−0.39,	7.26 (d, J=8)
	−0.19,	7.93 (d, J=8)	−0.02,	8.10 (d, J=8)

Molecular Orbital Calculations. The electronic structures of substituted cinnamic acids as model compounds in excited states were calculated by the CNDO/S-CI method with standard parameters.[6] The planar structure (C_s symmetry) was assumed, and standard bond lengths and bond angles were employed for the geometric parameters.[7] Two-center two-electron repulsion integrals were evaluated according to the Mataga-Nishimoto formula.[8] In the CI procedure 20 singly excited configurations below 16 eV were used.

Results and Discussion

Nitro-Substituent Effect. The progressive spectral changes of trimethylene bis(3-nitrocinnamate)s (**4c**) and trimethylene bis(4-nitrocinnamate)s (**5c**) are

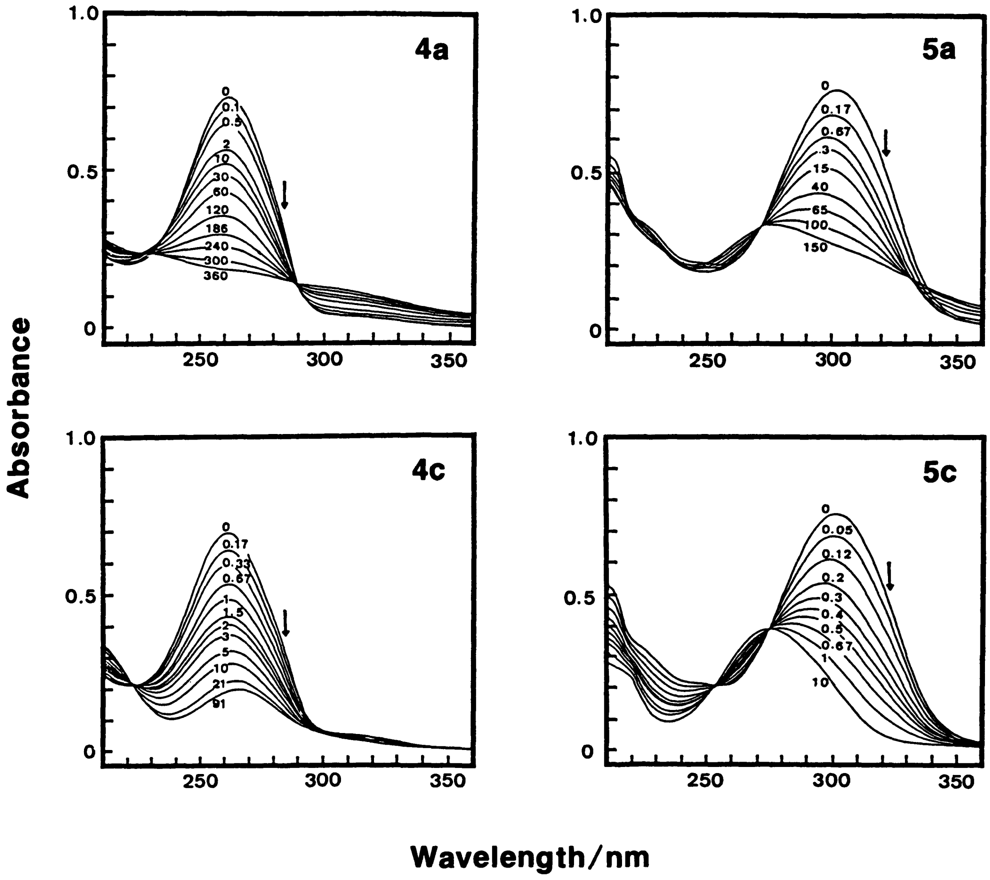


Fig. 1. Electronic spectral changes upon UV irradiation of methyl cinnamates and trimethylene dicinnamates. The arrows and numerical values in each spectrum indicate the irradiation wavelength and irradiation time (min), respectively.

shown in Fig. 1 together with those of methyl 3- and 4-nitrocinnamate (**4a** and **5a**) as unchained compound models for comparison.

It is seen from Fig. 1 that, on irradiation of methyl 3- and 4-nitrocinnamate (**4a** and **5a**), the absorption of the starting **4a** and **5a** decreased rapidly with isosbestic points at 235 and 272 nm, respectively. In the later stage of the reaction, such points disappeared or became faint. This result indicated that trans-cis photoisomerization proceeded until a photoequilibrium state was attained and then photocyclization occurred as an ensuing process in both cases. On the other hand, for trimethylene bis(3-nitrocinnamate)s (**4c**) and trimethylene bis(4-nitrocinnamate)s (**5c**), the decrease of the absorption of **4c** and **5c**, especially **5c**, was faster than that in the corresponding unchained compound **4a** and **5a**, and the isosbestic point was observed at 224 nm for **4c**, and 255 and 275 nm for **5c** throughout the reaction.

This result clearly indicated that the reaction of **4c** and **5c** involved a single photochemical process of photocyclization, and the rates of the photocyclization are far higher than those for the corresponding unchained cinnamates, due to the effect of the trimethylene chain.

The dependency of the relative quantum efficiencies for photocyclization on chain length were investigated and are shown in Fig. 2 together with those of the methoxy derivatives.

In fact, for the trimethylene compounds, the photocyclization of the 4-nitro derivative **5c** was three times as efficient as for 3-methoxy **2c** and 3-nitro **4c**. The quantum efficiencies diminished markedly with an increase or decrease in the number of methylene groups relative to those of the trimethylene compounds.

In order to compare the nature of the nitro substituent effect with that of methoxyl substituent on the photocylization, the electronic structure of the excited states of 3- and 4-nitrocinnamic acid (**4a′** and **5a′**) as model compounds were calculated by the CNDO/S-CI method. The reliability of this method for reproducing the experimental values of the lower transition energies of cinnamate derivatives has been proven in our previous paper.[4]

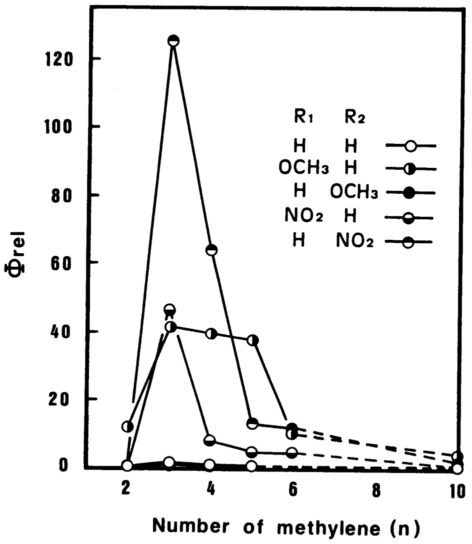


Fig. 2. Substituent effect on the photolability toward [2+2] cycloaddition on polymethylene dicinnamates.

The calculated electronic structural features for **4a′** and **5a′** were summarized in Table 3.

The correlation between the experimental absorption wavelengths of **4a** and **5a** and the calculated transition energies of **4a′** and **5a′** was examined by a least square method. In fact, the lower transition energies of nitro derivatives were also found to be well reproduced and those thus corrected were shown in Fig. 3.

In general, the reactivity of a photochemical reaction can be discussed more reasonably on the basis of the partial atomic orbital population of the singly occupied orbital (SOMO) than of the total atomic orbital population. Thus the substituent effect on the reactivity for photocyclization can be estimated on the basis of the odd electron densities

Table 3. Computed Electronic Features for Excited States of Substituted Cinnamic Acids

Substituent		State	Transition energies	Oscillator strength	Odd electron density		π Charge density				π Bond order
R_1	R_2		eV/nm		C_α	C_β	C_α	C_β	Benzene ring	Nitro group	$C_\alpha=C_\beta$
NO_2	H	S_0	—	—	—	—	1.0825	0.8810	5.9115	4.0634	0.9039
		$S_1^{n\to\pi*}$	3.9535 (314)	0.0001	0.0261	0.0522	1.0899	0.8860	6.2778	4.6814	0.8978
		$S_3^{\pi\to\pi*}$	4.0562 (306)	0.0538	0.2406	0.1029	0.8686	0.8126	5.6971	4.6015	0.7390
		$S_5^{\pi\to\pi*}$	4.8975 (253)	1.1413	—	—	1.0449	0.9197	5.5374	4.4091	0.7504
		$T_1^{\pi\to\pi*}$	2.4793 (500)	—	0.0174	0.0160	1.0987	0.8954	6.2816	3.6530	0.8871
H	NO_2	S_0	—	—	—	—	1.0556	0.8931	5.9269	4.0666	0.9049
		$S_1^{n\to\pi*}$	3.3795 (367)	0.0000	0.0966	0.0848	1.1470	0.9719	6.2573	4.5079	0.8229
		$S_3^{\pi\to\pi*}$	4.2738 (290)	0.8008	0.3093	0.1355	0.8905	0.8320	5.7442	4.4980	0.6919
		$T_1^{\pi\to\pi*}$	2.7228 (455)	—	0.2886	0.1446	0.9082	0.8577	5.7586	4.4264	0.6970

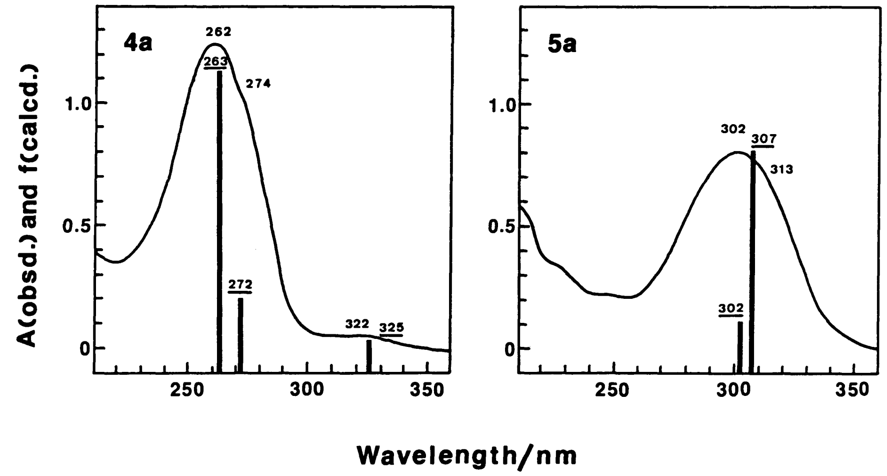


Fig. 3. Comparisons between the observed UV spectrum (solid curves) and the computed transition energy with correction (stick plot spectrum).
4a: Methyl 3-nitrocinnamate (ε=120000)
5a: Methyl 4-nitrocinnamate (ε=88000)

(Q_{odd}) of the lowest π-π* excited state (S3) calculated by the following formula, since S3 state has a large value of Q_{odd} on C_α with the large oscillator strength.

$$Q_{odd} = \sum_i \alpha c_i^2, \quad \alpha = \sum_j C_i^2$$

c_i: The coefficient of i th MO (SOMO).
C_i: The CI coefficient of i th MO (SOMO) composed of each electronic configuration in S_3 state.
j: The number of electronic configuration involved i th MO (SOMO).

The correlation between the calculated Q_{odd} of the C_α at the lowest $S^{\pi-\pi^*}$ state (S3) including those for methoxy derivatives of which detailed electronic structures were reported in a previous paper[4] and the relative quantum efficiencies (Φ_{rel}) for photocyclization of the trimethylene compounds was plotted, and is shown in Fig. 4.

It can be seen that the plots are linear demonstrating that the reactivity of the cinnamate derivatives was well correlated with the odd electron densities of the olefinic double bond at the lowest $S^{\pi-\pi^*}$ state. However, the plot of **5a** deviated considerably from the line. In the characteristics for the electronic structure of **4a′** and **5a′**, in the ground state the π-charge densities of the benzene ring are lower than that of cinnamic acid (=5.9664[4]) owing to a nitro group. In the S3 state the further decrease in the π-charge density of the benzene ring was shown at the expense of the greater increase in that of the nitro group. These electronic features were considerably greater than those of the methoxy derivatives. This characteristic may cause electronic repulsion between the aromatic moiety in the excited state and that in the ground state. This repulsion would effect the transition state of the photocyclization reducing the exciplex formation. We believe this is one of the major reasons for the large deviation of 4-nitro derivatives shown in Fig. 4.

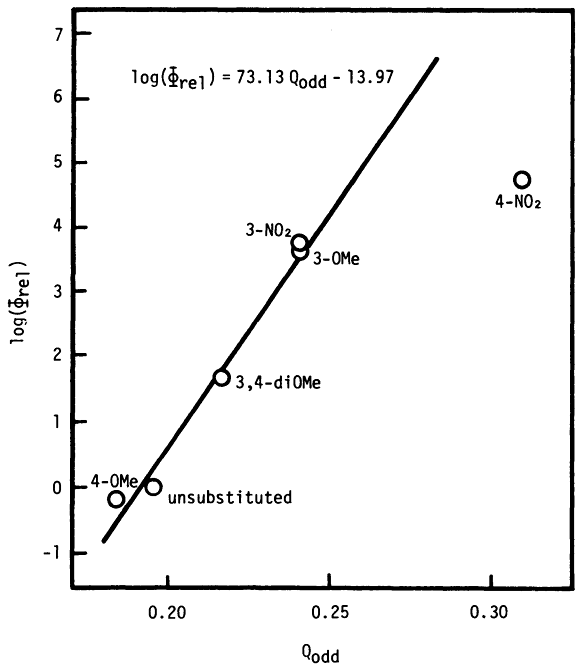


Fig. 4. Relationship between the calculated odd electron densities (Q_{odd}) of the C_α at the lowest $S^{\pi-\pi^*}$ state and the relative quantum efficiencies (Φ_{rel}) for photocyclization.

Stereochemistry of Photoproduct. The dependence of the stereochemistry of the photoproduct on the 4-nitro substituent and the number of methylene groups are shown in Fig. 5 together with those of other derivatives **1**—**3**.

As a general feature of Fig. 5, β-truxinate was exclusively formed for n=2, because of a difficulty in the production of δ-truxinate due to the geometrical

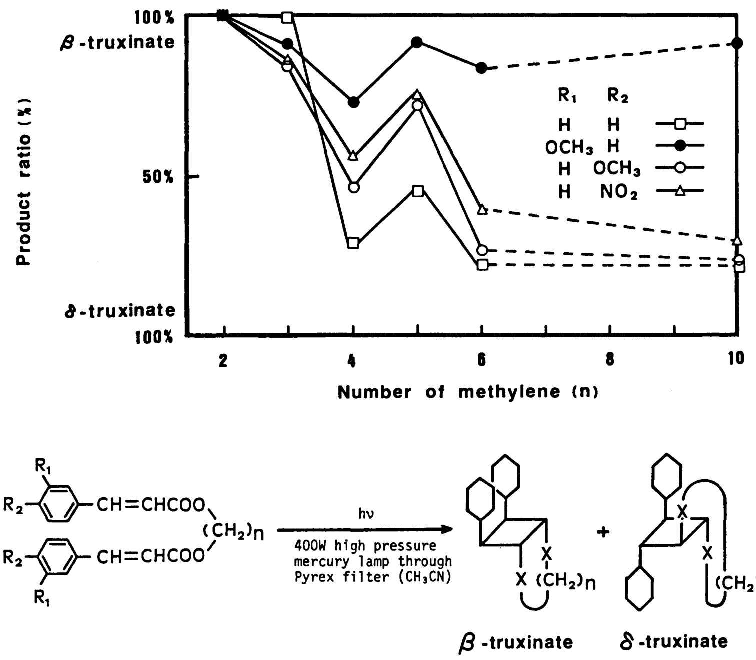


Fig. 5. Dependence of the stereochemistry of photoproduct upon alkane chain length and substituent.

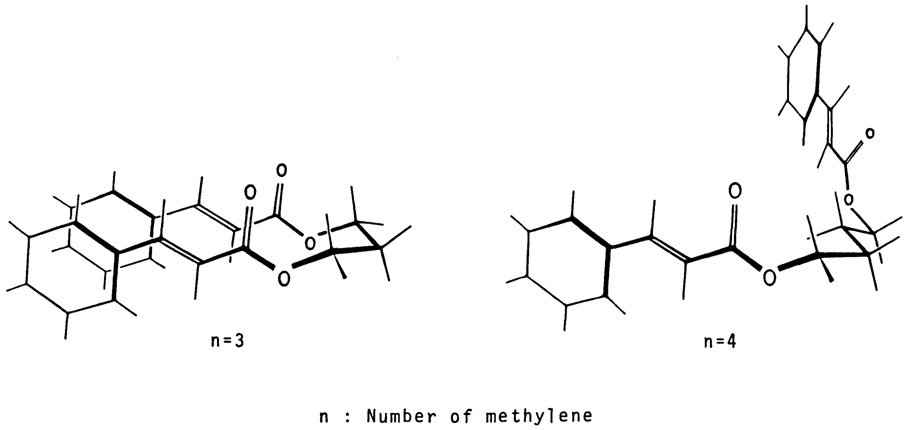


Fig. 6. The odd-even alternating effects of polymethylene chain on parallel arrangement of two cinnamoyl groups (Alkane chains are assumed to take an extended trans form).

restriction of ethylenic moiety. This tendency was shown also for n=3 and δ-truxinate was the main product. However, it was shown that the ratio of δ-truxinate in the total photoproduct markedly decreased for n=4 and that such a ratio increased again for n=5. These results indicated that the stereochemical course of the photoproduct are strongly depended on the odd or even number of the polymethylene chain. The most plausible geometrical situations of polymethylene dicinnamates are illustrated in Fig. 6 for n=3 and n=4 as representative examples.

Thus, an odd-even alternating effect of the methylene chain can be interpreted in terms of the vast difference in the geometric alignment between the two cinnamoyl moieties.[9,10] Another noteworthy feature in Fig. 5 is that only for 3-methoxy derivatives, was β-truxinate the main photoproduct irrespective of the number of methylene groups, unlike the case of the other derivatives.

From the above experimental results, it can be concluded that the high photocyclization efficiency of the trimethylene bis(4-nitrocinnamate)s (**5c**) is due to the high odd electron density in the olefinic moiety and the greater decrease of the efficiency and the less stereospecificity for the formation of β-truxinate product is due to the low efficiency for exciplex formation.

Conclusion

Pseudo-dimerization of the two cinnamoyl moieties of polymethylene dicinnamates proceeds through both singlet and triplet pathways, but predominantly through the singlet pathway. The singlet pathway consists of two steps, i.e. the formation of an exciplex and its subsequent pseudo-dimerization. The topotactic assistance by the polymethylene chain mainly affects the formation of the exciplex and concomitantly the stereochemistry of the photocyclization; for $n=3$ the two cinnamoyl groups can assume the most preferable alignment for the formation of the exciplex resulting in the highest reactivity.[4,9] On the other hand, substituent perturbation could affect both steps. That is, the π-charge density of the benzene moiety and the odd electron density in the olefinic moiety affects the formation of the exciplex and the photodimerization, respectively. Thus, the observed rate enhancement of the pseudo-dimerization of 3-methoxy derivative can be concluded to be assisted by facile exciplex formation; accordingly the high stereoselectivity of the photoproducts was observed. That of the 4-nitro derivative can be ascribed to the high odd electron density of the olefinic double bond, not to the formation of the exciplex, demonstrated by the less stereoselectivity of the photoproduct of the derivatives linked with a longer polymethylene chain.

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