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A Sudden-polarization Model to Predict Excited State Reactivity of *β*-*t*-Butylstyrene

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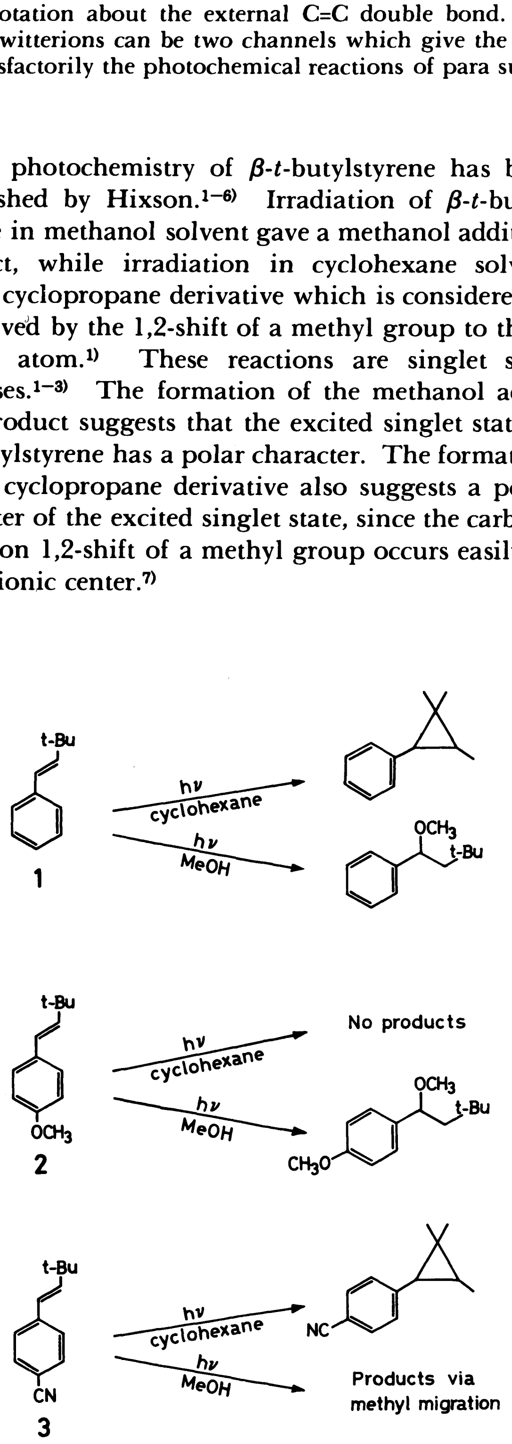
A model in which two zwitterions play a significant role was employed to account for solvent and substituent effects on photochemical reactions of *β*-*t*-butylstyrene. These zwitterions are formed by 90° rotation about the external C=C double bond. Semi-empirical MINDO/3 calculations showed that these zwitterions can be two channels which give the observed reacation products. The model also elucidated satisfactorily the photochemical reactions of para substituted *β*-*t*-butylstyrenes.

The photochemistry of *β*-*t*-butylstyrene has been established by Hixson.[1–6] Irradiation of *β*-*t*-butylstyrene in methanol solvent gave a methanol addition product, while irradiation in cyclohexane solvent gave a cyclopropane derivative which is considered to be derived by the 1,2-shift of a methyl group to the *β* carbon atom.[1] These reactions are singlet state processes.[1–3] The formation of the methanol addition product suggests that the excited singlet state of *β*-*t*-butylstyrene has a polar character. The formation of the cyclopropane derivative also suggests a polar character of the excited singlet state, since the carbon-to-carbon 1,2-shift of a methyl group occurs easily to the cationic center.[7]



Scheme 1.

From the pairing theorem of the Hückel MO framework, the electron population of the HOMO→LUMO excited state of an even-alternant hydrocarbon is identical with that of the ground state, and the polarization of the excited singlet state of the hydrocarbon should not be large, even if a more sophisticated MO theory is applied to it. Thus the photochemical reaction of *β*-*t*-butylstyrene, which indicates the ionic character of the excited states, is very interesting from a mechanistic point of view.

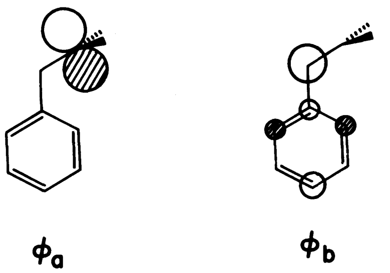
The zwitterions, which have negative and positive charges separately, are formed by a rotation about the C–C double bond of an olefin.[8] This is "sudden-polarization" appeared in the 90 °-twisted olefin. The sudden-polarization model is capable of elucidating the ionic character observed in the excited states of non-polar species. Some photochemical reactions have been well elucidated on the basis of this model.[9,10] In this paper we use the sudden-polarization model to explain the excited state reactivities of *β*-*t*-butylstyrene and its derivatives.

The closed-shell and open-shell SCF methods as well as two-configuration SCF method were employed for the calculation of the 90°-twisted structure within the semi-empirical MINDO/3 approximation.[11] The MINDO/3 CI method was used for the potential energy curves calculation along the rotation about the double bond of styrene.

Results and Discussion

Twisted Styrene. The $\pi \rightarrow \pi^*$ singlet state of an olefin is stabilized by a double-bond rotation which gives the 90°-twisted structure. The potential energy curves along this rotation of styrene were calculated by means of MINDO/3 CI which involves 50 and 48 configuration functions for the singlet and triplet states, respectively. Three lower singlet states and the lowest triplet state are shown in Fig. 1.

The 90°-twisted styrene has two non-bonding type MO's: one is the in-plane MO localized on the terminal carbon atom, ϕ_a, and the other is a π MO of the benzyl group, ϕ_b. The lowest singlet state of the 90°-twisted styrene is the ^1D diradical state in which each non-



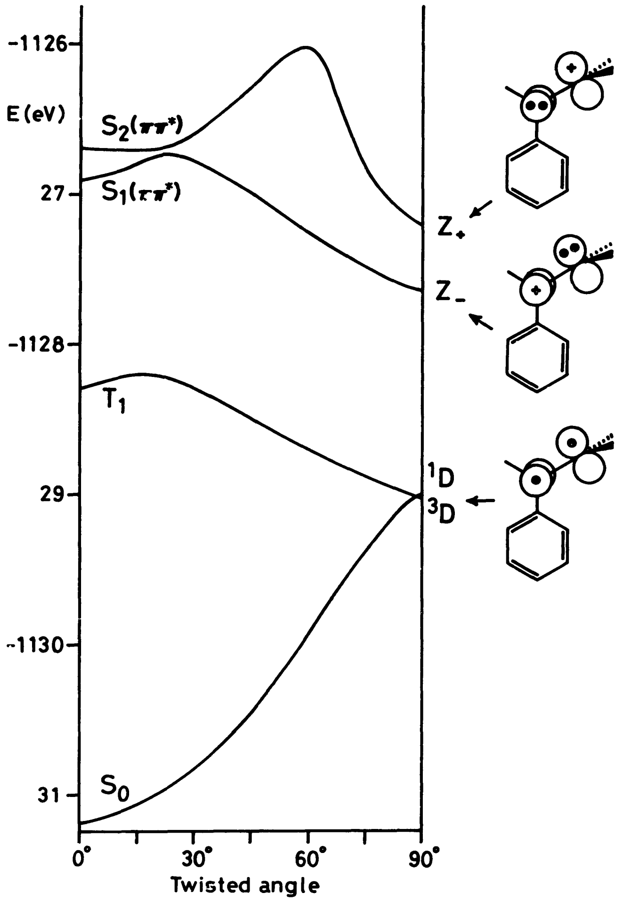


Fig. 1. Potential energy curves of styrene along the rotation about the double bond.
The structures employed were obtained by twisting the optimized ground state geometry. Three lower singlet and lowest triplet states are shown.

bonding MO is occupied by an unpaired electron. The lower excited singlet states involve the Z_- and Z_+ zwitterionic states, in which a pair of electrons occupy the ϕ_a orbital (Z_-) or ϕ_b orbital (Z_+). The electron occupations of these states are shown in Fig. 1.

As may be seen from Fig. 1, the Z_- state is lower in energy than the Z_+ state if the ground-state-twisted structure is considered. However, Bruckmann and Salem[12] pointed out that if the optimized structures corresponding to the Z_- and Z_+ zwitterions are sufficiently different from each other, both of the Z_- and Z_+ zwitterions should lie on the same lowest excited singlet energy surface at their optimized structures. This concept may rationalize the reaction processes of Scheme 1; the methanol addition product is derived from the Z_- zwitterion, while the cyclic isomerization product is from the Z_+ zwitterion *via* the 1,2-shift of a methyl group.

The electronic structure of the 90°-twisted styrene can be expressed in terms of three configurations:[13]

$$|a^2\rangle = |\cdots\phi_a\bar{\phi}_a|$$

$$|b^2\rangle = |\cdots\phi_b\bar{\phi}_b|$$

$$|ab\rangle = \frac{1}{\sqrt{2}}\{|\cdots\phi_a\bar{\phi}_b| + |\cdots\phi_b\bar{\phi}_a|\}$$

The nearly degenerate orbitals of the 90°-twisted styrene, ϕ_a and ϕ_b, belong to different irreducible representations of the molecular symmetry group. The diradical ^1D state is thus expressed by the open-shell wavefunction, $|ab\rangle$, while the zwitterionic states are expressed by two-configuration wavefunctions:

$$\begin{aligned} \Psi(Z_-) &= \lambda|a^2\rangle - \sqrt{1-\lambda^2}|b^2\rangle \\ \Psi(Z_+) &= \sqrt{1-\lambda^2}|a^2\rangle + \lambda|b^2\rangle \end{aligned} \qquad (\lambda \geqq 1/\sqrt{2})$$

For the 90°-twisted styrene, the mixing of $|a^2\rangle$and $|b^2\rangle$ is expected to be very small, since ϕ_a and ϕ_b have different symmetries and the value of $\langle a^2|H|b^2\rangle$ is small.[14] Thus the zwitterionic states of the 90°-twisted styrene were calculated by the closed-shell SCF method, while the diradical state was calculated by the open-shell SCF method. The optimized structures of these states are shown in Fig. 2. The unpaired electron density of the ^1D state and the charge distributions of the Z_- and Z_+ states are shown in Fig. 3.

In order to understand the potential energy surface of the lowest excited singlet state of the 90°-twisted styrene, the energies of the diradical and zwitterionic states were calculated for three structures, II, III, and the ground-state twisted structure. The qualitative shapes of energy surfaces along the structural change among these three structures were obtained by simple interpolation (Fig. 4). The lowest excited singlet state has two energy minima corresponding to different polarizations, Z_- at the structure II and Z_+ at the structure III. The energy difference between these two minima was calculated to be small (22 kJ mol^{-1}).

Twisted β-t-Butylstyrene. Calculations on the 90°-twisted styrene showed two ionic channels on the energy surface of the lowest excited singlet state. This indicates two distinct photochemical pathways of styrene in which two zwitterions act as intermediates.[12]

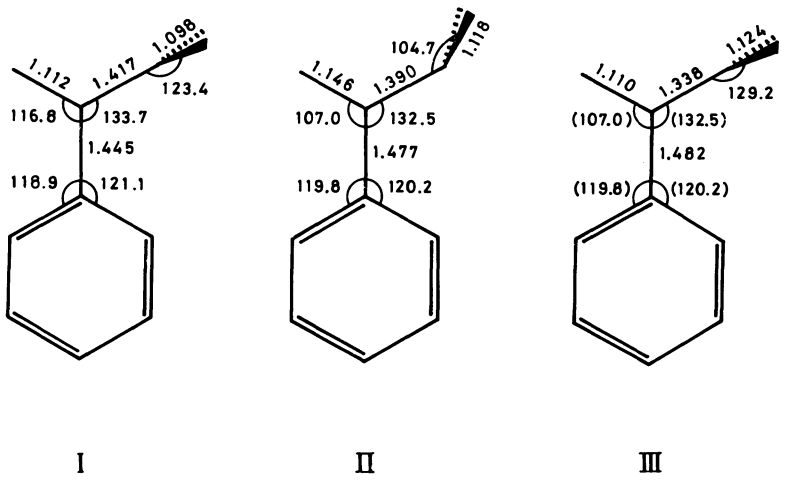


Fig. 2. Optimized structures of the 90°-twisted styrene.
I: Diradical structure, II: Z_- zwitterionic structure, III: Z_+ zwitterionic structure.
In the optimization of III the variables in parentheses were fixed.

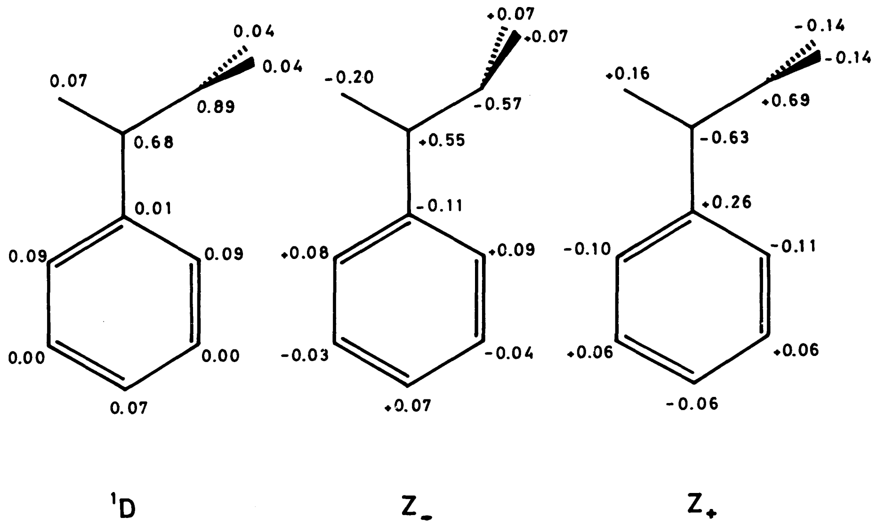
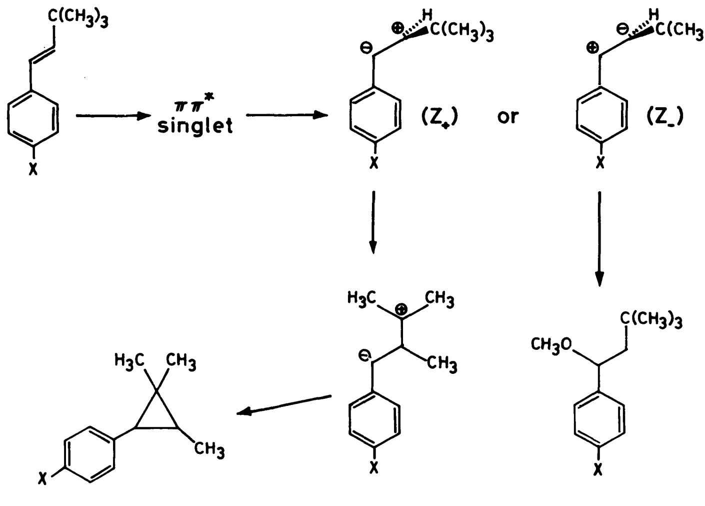


Fig. 3. Unpaired electron densities for the ^{1}D state and charge densities of the zwitterionic states.



Scheme 2.

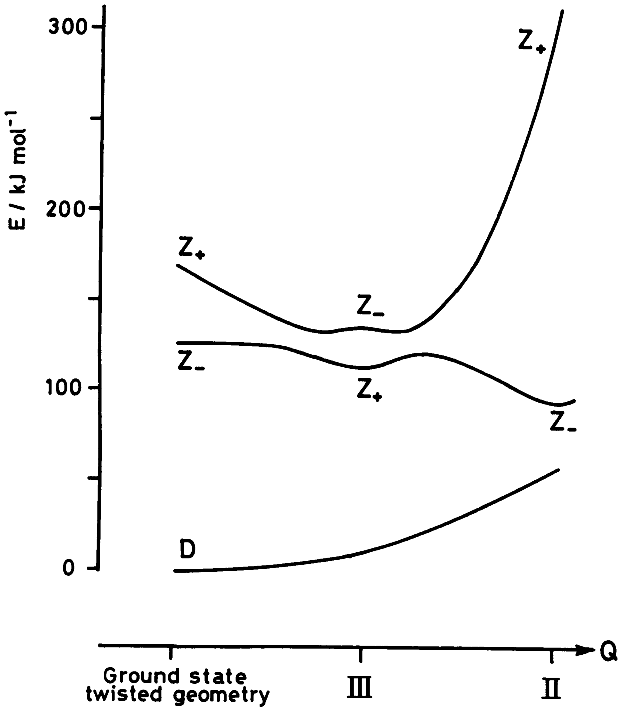
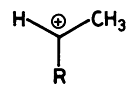


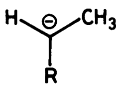
Fig. 4. Qualitative potential energy curves for the lowest singlet states of 90°-twisted styrene.
The coordinate Q indicates the structure of 90°-twisted styrene and is obtained by linear interpolation from the ground-state twisted structure to III, and from III to II; the structures II and III are shown in Fig. 2 and the ground-state twisted structure is obtained by 90° twisting of the ground state structure. The energies of the ^{1}D, Z$_-$, and Z$_+$ states were calculated for only these three structures and the energy curves were estimated by simple interpolation.

The photochemical reaction of β-*t*-butylstyrene can well be explained according to this concept (Scheme 2). The Z$_+$ zwitterion undergoes 1,2-methyl migration to the positive β carbon atom. This migration occurs very fast and is followed by cyclization to give the cyclopropane derivatives. In the Z$_-$ zwitterion, the methyl migration to the β carbon atom which has negative charge does not occur. The methanol addition product at the α carbon atom is obtained from the Z$_-$ zwitterionic state.

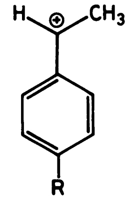
For the twisted styrene, the Z$_-$ state is more stable than the Z$_+$ one. In the case of β-*t*-butylstyrene, the Z$_+$ state may be stabilized by a *t*-butyl group. In order to estimate the relative stabilities of the Z$_-$ and Z$_+$ states of the 90°-twisted β-*t*-butylstyrene and its derivatives, the energies of ions **4**—**7** were calculated for their optimized geometries (Table 1). The change in the relative energy of the Z$_-$ and Z$_+$ states caused by the substitution of a *t*-butyl group at the β position was calculated by:



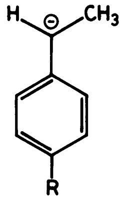
4a, R=H
b, R=C(CH$_3$)$_3$



5a, R=H
b, R=C(CH$_3$)$_3$



6a, R=H
b, R=CN
c, R=OCH$_3$



7a, R=H
b, R=CN
c, R=OCH$_3$

$$\{E(\mathbf{4a})-E(\mathbf{4b})\}-\{E(\mathbf{5a})-E(\mathbf{5b})\} = 37\ \mathrm{kJ\,mol^{-1}}$$

This indicates that a *t*-butyl group at the β position stabilizes the Z$_+$ state by 37 kJ mol^{-1} in comparison with the Z$_-$ state. Since the Z$_+$ state of the unsubstituted styrene is 22 kJ mol^{-1} less stable than the Z$_-$ state, the Z$_+$ state of the 90°-twisted β-*t*-butylstyrene is expected to be 15 kJ mol^{-1} more stable than the Z$_-$ state. This energy difference is small and both of the Z$_+$ and Z$_-$ states of 90°-twisted β-*t*-butylstyrene can be the channels from which the methanol addition product and the cyclopropane derivative are formed. This agrees well with the dual pathways observed in the photochemical reaction of β-*t*-butylstyrene.[1]

The energy differences between the Z$_+$ and Z$_-$ states of the *p*-OCH$_3$ and *p*-CN derivatives were estimated similarly. The results are shown in Table 2. The electron-withdrawing group (CN) at the para position stabilizes the Z$_+$ state, and the energy difference between the Z$_+$ and Z$_-$ states of 90°-twisted *p*-cyano-β-*t*-butylstyrene, 54 kJ mol^{-1}, is larger than that of β-*t*-butylstyrene. This indicates that in the photochemical reaction of *p*-cyano-β-*t*-butylstyrene, the Z$_+$ state may be the only channel from which the reaction product is

Table 1. MINDO/3 Energies of ions **4**—**7**

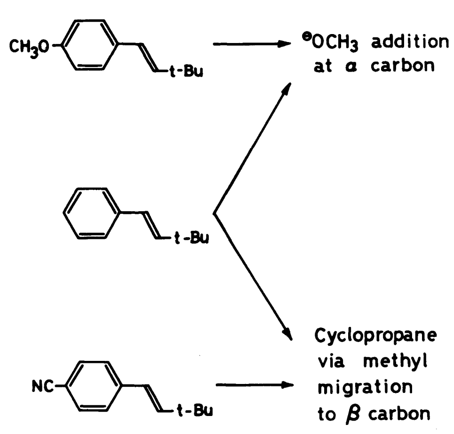
Ion	Energy/eV[a]
4a	−318.272
4b	−944.548
5a	−326.057
5b	−951.952
6a	−1138.774
6b	−1442.322
6c	−1607.232
7a	−1146.283
7b	−1450.229
7c	−1614.233

a) All the geometries except the benzene ring were optimized.

Table 2. Relative energies (kJ mol^{-1}) of two zwitterions of twisted β-*t*-butylstyrenes

β-*t*-Butylstyrene	Z_-	Z_+
1	0	−15
2	0	+34
3	0	−54

formed. The Z_+ state will give the cyclopropane derivative, which agrees well with experiment.1) In the case of *p*-methoxy-β-*t*-butylstyrene, the Z_- state was calculated to be 34 kJ/mol more stable than the Z_+ state, indicating that the photochemical reaction *via* the excited singlet state of *p*-methoxy-β-*t*-butylstyrene gives the methanol addition product from the Z_- zwitterion. This also agrees well with experiment.1)



The photochemical reactions of β-*t*-butylstyrene and its derivatives were satisfactorily elucidated on the basis of the sudden-polarization model which involves the 90°-twisted structure. Existence of the twisted structure of β-*t*-butylstyrene was supported indirectly by experiment.2) The trans and cis forms of *p*-cyano-β-*t*-butylstyrene gave the same primary reaction product, indicating a common intermediate of the 90°-twisted structure.2) Another fact which may support the twisted structure of styrene is the formation of carbene intermediates2,7) in the photochemical reactions of styrene derivatives, since carbenes would be expected to be derived easily from the 90°-twisted structure of olefins.15) It has been shown here that the present modeling is useful to understand the photochemical reactions which appear to involve polar species.

The present results indicate that the excited-state reactivity of olefins can well be described by the MINDO/3 approximation if the correct configuration functions are employed. The energy diagram along the 1,2-hydrogen shift of the 90°-twisted ethylene has been obtained by *ab initio* 4-31G calculation.15) For this reaction, the similar diagram was obtained when the MINDO/3 CI calculation was carried out. Also, the small CI calculation with the MINDO/3 approximation reproduced well the observed excitation energies of *s-trans*-butadiene and *s-trans*-acrylaldehyde.16) Thus we feel the MINDO/3 method can be employed for the qualitative analysis of the excited state reactivity, although its parameters were determined so as to reproduce the ground state properties of organic molecules.

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