May, 1994] © *1994 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *67*, *1405—1411(1994)* 1405

The Polarized Absorption Spectrum of 1,3-Diphenyl-1,2-propadiene: Interaction between Mutually Perpendicular Equivalent π-Electronic Systems

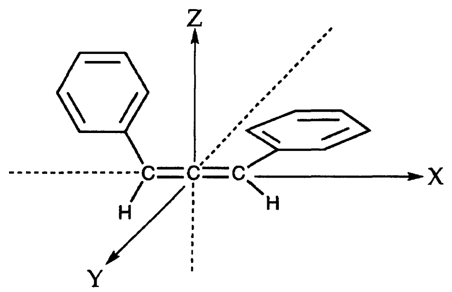
Jun Okubo,* Takayasu Shimazaki, Shin-ichi Sato, and Hiraku Shinozaki
Department of Natural Science for General Education, Faculty of Engineering, Tokyo Denki University,
Inzaimachi, Inba-gun, Chiba 270-13

(Received November 22, 1993)

The polarized UV absorption spectrum of 1,3-diphenyl-1,2-propadiene (DPA) was measured in a stretched polymer film at 101 K, and the polarization directions of the electronic absorption bands were determined. Pariser–Parr–Pople (PPP) calculations extended to three dimensions were performed, and the position, intensity, and polarization of each absorption band of DPA were obtained from the calculations. The observed 289.8 and 265.2 nm bands polarized along the longer molecular axis were assigned to the calculated $S_1 \leftarrow S_0$ and $S_3 \leftarrow S_0$ transitions, respectively, and the 237.1 nm band along the shorter molecular axis was assigned to the $S_4 \leftarrow S_0$ transition. The results of configuration analysis indicate that the second transitions (at 260.5 nm) of two styrenes, whose π-electronic systems are perpendicular to each other, contribute equally to the third and fourth transitions observed at 265.2 and 237.1 nm of DPA. In addition, it was clarified that the first absorption band of DPA corresponding to Parity's forbidden transition was intensified by an increase of the ionization energy of the *sp* hybridized carbon atom in the allenic moiety.

An allenic group has two π-electronic systems which are perpendicular to each other. A molecule of 1,3-diphenyl-1,2-propadiene (1,3-diphenylallene, abbreviated to DPA) has two styrene π-electron systems, and belongs to the D_{2d} point group (Chart 1).[1,2] The physicochemical properties have been studied in detail from the point of view of the unique stereostructure and reactivities of allene derivatives.[3—7] Runge et al. studied the electronic- and stereo-structures of phenylallenes and related compounds such as styrene and phenylacetylene by means of UV, He I photoelectron and ^{13}C NMR spectroscopic methods, together with MO calculations.[5] According to their studies, the twist angle of the phenyl ring in 3-phenyl-1,2-butadiene is estimated to be 20°, and the UV absorption spectrum of phenylallene shows four bands at 289, 254, 228, and 212.8 nm in isooctane. So far, there have been several investigations on the electronic structures and conformations of allene derivatives,[3—7] however, little is known about the nature and the polarizations of the absorption bands of DPA itself.

In the present investigation, the polarized absorption spectrum of DPA was measured in a stretched poly(vinyl alcohol) (PVA) film at 101 K. From the results of the spectral data together with improved PPP calculations extended to three dimensions, in which intramolecular orbital interactions between two perpendicular π-systems were taken into account, the origin of each electronic absorption band of DPA has been identified. In addition, the mechanism of an intramolecular orbital interaction between the perpendicular π-systems in DPA is discussed.



1,3-Diphenyl-1,2-propadiene (Diphenylallene (DPA))

Chart 1.

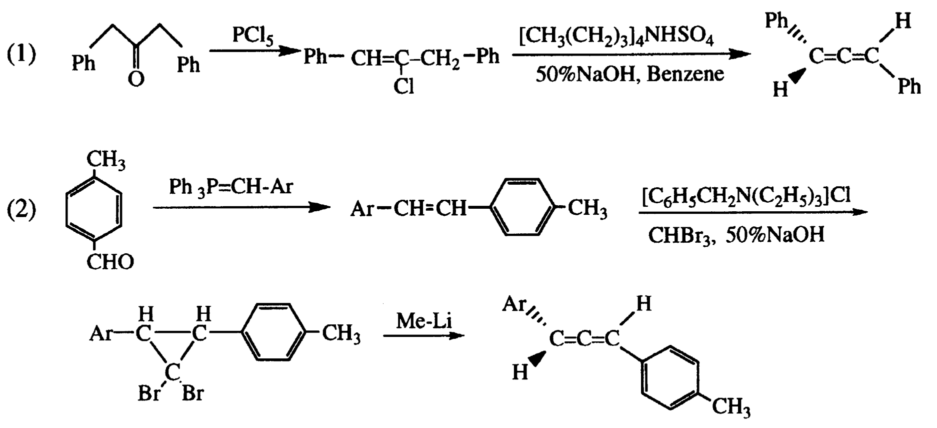
Experimental

Materials. The syntheses of 1,3-diphenyl-1,2-propadiene (DPA), 1-phenyl-3-(*p*-tolyl)-1,2-propadiene (PTA), and 1,3-di-*p*-tolyl-1,2-propadiene (DTA) are summarized in Scheme 1. PTA and DTA were prepared by a modification of the literature procedures.[8]

1,3-Diphenyl-1,2-propadiene (DPA).[4] Dibenzyl ketone was converted into 2-chloro-1,3-diphenylpropene (48%, bp 138—143 °C/2 mmHg) (1 mmHg=133.322 Pa).[9] A mixture of 2-chloro-1,3-diphenylpropene (10 mmol), tetrabutylammonium hydrogensulfate (1.2 mmol), 50% NaOH (4 ml), and benzene (6 ml) was stirred at room temperature for 3 h, then washed with water and saturated aqueous NH_4Cl. The organic extract was dried over anhydrous Na_2SO_4 and the residue was chromatographed on silica gel with hexane to give crude solids that were further purified by recrystallization from hexane at 5 °C to give DPA as colorless crystals (20%): Mp 48—51 °C; ^{1}H NMR ($CDCl_3$) δ=6.59 (s, 2H, CH) and 7.25—7.32 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$) δ=98.43, 126.98, 127.28, 128.72, 133.62, and 207.77; IR (KBr) 1930 cm^{-1} (C=C=C); MS *m/z* 192 (M^+).

1-Phenyl-3-(*p*-tolyl)-1,2-propadiene (PTA). PTA was obtained in a yield of 72.7% from dibromocyclopropane as an unstable colorless oil: ^{1}H NMR ($CDCl_3$) δ=2.32 (s, 3H, CH_3), 6.54 (s, 2H, CH), and 7.05—7.36 (m, 9H, ArH); ^{13}C NMR ($CDCl_3$) δ=21.22, 98.24, 98.32, 126.90, 126.96, 127.20, 128.69, 129.45, 130.59, 133.81, 137.14, and 207.52.

1,3-Di-*p*-tolyl-1,2-propadiene (DTA).[10] DTA was obtained in a yield of 73.5% from dibromocyclopropane as



Ar = C_6H_5; 1-Phenyl-3-(*p*-tolyl)-1,2-propadiene (PTA)

= 4-CH_3-C_6H_4; 1,3-Di-(*p*-tolyl)-1,2-propadiene (DTA)

Scheme 1.

colorless crystals recrystalized from hexane at 5 °C: Mp 76—77 °C; ^{1}H NMR ($CDCl_3$) δ=2.33 (s, 6H, CH_3), 6.54 (s, 2H, CH), 7.10 (d, J=8.3 Hz, 4H), and 7.25 (d, J=8.3 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ=21.17, 98.01, 126.85, 129.40, 130.75, 137.01, and 207.58; IR (KBr) 1935 cm^{-1} (C=C=C).

Commercially available poly(vinyl alcohol) (PVA) (Koso Chemical Co., Ltd., polymerization degree=1400) and ethanol (Wako Pure Chemical Co., Ltd.) were used without purification. The stretched PVA film including sample molecules was prepared as described previously by Hoshi et al.[11,12] Styrene was obtained from Kanto Chemical Co., Ltd., and was purified by distillation under reduced pressure before use.

Measurements. The UV absorption spectra, in solution, were recorded on a Hitachi UV-3210 spectrophotometer. The polarized absorption spectrum at low temperature was recorded on a Shimadzu UV-360 type spectrophotometer equipped with a Rochon-type polarizer and an N_2 cryostat.

MO Calculations. Molecular orbital calculations were carried out by the PPP method extended to three dimensions, in which interactions between two perpendicular π-orbitals were taken into account through electron repulsion terms in both matrix elements of Fock and configuration interactions (CI).[13,14] In these calculations, the valence state ionization energy (Ip(C)) and electron affinity (Ea(C)) of the carbon atoms used were $Ip(\mathrm{C})=11.22$ and $Ea(\mathrm{C})=0.62$ eV, respectively. The resonance integrals (β_{cc}) between the carbon atoms were computed by means of the variable β approximation of Nishimoto–Forster,[15] and all differential overlap integrals were conventionally neglected. All singly excited 64 configurations were taken into account in the CI calculation.

Results and Discussion

The Solution and Polarized Absorption Spectra of DPA. Studies on the UV absorption spectra of some phenylallenes have been carried out by Runge et al.[5] They reported that phenylallene shows four absorption bands in the ultraviolet wavelength region, and the 0–0 band positions are at 34600, 39300 (band maximum), 43800, and 47000 cm^{-1} in isooctane. However, the nature of these electronic transitions was not clarified, and the electronic natures of other phenylallenes were not reported in detail. It seems that, thus far, there is little information concerning the electronic absorption spectrum and structure of DPA itself.

The absorption spectrum of DPA measured in ethanol is shown in Fig. 1a. This compound shows three peaks at 289.0, 255.4, and 206.8 nm, and shoulders around 280, 262, 236, 228, and 215 nm. For comparison, the absorption spectrum of styrene measured under the same conditions is shown in Fig. 1b. Both spectra are very similar to each other, but the main absorption band of DPA at 255.4 nm is red-shifted, and the first band of DPA at 289 nm is slightly blue-shifted and strengthened, compared with those of styrene. Furthermore, in the spectrum of DPA additional bands exist around 236 nm, which are not found in the styrene spectrum. Since the π-electronic system of styrene is equivalent to one half of the π-electronic systems of DPA, if the two π-systems in DPA do not interact with each other, the spectral shape of DPA would be the same as that of styrene, and the molar absorptivity for styrene would be half that of DPA. However, it is obvious that there are some differences in both spectra (Figs. 1a and 1b). This may indicate that the two perpendicular π-systems of DPA interact with each other.

In order to determine the polarizations of the absorption bands of DPA, the polarized absorption spectrum was measured by means of the stretched polymer film technique. Figure 2 shows the spectrum in the stretched PVA film at 101 K. In this figure, $D_{/\!/}$ and $D_{\perp}$ denote absorbances measured with polarized light beams whose electric vectors are respectively parallel and perpendicular to the stretching direction of the PVA film. R_d is the ratio of $D_{/\!/}$ and $D_{\perp}$ ($D_{/\!/}/D_{\perp}$). R_s is a stretching ratio. Generally, a molecule included in a polymer

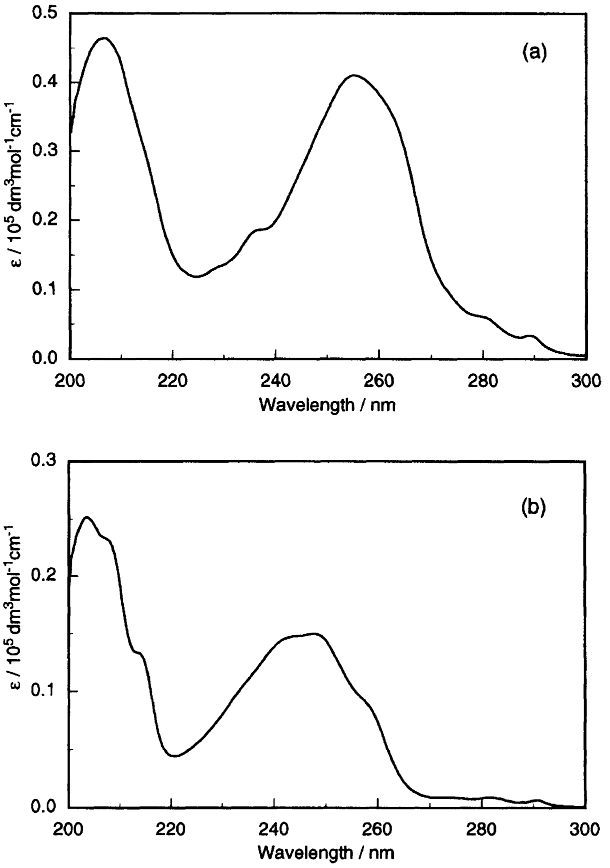


Fig. 1. The absorption spectra of 1,3-diphenyl-1,2-propadiene (a) and styrene (b) in ethanol.

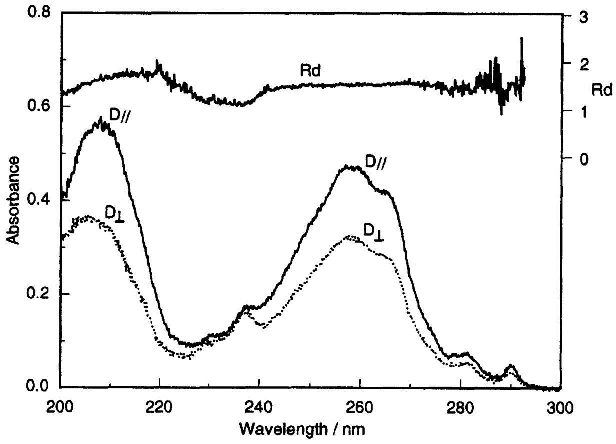


Fig. 2. The polarized absorption spectrum of 1,3-diphenyl-1,2-propadiene (DPA) in the stretched PVA film at 101 K. $R_s=5.2$.

film is preferentially oriented with the longer molecular axis along the stretched direction. Consequently, when the direction of the transition moment is along the long molecular axis, the R_d value becomes higher, and when the direction is along the shorter axis, the R_d value becomes lower.

The 0–0 band of the first absorption band system appears at 289.8 nm, accompanying the peak at 281.5 nm on the higher energy side. Since R_d curves corresponding to these bands are relatively high, it is clear that both are polarized along the longer molecular axis. The origin of the 281.5 nm bands, at present, is not clear, and will be discussed later from the comparison of the results of the MO calculations and the absorption spectra of tolylallenes. The main absorption band, whose 0–0 band may be at 265.2 nm, has a high R_d value, and the R_d curve is flat. This suggests that only a single band with a transition moment along the longer molecular axis exists in the wavelength region 240—270 nm. Weak bands appear at 237.1 and 229.6 nm, and the corresponding R_d values are lower than those of neighboring bands. These bands are, therefore, polarized along the shorter molecular axis, and the 229.6 nm band is considered to be a vibronic band of the 237.1 nm band. The behavior of the spectrum in the region 200—220 nm is somewhat complicated, i.e., the peak positions in the $D_{//}$ and $D_{\perp}$ curves deviate slightly, the band peaks are located at 208 and 204 nm, and the R_d curve is lowered towards the higher energy side of the wavelength. That is, these 208 and 204 nm bands are polarized along the longer and shorter molecular axes, respectively. In addition, since the R_d curve shows a maximum at 219 nm, a very weak band with long axis polarization might be hidden in this region.

Assignment of the Electronic Bands. In the PPP calculations, the two phenyl rings in DPA are assumed to be perpendicular to each other. The observed and calculated results are summarized in Table 1. It is clear from transition energy, intensity, and polarization data, that the long-axis polarized main band at 265.2 nm can be assigned to the calculated $S_3 \leftarrow S_0$ transition, and the shorter polarized 237.1 nm band to the $S_4 \leftarrow S_0$ transition. From the assignment process mentioned above, it seems reasonable to suggest that the long-axis polarized 208 nm and the short-axis polarized 204 nm bands correspond to the $S_7 \leftarrow S_0$ and $S_8 \leftarrow S_0$ transitions, respectively. In addition, the 219 nm band, which is represented by the presence of a peak in the R_d curve, should probably be assigned to the $S_5 \leftarrow S_0$ transition. The band corresponding to the calculated $S_6 \leftarrow S_0$ transition was not observed in this experiment.

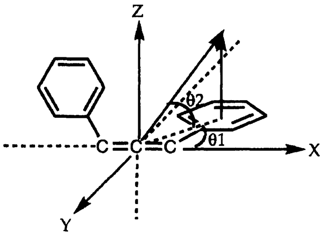
As for the origin of the weak 289.8 and 281.5 nm bands along the long molecular axis, two interpretations are possible. Firstly, the 289.8 nm band is derived from a different kind of electronic transition to the 281.5 nm band, and the 289.8 and 281.5 nm bands are assigned to the calculated $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions respectively, which may be split by an anisotropic perturbation force such as a dipole of the solvent and/or the Yahn–Teller effect.[2)] Alternatively, the 281.5 nm band is a vibronic structure of the 289.8 nm band, and the latter band corresponds to the $S_1 \leftarrow S_0$ transition.

If the first interpretation is the case, then the splitting width between the two bands would be changed by an unsymmetrical perturbation of the π-electronic

Table 1. Comparison of the Calculated and Observed Data of Transition Energy, Intensity, and Polarization of 1,3-Diphenylallene

	Transition energy/nm		Intensity		Polarization		
	Calcd	Obsd[a]	Calcd	Obsd[b]	$\theta 1$ Calcd[c]	$\theta 2$ Calcd[d]	Obsd[e]
S_1	292.7	289.8	Forbidden	3390			L
S_2	292.7		Forbidden				
S_3	269.6	265.2	0.9689	41100	24.5°	67.5°	L
S_4	253.3	237.1	0.2806	18600	90.0°	−45.0°	S
S_5	214.1	219	0.4713	≈15000	−34.9°	−60.2°	L
S_6	213.5		0.2356		90.0°	−45.0°	
S_7	208.9	208	1.2007	≈46000	8.3°	81.8°	L
S_8	205.3	204	0.2306		90.0°	−45.0°	S
S_9	202.1		Forbidden				
S_{10}	202.1		Forbidden				

a) Measured in the PVA film. b) Molar absorptivity in ethanol/dm^3 mol^{-1} cm^{-1}.
c) The angle with respect to the X axis. d) The angle with respect to the XY plane.
e) L and S indicate long and short axes of the molecule, respectively.



systems of DPA. To confirm this hypothesis, 1-phenyl-3-(*p*-tolyl)-1,2-propadiene (PTA) was synthesized. The π-electronic system of PTA is isoelectronic with that of DPA and is unsymmetrically perturbed by the addition of a methyl group to one phenyl ring of DPA. The absorption spectrum of PTA in cyclohexane is shown in Fig. 3 together with those of 1,3-di-*p*-tolyl-1,2-propadiene (DTA) and DPA. The intensities of these spectra are normalized at the peak position of the main band of DPA. The PTA spectrum (2) shows a weak band at 294.5 nm and shoulders around 289 and 283 nm. The existence of these bands is clearer from the differential spectrum of PTA (see the inserted figure in Fig. 3). On the other hand, on the DTA spectrum (3), the 289 nm band disappears and new bands emerge at 294.7 and 284 nm. But, in fact, the 289.8 nm band of DPA and the 294.7 nm band of DTA exist simultaneously in the 280—300 nm band region of PTA. The splitting width of the 289 and 283 nm bands of PTA is not changed by the unsymmetrical perturbation to one phenyl ring of DPA. This rules out the possibility of the first interpretation. Accordingly, the long-axis-polarized 281.5 nm band of DPA is ascribed as a vibronic structure of the 289.8 nm band which can be assigned to the $S_1\leftarrow S_0$ transition.

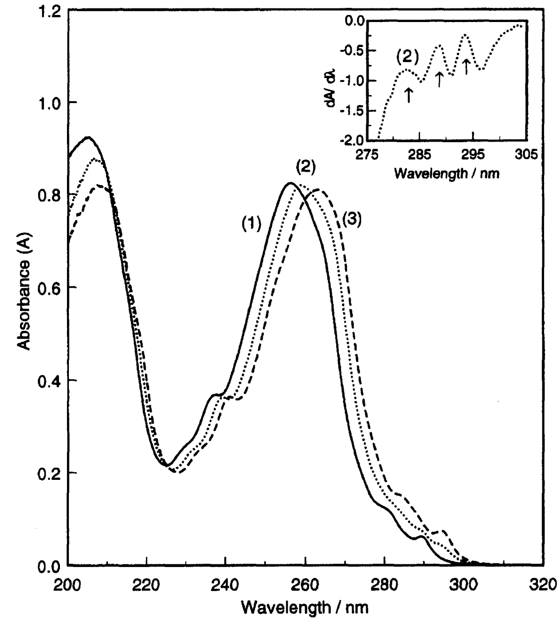
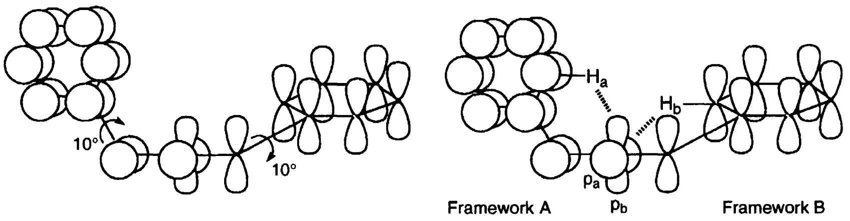


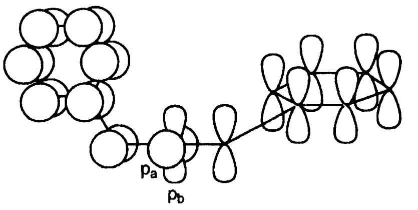
Fig. 3. The absorption spectra of 1,3-diphenyl-1,2-propadiene (DPA) (1), 1-phenyl-3-(*p*-tolyl)-1,2-propadiene (PTA) (2) and 1,3-di-*p*-tolyl-1,2-propadiene (DTA) (3) in cyclohexane. Inserted figure: The differential spectrum of PTA in the wavelength region 275—305 nm.

The degenerated $S_1\leftarrow S_0$ and $S_2\leftarrow S_0$ transitions have a forbidden character. In practice, however, the 289.8 nm band corresponding to this calculated transition has a degree of intensity ($\varepsilon=3390$ in ethanol), and then was observed as an allowed transition. This discrepancy may be explained by the following reasons: (I) in this calculation, the two phenyl rings of DPA are assumed to be completely perpendicular to each other,[5,16] (II) all σ–π interactions[6] are neglected, and (III) each π-electronic system of DPA is regarded as that of an alter-



Structure I

Structure II (Ip(Csp) = 12.22 eV)



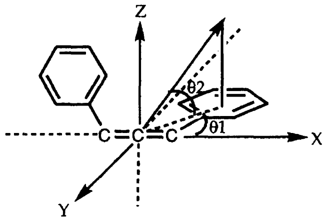
Structure III (Ip(Csp) = 15.22 eV)

Chart 2.

Table 2. The Calculated Results for the Assumed Structures I, II, and III of DPA

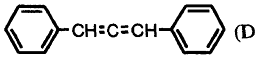
	Structure I (Twist angle of the phenyl rings=10°)				Structure II ((*Ip*(C_{sp}))=12.22 eV)				Structure III ((*Ip*(C_{sp}))=15.22 eV)			
	TE[a)]/nm	Intensity[b)]	Polarization		TE[a)]/nm	Intensity[b)]	Polarization		TE[a)]/nm	Intensity[b)]	Polarization	
			$\theta 1$[c)]	$\theta 2$[d)]			$\theta 1$[c)]	$\theta 2$[d)]			$\theta 1$[c)]	$\theta 2$[d)]
S_1	292.3	forb.			292.5	0.0005	−51°	52°	292.6	0.0046	−43°	−56°
S_2	292.3	forb.			292.4	0.0002	90°	−45°	292.6	0.0023	−90°	−45°
S_3	268.5	0.9593	24°	67°	266.5	0.9449	25°	67°	260.7	0.8587	26°	66°
S_4	252.6	0.2751	−90°	−45°	250.2	0.2723	90°	−45°	245.8	0.2459	90°	−45°
S_5	213.1	0.4453	−31°	−51°	213.6	0.4787	−36°	60°	212.8	0.5317	−34°	61°
S_6	208.8	0.2510	−90°	45°	212.8	0.2437	90°	−45°	212.1	0.2325	90°	−45°

a) Transition energy. b) Oscillator strength. c) The angle with respect to the *X* axis. d) The angle with respect to the *XY* plane.



nant hydrocarbon, and the ionization energies (*Ip*(C)) of all the carbon atoms are assumed to be equivalent.[17)] Thus, the MO calculations were performed again by taking into account the following conditions shown in structures I, II, and III (Chart 2). In structure I both terminal phenyl rings are twisted by 10° around the bond between the phenyl group and the allenic one. In structure II the p-orbitals of the central *sp*-hybridized carbon atom are perturbed by the σ-electronic system including the hydrogen atoms. Since the π-electronic system of Framework A is coplanar with the σ-electronic system of Framework B and vice versa, it can be assumed that hydrogens H_a and H_b mainly affect the nearby p-orbitals P_b and P_a, respectively, on the central *sp* carbon atom, affording a slight increase in the ionization energy of p-orbitals P_a and P_b. In structure III, the ionization energy of the *sp*-hybridized carbon atom is estimated to be about 15.22 eV.[18)] The results of these MO calculations are summarized in Table 2. If the twistings of the phenyl rings of DPA are taken into account, the energies for the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions are in agreement with the observed results, but these transitions remain forbidden. In the calculated results for structure II, the $S_1 \leftarrow S_0$ transition is allowed slightly, but the oscillator strength of the first transition seems to be too weak to explain the intensity of the 289.8 nm band. In the case of structure III, both Parity's forbidden transitions, $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$, are allowed, and their intensitties are satisfactorily enhanced. The calculated energy, intensity, and polarization data of other transitions of structure III are also in fair agreement with the observed results. This indicates that the 289.8 nm band of DPA is intensified by an increase of the ionization energy of the *sp*-hybridized

Table 3. Result of Configuration Analysis for DPA (in Weight Percent)[a)]


(DPA)

			Ψ_G	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_7	Ψ_8	……	Ψ_{14}	Ψ_{15}	Ψ_{16}
		obsd*		289.8		265.2	237.1	219		208	204				
	Ψ_G^0		100												
	Ψ_1^{01}	291.9		100											
	Ψ_2^{01}	260.5				49.5	49.5								
Styrene 1	Ψ_3^{01}	ca.222						49.0	49.6	1.0					
	Ψ_4^{01}	216.8								48.8	49.2				
	Ψ_5^{01}														
	Ψ_6^{01}														
	Ψ_1^{02}	291.9			100										
	Ψ_2^{02}	260.5				49.5	49.5								
Styrene 2	Ψ_3^{02}	ca.222						49.0	49.6	1.0					
	Ψ_4^{02}	216.8								48.8	49.2				
	Ψ_5^{02}														
	Ψ_6^{02}														
	$\Psi_{1\to2}^{CT}$												97.1		
	$\Psi_{2\to1}^{CT}$													97.1	

a) obsd*, the λ_{max} (nm) for styrenes and DPA were measured in the PVA film; Ψ_G and Ψ_G^0, the wavefunctions of configurations of DPA and a reference molecule in the ground state, respectively; Ψ_i, the total wavefunction in the *i*th excited state of DPA; Ψ_j^{oi}, the total wavefunction of the *j*th excited state of the *i*th styrene; $\Psi_{1\to2}^{CT}$ and $\Psi_{2\to1}^{CT}$, the total wavefunctions of the charge transfer configuration from styrene 1 to styrene 2 and vice versa.

carbon atom in the allenic group. Furthermore, a weak σ–π interaction in the molecular framework may contribute in part to the increase of the band intensity.

Configuration Analysis for DPA. In order to understand the nature of each electronic transition of DPA in more detail, configuration analysis (CA) was performed[19)] and the results are shown in Table 3. In the analysis, two styrenes were used as a reference molecule. The first excited state wavefunction of DPA, Ψ_1, which corresponds to the observed 289.8 nm band, has a contribution weight of 100% of the first band of styrene 1 at 291.9 nm. The Ψ_2 wavefunction is related to the first band of styrene 2 in the same way. That is, the first and second transitions of DPA do not mix with each other. On the other hand, the second excited wavefunctions of the two styrenes, styrene 1 and styrene 2, equally contribute to the third and fourth excited state wavefunctions of DPA, Ψ_3 and Ψ_4, having a contribution weight of 49.5%. Wavefunction Ψ_3 corresponds to the longer axis-polarized 265.2 nm band and Ψ_4 to the shorter axis polarized 237.1 nm band. Both the longer axis-polarized 208 nm and the shorter axis-polarized 204 nm bands similarly originate from the mixing of the ca.222 nm bands of the styrenes.

The authors would like to thank Assistant Professor Jeanette M. McLean of Tokyo Denki University for her helpful advice.

References

1) D. R. Taylor, "The Chemistry of Allenes," *Chem. Rev.*, **67**, 317 (1967).

2) F. Brogli, J. K. Crandall, E. Heilbronner, E. Kloster-Jensen, and S. Sojka, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 455 (1973).

3) W. D. Celmer and I. A. Solomons, *J. Am. Chem. Soc.*, **75**, 1372 (1953).

4) T. L. Jacobs and D. Dankker, *J. Org. Chem.*, **22**, 1424 (1957).

5) W. Runge, W. Kosbahn, and J. Kroner, *Ber. Bunsenges. Phys. Chem.*, **79**, 371 (1975).

6) P. Bischof, R. Gleiter, H. Hopf, and F. T. Lenich, *J. Am. Chem. Soc.*, **97**, 5467 (1975).

7) R. J. Bushby, A. S. Patterson, G. J. Ferber, A. J. Duke, and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 2*, **1987**, 807.

8) a) K. Maruyama and H. Imahori, *J. Org. Chem.*, **54**, 2692 (1989); b) L. Skattebol, *Acta Chem. Scand.*, **17**, 1683 (1963).

9) T. A. Bryson and T. M. Dolak, "Organic Syntheses," ed by W. E. Noland, John Wiley & Sons, New York (1988), Coll. Vol. 6, pp. 505—507.

10) K. A. Reynolds, P. G. Dopico, M. J. Sundermann, K. A. Hughes, and M. G. Finn, *J. Org. Chem.*, **58**, 1298 (1993).

11) T. Hoshi and Y. Tanizaki, *Z. Phys. Chem., Neue Folge (Munich)*, **71**, 230 (1970).

12) T. Hoshi, J. Okubo, T. Kawashima, K. Iijima, H. Inoue, and T. Sakurai, *Nippon Kagaku Kaishi*, **1987**, 1.

13) M. Kobayashi, T. Hoshi, J. Okubo, H. Hiratsuka, T.

Harasono, M. Nakagawa, and Y. Tanizaki, *Bull. Chem. Soc. Jpn.*, **57**, 2905 (1984).

14) T. Hoshi, J. Okubo, M. Kobayashi, and Y. Tanizaki, *J. Am. Chem. Soc.*, **108**, 3867 (1986).

15) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta* (*Berlin*), **3**, 407 (1965).

16) Y. Ni, J. S. Siegel, V. L. Hsu, and D. R. Kearns, *J. Phys. Chem.*, **95**, 9211 (1991).

17) T. Hoshi, H. Yamamoto, T. Miyauchi, S. Mori, M. Kobayashi, and Y. Tanizaki, *Ber. Bunsenges. Phys. Chem.*, **86**, 330 (1982).

18) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

19) H. Baba, S. Suzuki, and T. Takemura, *J. Chem. Phys.*, **50**, 2078 (1969).