Alternant Conjugate Systems. IV. Ultraviolet Spectroscopic Properties and Photoisomerization of Geometrical Isomers of p-Distyrylbenzenes, p, p′-Distyrylstilbenes and Related Compounds

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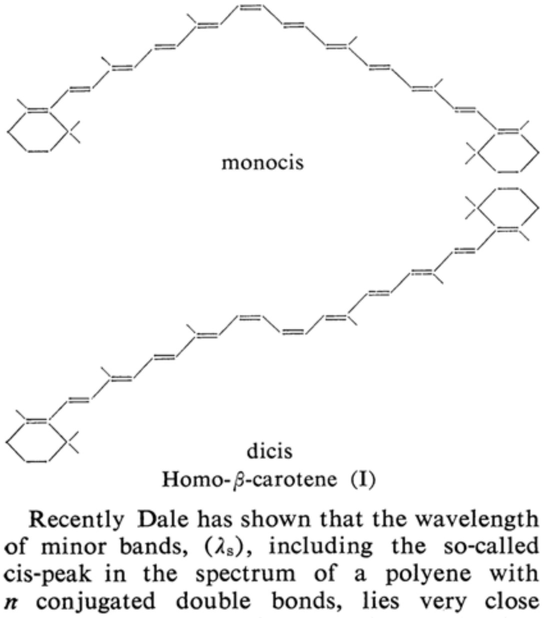
(Received March 23, 1961)

Zechmeister and his co-workers have observed the appearance of a new absorption maximum in the near ultraviolet region when various kinds of all trans isoprenic conjugated polyolefins were irradiated(1). They have attributed the new absorption band to the presence of unhindered cis ethylenic linkage formed by a photochemical stereomutation of trans linkage. The so-called " cis-peak rule " was proposed by them to correlate the wavelength and the intensity of the new absorption maximum with the geometry of the cis-isomer. It has been proved that this rule is valid for a wide variety of carotenoids, such as central cis-β-carotene, central cis-bixin methyl ester, monocis- and dicis-homo-β-carotenes (I)(2) and the straight conjugated system, i. e., diphenylpolyenes(1).



Homo-β-carotene (I)

Recently Dale has shown that the wavelength of minor bands, (λ_s), including the so-called cis-peak in the spectrum of a polyene with n conjugated double bonds, lies very close to the wavelength of the main band of a corresponding polyene with n/s conjugated double bonds (where n/s does not need to be an integral)(3). He has also shown that this simple relationship holds also in the conjugated system containing benzene nuclei such as diphenylbutadiene, stilbene, etc. From these results, he has concluded that the appearance of minor bands in a conjugated polyene can not be attributed to the operation of independent partial chromophores, but is ascribable to the higher order transition of the total chromophore system. According to this argument, Zechmeister's cis-peak can be regarded as the first overtone band of the full chromophore system.

On the other hand, it has been found that isoprenic diphenylpolyenes containing sterically hindered cis ethylenic linkage exhibit no distinct cis-peak(4). Oroshnik and his co-workers(5) have attributed the absorption band at a shorter wavelength in the spectra of hindered retrovitamin A methyl ether and related compounds to an overlap of the cis-peak with an absorption arising from the partial chromophore systems. He has pointed out that the contribution of the cis-peak and the partial chromophore can not be distinguished in these cases and that Zechmeister's cis-peak rule seems to be inapplicable in its original form to a conjugated system with sterically hindered cis olefinic linkage.

As reported in the preceding papers of this series(6), the present authors have synthesized several geometrical isomers of stilbene homologues and the acetylenic analogues, including sterically hindered cis-isomers (Fig. 1). The

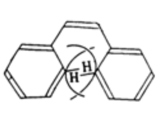


Fig. 1

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(1) L. Zechmeister, L. Pauling et al., *J. Am. Chem. Soc.*, **65**, 1940 (1943); L. Zechmeister, *Chem. Revs.*, **34**, 267 (1944); *Experientia*, **10**, 1 (1954).

(2) H. H. Inhoffen et al., *Ann.*, **570**, 54 (1940); **573**, 1 (1951); **592**, 214 (1955); L. Zechmeister, *Fortschr. Chem. org. Naturstoffe*, **18**, 223 (1960).

(3) J. Dale, *Acta Chem. Scand.*, **8**, 1235 (1954); **11**, 971 (1957).

(4) P. Karrer et al., *Helv. Chim. Acta*, **35**, 1850 (1952); **36**, 562 (1953).

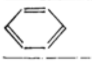
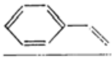
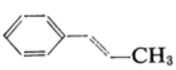
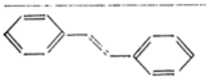
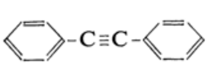
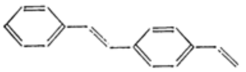
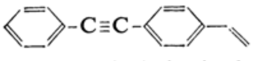
(5) W. Oroshnik et al., *J. Am. Chem. Soc.*, **76**, 5719 (1954).

(6) Part II and III, This Bulletin, **34**, 1833 (1961); **35**, 135 (1962).

present paper deals with the ultraviolet spectroscopic properties and the photoisomerization of these geometrical isomers.

Spectroscopic Properties. — In the series of *p*-distyrylbenzene, the t–t isomer* showed a main maximum at the longest wavelength as compared with other geometrical isomers and the acetylenic analogues, as illustrated in Figs. 1 and 2 in Part II of this series. (The numerical data are summarized in Table I of Part II.) Substitution of the trans-linkage with cis- or acetylenic bonds caused a shift of the absorption maximum to shorter wavelength and a decrease of the absorption intensity. The decrease of absorption intensity was found to be much larger in the case of the insertion of cis-linkage than that of acetylenic bond, in spite of the same degree of hypsochromic shift in both cases. This fact is quite understandable from the fact that the coplanarity of the cis-molecule is broken as the result of the steric hindrance of hydrogen atoms in the *o*- and *o'*-positions of the benzene rings adjacent to the cis-linkage (Fig. 1). On the contrary, the absorption intensity of the band near 230 mμ is larger in the case of the cis-isomer than in that of the trans-isomer. The sequence of intensity of this absorption peak was found to be c–c>t–c>t–t and A–c>A–t. The ultraviolet spectra of the three compounds containing no cis-linkage, i. e., t–t, t–A and A–A, each exhibit a distinct absorption minimum in the region of 250~290 mμ. But an absorption maximum at about 270 mμ was observed in the spectra of the corresponding cis-isomers, i. e., t–c, c–c and A–c. An examination of the spectra of reference substances which can be regarded as the possible partial chromophores of the abovementioned *p*-distyrylbenzenes and *p*-styryltolan indicates that the absorption maximum at ca. 270 mμ can not be attributed to a contribution of any partial chromophores (Table I). For instance, styrene, stilbene and vinylstilbene may be the possible partial chromophores for the t–c isomer, but it seems to be quite difficult to find out the contribution of the ultraviolet absorption of these compounds from the spectrum of the t–c isomer. Tolan, styrene and vinyltolan may be the possible partial chromophores of A–c isomer. Also, the shape of the absorption curve of the A–c isomer indicates that the participation of the partial chromophores is negligible.

TABLE I. ULTRAVIOLET ABSORPTION OF POSSIBLE PARTIAL CHROMOPHORES

	λ_{max} mμ	ε_{max}	Solv.*	Ref.
	198 255	8000 230	b	
	244 282	12600 500	a	7
	250 284 293	17300 1100 780	a	8
	226 295 310	15000 27000 25000	a	9
	265 281 289 298	21000 29000 20000 25000	c	10
	323	34000	b	11
	301	43000	b	11

* a=alcohol, b=hexane, c=cyclohexane.

The same situation was found in the spectra of the higher homologues; the isomeric *p,p'*-distyrylstilbenes and the related compounds (t–c–t, t–c–A and A–c–A) exhibit broad and most intense absorption maxima at the wavelength region of 280~320 mμ (cf. Fig. 2 in Part III of this series). An examination of the spectra of the reference substances corresponding to the partial chromophores also

TABLE II. ULTRAVIOLET ABSORPTION OF STEREOISOMERIC *p,p'*-DISTYRYLSTILBENES AND RELATED COMPOUNDS

	λ_{max}, mμ ($\varepsilon_{max}\times10^{-2}$)				Solv.*
t–t–t	238(359)	270(186)		384(893)	a
t–t–A	237(321)	266(208)		374(787)	a
t–A–t	243(432)			361(843)	a
A–t–A	235(297)	262(144)		362(801)	a
A–A–A	236(370)	256(89)		340(709)	c
t–t–c	237(285)			372(681)	a
t–c–t	236(229)		316(521)	353(410)	a
	232(224)		312(492)	348(409)	b
c–t–c	238(368)			359(488)	a
t–c–A	235(290)	270(241)	302(457)	346(376)	a
	232(271)	268(230)	298(457)	341(387)	b
A–c–A			295(453)	330(365)	a

* a=tetrahydrofuran, b=*n*-hexane, c=chloroform

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* t, c and A denote trans-, cis- and acetylenic bonds respectively. Therefore, for example, t-t isomer and t-c-A isomer represent *trans*, *trans-p*-distyrylbenzene and *p-trans*-styryl-*p'*-phenylethynyl-*cis*-stilbene respectively.

7) H. P. Koch, *J. Chem. Soc.*, **1949**, 387; W. W. Robertson and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5250 (1950).

8) R. Y. Mixer, R. F. Hech, S. Winstein and W. G. Young, *J. Am. Chem. Soc.*, **75**, 4094 (1953).

9) A. Eucken and K. H. Hellwege, " Landolt-Börnstein Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik ", 6 Aufl., Band I, Teil. 3, Springer-Verlag (1951).

10) R. A. Friedel and M. Orchin, " Ultraviolet Spectra of Aromatic Compounds ", John Wiley & Sons, Inc. (1951).

11) G. Drefahl, G. Plötner and F. Rudolph, *Chem. Ber.*, **93**, 998 (1960).

reveals that the operation of partial chromophores is not reflected in the spectra of the distyrylstilbenes and their analogues. The absorption maximum at 312 mμ and the inflection at ca. 300 mμ in the spectrum of the t–c–t isomer seem to be attributable to the participation of the absorption of stilbene, an possible partial chromophore, which has a strong maxima at 297 and 310 mμ, while the presence of an absorption minimum at 326 mμ in the spectrum of t–c–t isomer excludes the possible operation of another partial chromophore, vinylstilbene, which has a strong maximum at the same wavelength (323 mμ). Also, the attribution of the $\lambda_{\max}$ at 293 mμ and the $\lambda_{\text{infl.}}$ at ca. 283 mμ in the spectrum of the A–c–A isomer to the contribution of a partial chromophore, tolan ($\lambda_{\max}$ 281 and 298 mμ), is inconsistent with the fact that the spectrum of this isomer shows a distinct $\lambda_{\min}$ at 307 mμ, while the spectrum of vinyltolan, another possible partial chromophore, exhibits a strong $\lambda_{\max}$ at about the same wavelength (301 mμ). Similarly, the absorption of the t–c–A isomer ($\lambda_{\max}$ 298 mμ, $\lambda_{\text{infl.}}$ ca. 290 mμ) could not be explained by the participation of either pair of the partial chromophores, stilbene-vinyltolan or tolan-vinylstilbene. Furthermore, the close resemblance of the shape of the absorption curve of the unsymmetrical t–c–A isomer to those of the symmetrical isomers (t–c–t and A–c–A) in this wavelength region seems to indicate the negligible participation of the partial chromophores. It may be reasonable to conclude from these observed results that the absorption maxima at ca. 270 mμ and at 280∼320 mμ in the spectra of the three benzene and the four benzene systems do not arise from the participation of partial chromophores, but arise from the second order electronic transitions of the total chromophore.

The absorption curves of the t–c and A–c each form a distinct peak at 270 mμ, while the spectrum of the c–c isomer forms a plateau at the same wavelength (Fig. 1 in Part II). Also, the t–c–t, t–c–A and A–c–A isomers each showed a very strong absorption at 280∼320 mμ (Fig. 2 in Part III). On the other hand, the t–t–c and c–t–c isomers did not exhibit a marked absorption peak at this region (Fig. 4 in Part III). These facts indicate that the probability of the second order transition is strongly affected by the geometry of the molecule. As illustrated in Fig. 2, the A–c and t–c isomers may have a dipolemoment perpendicular to the long axis of the conjugated system, whereas the most probable configuration of c–c isomer (a) has no dipolemoment perpendicular to the long axis, and the contribution of a configuration such as (b) which has the above-mentioned dipolemoment seems to be highly improbable owing to its great steric hindrance. Similarly, the t–c–t, t–c–A and A–c–A isomers which may have large dipolemoment perpendicular to the long axis exhibit a distinct second order absorption maximum, and the t–t–c and c–t–c isomers having minor dipolemoment show only a weak shoulder at the corresponding wavelength position. The same trend has been pointed out by Zechmeister[1] in carotenoid series containing unhindered cis-linkage or cis-linkages.

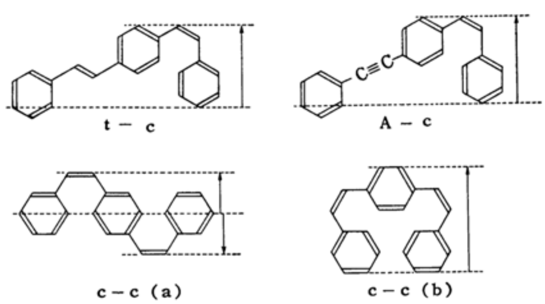

Fig. 2

If the appearance of the second absorption maximum in the spectra of cis-compounds could be attributed to the second order transition of the total chromophore, the all-trans isomer and the acetylene-trans compounds would also have an absorption in the same wavelength, even if it is extremely weak in its intensity. In fact, the spectra of t–t, t–A and A–A compounds exhibit a weak inflection at ca. 270 mμ (Figs. 1 and 2 in Part II). In the same way, a weak inflection at 290∼310 mμ was observed in the spectra of t–t–t, t–A–t, t–t–A, A–t–A and A–A–A compounds (Figs. 3 and 4 in Part III). The existence of these inflections at the wavelength corresponding to the second absorption maximum of the cis-compound clearly indicates that the second order transition contributes to the spectra of the alternant conjugate systems lacking cis-linkage.

All compounds belonging to the four benzene system showed an absorption maximum at the wavelength of 260∼280 mμ. This maximum was observed as a weak inflection in the cis-series. On the other hand, a fairly distinct peak was observed in the spectra of the trans- and acetylene-series. This absorption and the absorption at a shorter wavelength (235∼245 mμ) can also be satisfactorily explained in terms of a third and of still higher order transitions of the total chromophore. It is to be noted that the probability of the xth order transition is larger in trans and/or acetylenic series than the corresponding cis-compounds when x is an even number. Conversely, when

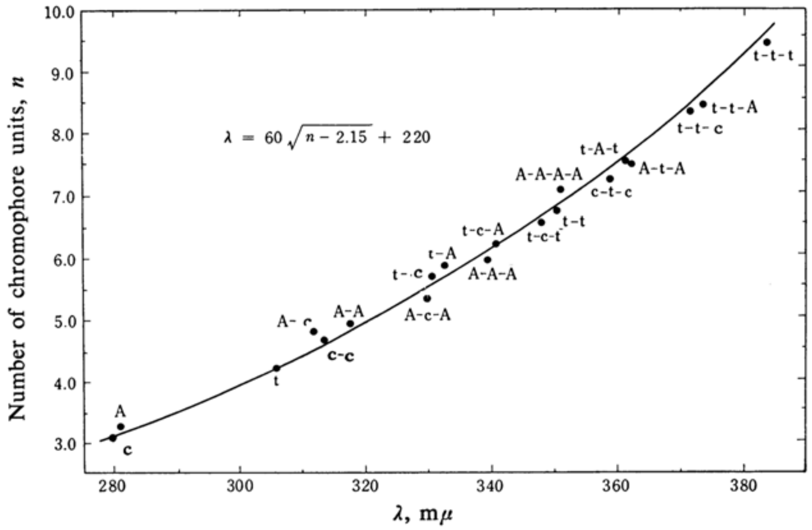

Fig. 3. The wavelength positions of the longest wavelength bands of the stereoisomers plotted against number of chromophore units.

TABLE III. CALCULATED AND OBSERVED VALUES OF LONGEST WAVELENGTH BANDS

	Number of chromophore units, n	Calcd. mμ	Obs. mμ	Solv.*
t	4.20	306	306	d
c	3.13	279	280	a
A	3.26	283	281	a
t–t	6.80	349	350	d
t–c	5.73	334	331	d
c–c	4.66	315	314	d
t–A	5.86	336	333	d
c–A	4.79	316	312	d
A–A	4.91	320	318	a
t–t–t	9.40	382	384	e
t–t–c	8.33	369	372	e
t–c–t	6.59	346	348	d
c–t–c	7.26	356	359	e
t–t–A	8.46	371	374	e
t–A–t	7.57	360	361	e
A–t–A	7.51	359	362	e
t–c–A	6.28	342	341	d
A–c–A	5.33	327	330	e
A–A–A	6.01	338	340	c
A–A–A–A	7.10	353	351	b

t, c and A denote trans-, cis- and acetylenic bond, respectively.

* a=alcohol, b=benzene, c=chloroform, d=n-hexane, e=tetrahydrofuran

x is an odd number, cis-compounds have larger xth order absorption maxima than the corresponding trans and/or acetylenic compounds (Figs. 3 and 4 in Part III).

As illustrated in Fig. 3, a smooth curve was obtained by plotting the position of the absorption maxima of the longest wavelength ($\lambda_{\max}$) against the number of chromophore units (n), where an ethylenic bond is taken as an unit, and each benzene ring and acetylenic bond is set equal to the 1.6 and 0.6 ethylenic bond respectively, and the effect of the blue shift caused by the presence of cis- and acetylenic bonds is corrected by introducing cis- ($f_C=0.33$) and acetylenic ($f_A=0.66$) factors. The calculated chromophore units of this series of compounds are summarized in Table III. The relationship between $\lambda_{\max}$ and n is well represented by the following empirical Eq. 1.

$$\lambda=60\sqrt{n-2.15}+220 \qquad (1)$$

A fairly good agreement of the calculated values with the observed values was obtained for almost all compounds of this series, as shown in Table III. The minor deviation of the calculated values in the four benzene series seems to be attributable to a solvent effect, since the spectra were measured using tetrahydrofuran or benzene as the solvent. n-Hexane and ethanol could not be used owing to the poor solubility of the compounds to these solvents. A red shift of about 2∼5 mμ was generally observed in the case of a solution in tetrahydrofuran or benzene as compared with those in aliphatic hydrocarbons. A slightly larger deviation between the predicted and observed values was observed in the cases of polytolans.

Photoisomerization. — In order to determine the relative rates of photoisomerization and to know the isomer ratios in the equilibrated mixtures, dilute solutions of each pair of the above-mentioned alternant conjugate systems

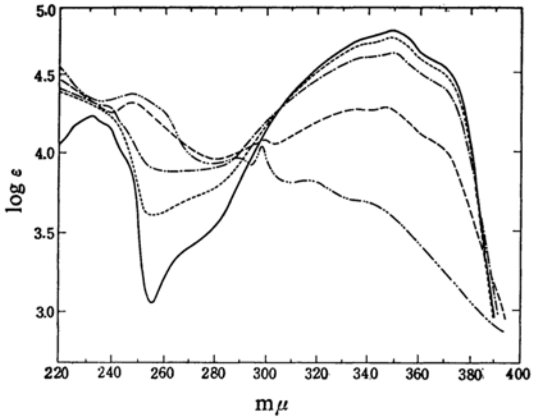

Fig. 4. The change of ultraviolet spectra on irradiation of *trans*, *trans*-*p*-distyrylbenzene (0 hr., ——; 1 hr., ------; 27 hr., —·—·; 100 hr., ----; 240 hr., —··—··) in *n*-hexane.

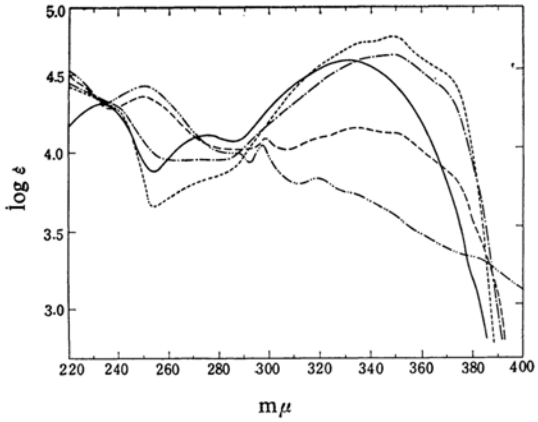

Fig. 5. The change of ultraviolet spectra on irradiation of *trans*, *cis*-*p*-distyrylbenzene (0 hr., ——; 1 hr., ------; 27 hr., —·—; 100 hr., ----; 240 hr., —··—··) in *n*-hexane.

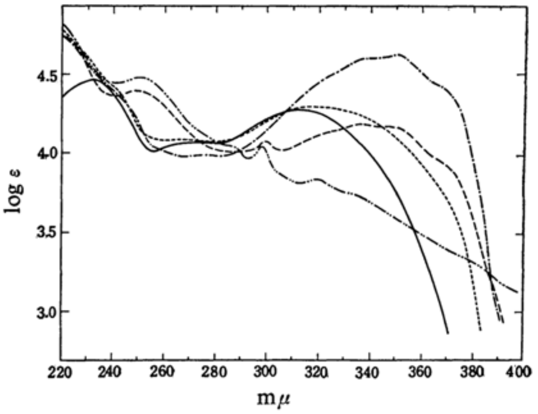

Fig. 6. The change of ultraviolet spectra on irradiation of *cis*, *cis*-*p*-distyrylbenzene in *n*-hexane (0 hr., ——; 1 hr., ------; 27 hr., —·—·; 100 hr., ----; 240 hr., —··—··).

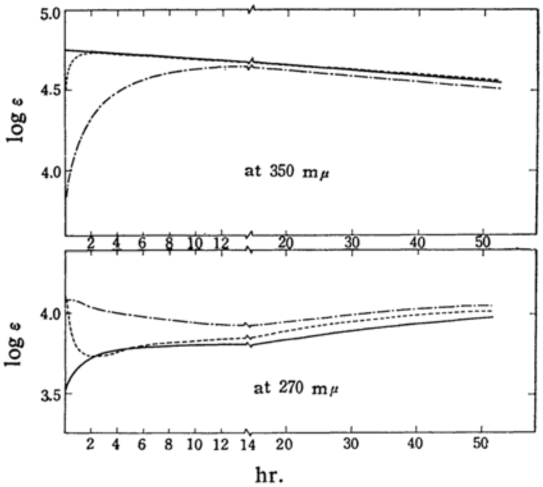

Fig. 7. The change of the extinction values of the ultraviolet spectra of three isomeric *p*-distyrylbenzenes in *n*-hexane by exposure to light at 10 cm. (t-t, ——; t-c, ------; c-c, —·—·).

were exposed to the light of a fluorescent tube under controlled conditions and the course of photoisomerization was followed, measuring the change of the spectra. It was observed that some kind of photocyclization presumably accompanied with photodegradation occurs on a prolonged irradiation. As a result of these side-reactions, it was found to be impossible to determine the composition of the equilibrium mixture.

The changes of ultraviolet spectra on irradiation of the three geometrical isomers of *p*-distyrylbenzene (t-t, t-c and c-c) are illustrated in Figs. 4, 5 and 6, and those of absorption intensities at 350 and 270 mμ of each isomer are shown in Fig. 7. The bands at the longest wavelength in the t-c and c-c isomer shifted to the red side, increasing their intensities in accord with the period of irradiation. It was observed that the t-c isomer is converted to an approximate equilibrium with the t-t isomer after 1 hr. of irradiation. On the other hand, in the case of the c-c isomer, an approximate equilibrium with the t-t isomer was attained only after 13 hr. irradiation. It is to be noted that the rate of photoisomerization is much slower in the case of the more hindered c-c isomer than the case of the less hindered t-c isomer.

Further change of the spectra were observed on prolonged irradiation. A slow decrease of the intensity at 350 mμ was accompanied with a gradual increase of the intensity at 232 mμ, and the latter maximum was buried in the strong absorption which appeared in the shorter wavelength region. The appearance of new inflections at 250 and 297 mμ was observed after exposure for ca. 54 hr. These inflections grew to the intense absorption maxima after exposure for 100 hr.

Also, the A–c and A–t isomers showed a distinct fine structure in their spectra after irradiation for a long time, suggesting the formation of phenanthrene nucleus by photochemical cyclization[12] (Figs. 8 and 9).

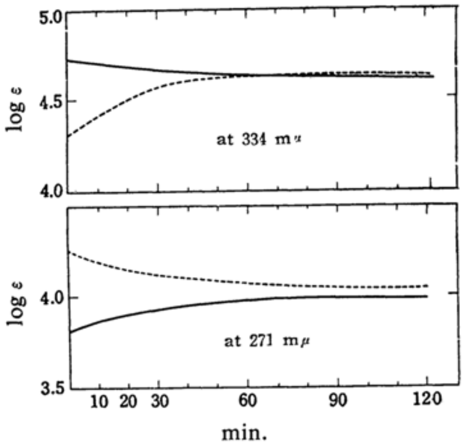

Fig. 8. The change of the extinction values of the ultraviolet spectra of stereoisomeric *p*-styryltolans in *n*-hexane by exposure to light at 10 cm. (A–t, ——; A–c, ------).

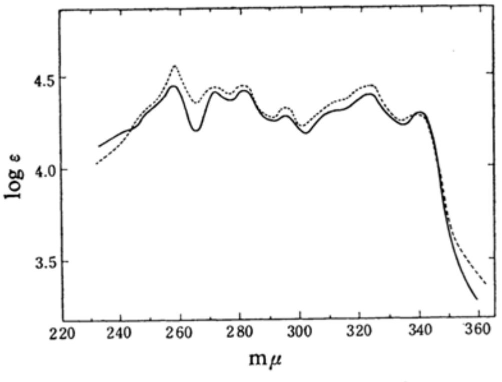

Fig. 9. The ultraviolet spectra of stereoisomeric *p*-styryltolans after irradiation for 213 hr. at 10 cm. (A–t, ——; A–c, ------).

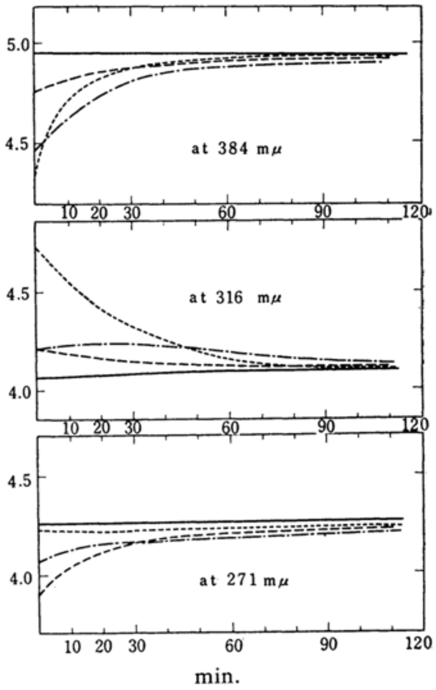

Fig. 10. The change of the extinction values of the ultraviolet spectra of four isomeric p,p'-distyrylstilbenes in tetrahydrofuran by exposure to light at 20 cm. (t–t–t, ——; t–c–t, ----; t–t–c, ------; c–t–c, —·—·).

The change of absorption intensities at three points of wavelength according to the progress of photoisomerization of the four geometrical isomers of p,p'-distyrylstilbene is illustrated in Fig. 10. The sequence of the rate of photochemical stereomutation was found to be t–c–t>t–t–c>c–t–c. The fact that the most hindered c–t–c isomer is most stable is consistent with the case of the c–c isomer. Also, it is an interesting fact that the isomer having a more intense cis-peak (in another word, absorption due to the second order transition of total chromophore) shows a larger rate of photoisomerization.

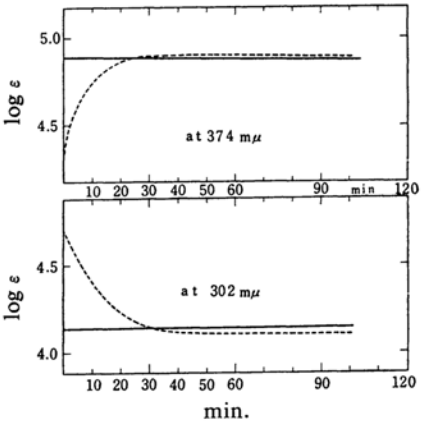

Fig. 11. The change of the extinction values of the ultraviolet spectra of isomeric *p*-styryl-p'-phenylethynyl-stilbenes in tetrahydrofuran by exposure to light at 10 cm. (t–t–A, ——; t–c–A, ------).

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[12] A. Smakula, *Z. physik. Chem.*, **B25**, 90 (1934); R. E. Buckles, *J. Am. Chem. Soc.*, **77**, 1041 (1955); P. Hugelshofer, J. Kalvoda and K. Schaffner, *Helv. Chim. Acta*, **43**, 1322 (1960).

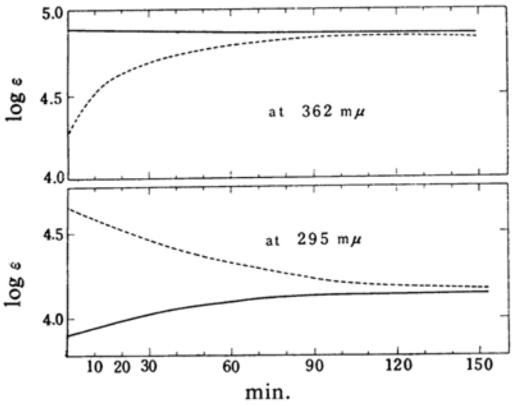

Fig. 12. The change of the extinction values of the ultraviolet spectra of isomeric *p*-bis-(phenylethynyl)stilbenes in tetrahydrofuran by exposure to light at 20 cm. (A-t-A, ——; A-c-A, ------).

The changes of the spectra by irradiation of other pairs of isomers of the four benzene series, t-t-A : t-c-A and A-c-A : A-t-A, are presented in Figs. 11 and 12. After prolonged irradiation, the spectra of these compounds showed distinct fine structures, indicating the formation of a condensed aromatic system.

The present authors are continuing the photochemical cyclization of these series of compounds.

Experimental

General Method of Photoisomerization.—The spectrum was measured in a sealed fused silica cell of 1.0 cm. thickness using a dilute solution (ca. 1 mg. of substance in 1000 ml. of solvent). Spectral grade *n*-hexane was used in the case of the compounds of the three benzene series. The compound of the four benzene series were dissolved in purified tetrahydrofuran. Two cells containing the solutions of the pair of isomers were irradiated with a fluorescent tube (10 W. daylight type). The change of spectrum and the change of intensities at particular wavelength were measured at an appropriate interval.

The authors are grateful to the Ministry of Education for the financial support for this wark.

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