

Ultraviolet Absorption Spectra of Chain Molecules Consisting of Alternating Benzene Rings and Ethylenic Bonds

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The electronic absorption spectra of styrene, stilbene, 1,4-diphenylbutadiene, *p*-distyrylbenzene, *p*-(phenylbutadienyl)stilbene, *p,p'*-distyrylstilbene and diphenylacetylene have been measured, most of them down to 195 $m\mu$. Mono-*cis*-isomers of *p*-distyrylbenzene and *p*-(phenylbutadienyl)stilbene have been prepared and their spectra also recorded. The observed bands are of three types: 1) a stationary band at 200—210 $m\mu$; 2) a semi-stationary band at 210—250 $m\mu$; and 3) polyene-like bands which can be interpreted as fundamental- and overtone-transitions of the full chromophore.

The spectra of the cross-conjugated compounds *m*-terphenyl and *m*-distyrylbenzene have been measured and compared with the spectra of biphenyl and stilbene.

The syntheses of *p,p'*-distyrylstilbene, *p*-chloro-*p'*-styryl-stilbene and *o*-chloro-*p'*-styryl-stilbene are described.

Compounds of structure intermediate between the polyphenyls and the pure polyenes are of considerable interest for the interpretation of electronic absorption spectra of conjugated chain molecules in general. The chemical structure of alternating benzene nuclei and ethylenic bonds is such that a multiplicity of "partial chromophores" would be expected to be active in addition to the "full chromophore", if it is at all justified to divide a conjugated system arbitrarily into independent partial chromophores in order to explain the more complex spectra. It has already been shown that the concept of partial chromophores had to be rejected in discussions of polyene and polyenyne spectra^{1,2} in favour of the simple, and more successful, overtone interpretation, which requires that the wave length position of the minor bands must be independent of the detailed structure and correspond to integral fractions of the total chromophore length. The transitions are, however, subject to selection rules which depend on the over-all shape of the molecule.

Among compounds of this type, styrene^{3,4}, as well as *cis*- and *trans*-stilbene^{5,6}, have already been investigated in the ultraviolet; for the stilbene isomers an interpretation based on rather implausible assumptions of several partial chromophores has been given by Braude⁷. For the first stilbene

homolog, *p*-distyrylbenzene, only an incomplete spectrum has been reported⁸. The solution spectra of these compounds have now been remeasured to down below 200 $m\mu$ (Figs. 1—3).

The next stilbene homolog, *p,p'*-distyrylstilbene, has been synthesized for the first time (see Experimental Part), but its extremely low solubility made it difficult to obtain a spectrum in the lowest wave length region (Fig. 4).

In addition, the closely related compounds, 1,4-diphenylbutadiene and *p*-(phenylbutadienyl)stilbene have also been investigated, the latter for the first time (Figs. 5—6).

The spectra of mono-*cis*-isomers of stilbene⁶ and 1,4-diphenylbutadiene⁹ have been redrawn from the literature (Figs. 2 and 5). Mono-*cis*-isomers of *p*-distyrylbenzene and *p*-(phenylbutadienyl)stilbene were not known and have been prepared by illumination of the all-*trans*-isomers; the spectra are given in Figs. 3 and 6.

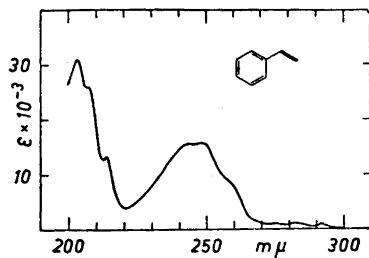


Fig. 1. Molecular extinction curve of styrene in hexane.

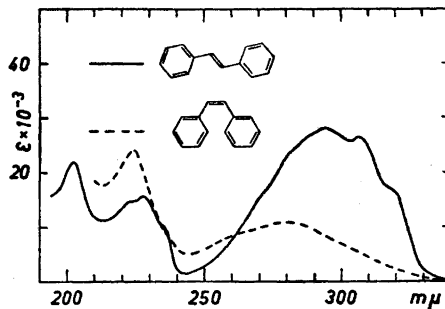


Fig. 2. Molecular extinction curves of *trans*-stilbene in hexane, and of *cis*-stilbene in ethanol (the latter curve from Beale and Roe⁶).

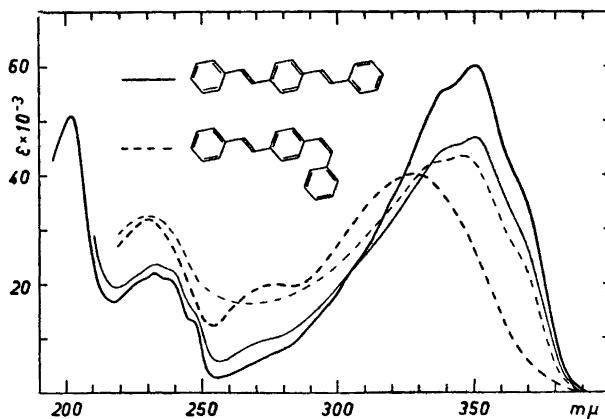


Fig. 3. Molecular extinction curves of all-*trans*- and of mono-*cis*-*p*-distyrylbenzene in hexane. Heavy lines represent fresh solutions; thin lines the same solutions after iodine catalysis.

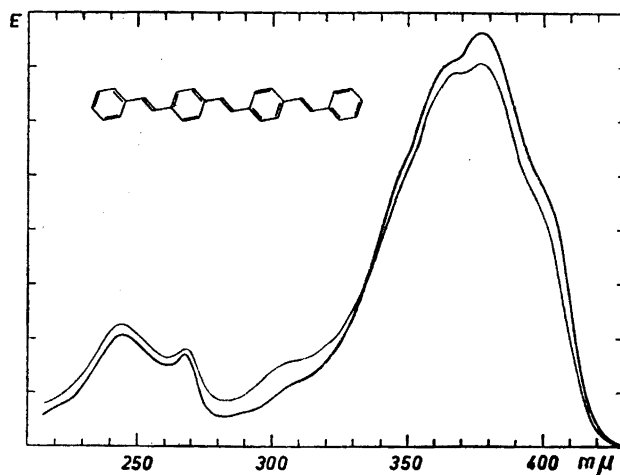


Fig. 4. Extinction curve of all-*trans*-*p,p'*-distyrylstilbene in cyclohexane. Heavy line represents a fresh solution; thin line the same solution after iodine catalysis. Cell length 5 cm.

None of the compounds mentioned above contain benzene nuclei linked in other than the *para* position. It was the plan of this work to prepare similar chains containing also *ortho*-disubstituted benzene links, but none of the numerous attempts were successful (see Experimental Part), either because the methods that were used may not be suitable, or because the compounds may not be obtainable in crystalline form. It is noteworthy that only one such compound has been reported in the literature, namely, *o*-distyrylstilbene, claimed to be obtained in a Meerwein reaction between *o*-aminostilbene and cinnamic acid¹⁰, and that a sample of this product proved, on closer examination, to be impure stilbene (see Experimental Part). The experience of the present writer indicates that the Meerwein reaction proceeds readily in the *para* position, but is replaced mainly by a Sandmeyer reaction in the *ortho* position (see Experimental Part). It should be mentioned, however, that chromatographically separated oily fractions showing the spectra expected for the desired *ortho* compounds could be obtained in some cases, but the quantities were far too small for identification.

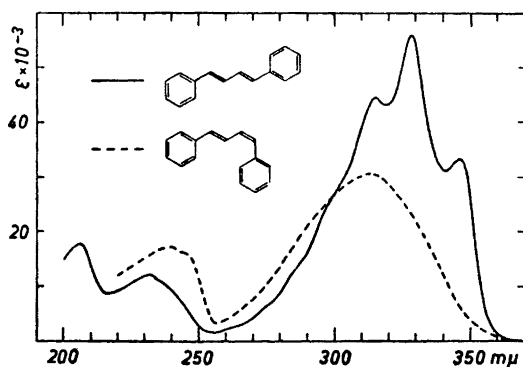


Fig. 5. Molecular extinction curves of all-*trans*- and of mono-*cis*-1,4-diphenylbutadiene in hexane (the latter curve from Pinckard, Wille and Zechmeister⁹).

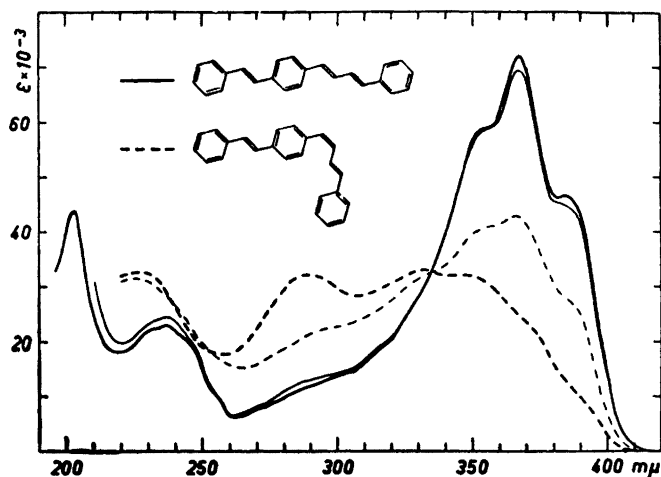


Fig. 6. Molecular extinction curves of all-*trans*- and of mono-*cis-p*-(phenylbutadienyl)-stilbene in hexane. Heavy lines represent fresh solutions; thin lines the same solutions after iodine catalysis.

In order to predict the wave length position of overtone bands¹ the wave lengths of the main bands have been plotted against the number of chromophoric units in Fig. 7. It was found that the smoothest curve could be obtained if each benzene ring is set equal to two ethylenic bonds. This choice is also in agreement with the molecular orbital picture of such systems⁴.

The predicted and observed wave lengths have been compared in Table 1.

The polyene-like bands

From Figs. 3, 4 and 6 it is at once seen that there are no bands in the spectra of these compounds that could be assigned to any of the partial chromophores that would seem most reasonable. For instance, in the spectrum

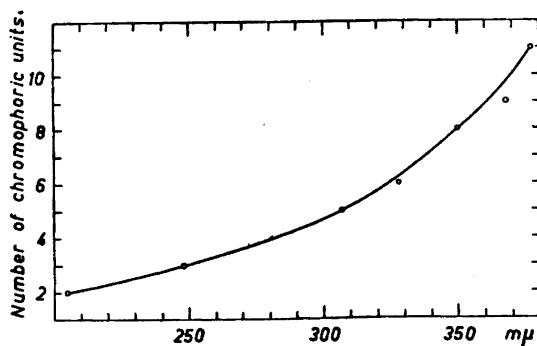


Fig. 7. Wave length position of the main band of the compounds from the preceding figures, plotted against number of chromophoric units (benzene ring = 2; ethylenic bond = 1).

Table 1. Predicted and observed wave lengths of overtone bands (in $m\mu$).

	Number of chromophoric units	λ_2		λ_3		λ_4	
		calc.	obs.	calc.	obs.	calc.	obs.
Stilbene	5	228	224				
1,4-Diphenylbutadiene	6	248	~ 246	205	(~ 207)		
<i>p</i> -Distyrylbenzene	8	280	~ 275	235	~ 230	205	
<i>p</i> -(Phenylbutadienyl)-stilbene	9	295	~ 288	248	(~ 246)	217	~ 225
<i>p,p'</i> -Distyrylstilbene	11	315	~ 305	270	268	240	(~ 244)

of *p*-distyrylbenzene (Fig. 3) there is no band in the 300 $m\mu$ region where the stilbene chromophore should absorb; and in the *p*-(phenylbutadienyl)stilbene spectrum (Fig. 6) no bands appear that can be due to either the stilbene- or the diphenyl-butadiene-chromophore. Furthermore, in the *p,p'*-distyrylstilbene spectrum (Fig. 4) bands corresponding to the stilbene- and the *p*-distyrylbenzene-chromophore are both lacking.

On the other hand, the spectra can be satisfactorily explained in terms of overtone transitions of the total chromophore (Table 1). Thus, in the region predicted for the first overtone (λ_2 -band) no bands are observed as long as the ethylenic bonds remain in the stable *trans*-configuration obtained by synthesis (no dipole moment for this transition in a straight chain), but bands appear upon *cis*-isomerization. This behaviour is just what should be expected¹, and the bands correspond with the "*cis*-peak" in polyene spectra. It can also be inferred from this spectral behaviour that the *p*-divinylbenzene system must assume the "*trans*-like" configuration already implied in the drawings of the skeleton models shown in the figures.

In the lower wave length region the situation is complicated by the presence of typical bands which are relatively stationary at 210—250 $m\mu$ and at 200—210 $m\mu$ through the whole series, and which apparently must have another origin than the polyene-like bands (for further discussion see below). Thus, in *cis*-stilbene (Fig. 2) a λ_2 -band at 224 $m\mu$ must be superimposed on the stationary band which is at 228 $m\mu$ in *trans*-stilbene, while in mono-*cis*-diphenylbutadiene (Fig. 5) the λ_2 -band is on the long wave side of the stationary band.

The λ_3 -band, which should be allowed in all isomers, seems to be superimposed on the short wave side of the stationary band in *p*-distyrylbenzene; it coincides with it in *p*-(phenyl-butadienyl)stilbene; and in *p,p'*-distyrylstilbene it appears well separated on the long wave side. A λ_4 -band must be held responsible for the increased absorption at 225 $m\mu$ in mono-*cis-p*-(phenylbutadienyl)stilbene (Fig. 6); it is forbidden in the all-*trans*-isomer¹.

The stationary bands

A discussion of the origin of the "stationary" bands is strictly beyond the scope of this paper, but it is tempting to correlate the strong band at 200—210 $m\mu$ with allowed transitions between orbitals with no longitudinal node

localized in each benzene ring, $e \rightarrow e$ in Platt's notation ⁴, although the intensity does not seem to be a clear function of the number of rings. The strongest band in the polyphenyl spectra is always found very constantly at the same wave length, and has been given this interpretation as a real "partial" ¹¹.

A further confirmation of these assignments could be obtained by checking experimentally a few predictions based on the following reasoning: In each benzene ring there are two sets of doubly degenerate π -orbitals, one filled and one empty, between which the electron jumps observable as absorption bands in the accessible ultraviolet region occur. When the rings are either mono-substituted or *para*-disubstituted links in a conjugated chain, one orbital of each set has a longitudinal node and remains isolated, whereas the other orbital of each set interacts with neighbouring π -orbitals to give polyene-like whole-molecular orbitals ⁴. If, however, a *para*-disubstituted link is replaced by a *meta*-disubstituted ring, one orbital of each set will interact mainly with one conjugated system, while the other two orbitals interact mainly with another conjugated system, so that, instead of through-conjugation, we get cross-conjugation in Dewar's sense ¹². The whole situation is very analogous to what happens if an allenic link is introduced into an aliphatic unsaturated system ^{13,14}. The effect is to break the conjugation; one double bond in the allenic grouping being conjugated with an unsaturated system in one plane, while the other allenic bond is conjugated with another planar system rotated by 90° from the former plane.

It is thus understandable that *m*-terphenyl should show a conjugation band corresponding to twice that of biphenyl ^{*}, which was already noted by Gillam and Hey in 1939 ¹⁶. In contrast, the band at $205 \text{ m}\mu$ should be expected to have the same intensity in both compounds since isolated orbitals will now be present only in the phenyl groups at both ends. This prediction could be

* The spectra of a series of polyphenyls containing *m*-disubstituted benzene rings ¹⁵, acting like insulating groups, can be similarly explained as superpositions of bands due to cross-conjugated partial chromophores corresponding to biphenyl, *p*-terphenyl or *o*-terphenyl.

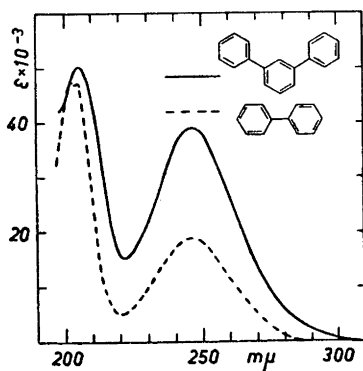


Fig. 8. Molecular extinction curves of *m*-terphenyl and biphenyl in hexane.

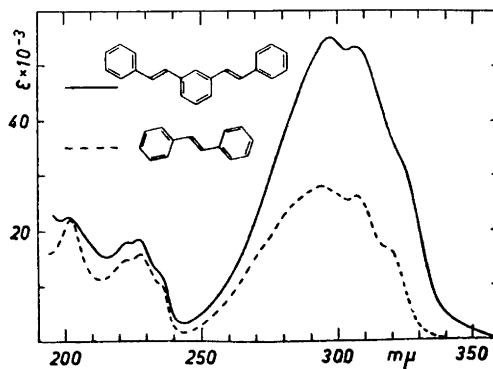


Fig. 9. Molecular extinction curves of *m*-distyrylbenzene and stilbene in hexane.

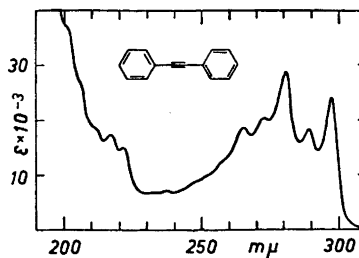


Fig. 10. Molecular extinction curve of diphenylacetylene (tolan) in hexane.

verified as shown in Fig. 8. Exactly the same relationships were found between the spectrum of *m*-distyrylbenzene and that of stilbene (Fig. 9).

The other "stationary" band at 228 $m\mu$ shows an intensity change intermediate between that of the conjugation band at 300 $m\mu$ and that of the true "partial" at 200 $m\mu$. With increasing length of the conjugated system it undergoes a slight red-shift, from about 228 $m\mu$ in stilbene to about 244 $m\mu$ in *p,p'*-distyrylstilbene, so that the band is really only semi-stationary. We may therefore have to do with the transitions between an isolated π -orbital (*e*) and a polyenelike π -orbital (*p*) discussed by Platt⁴. The difficulty is that there is no counterpart in the polyphenyl spectra; furthermore, there should be two different transitions, $e \rightarrow p$ and $p \rightarrow e$ in Platt's notation, and they should be weak. There does not seem to be more than one band, and it is rather strong. The alternative assignment of both stationary bands to $e \rightarrow p$ and $p \rightarrow e$ transitions has been proposed¹⁷, but the arguments do not seem decisive.

It may be significant that the pattern of vibrational structure in the semi-stationary band is very similar to that of the conjugation band⁶. Even for styrene this feature is apparent; it now seems to overlap on the long wave side of the stationary band at 204 $m\mu$ (Fig. 1). When the vibrational spacings of the conjugation band change and the peaks sharpen, as upon replacement of the ethylenic bond in stilbene with an acetylenic bond (Fig. 10), the structure of the semi-stationary band, now at 205–25 $m\mu$, changes correspondingly.

Band width and steric hindrance

The absorption spectrum of mono-*cis-p*-(phenyl-butadienyl)stilbene requires a few comments. As is well known, the introduction of sterically hindered *cis*-bonds in a polyene- or diphenylpolyene-chain *etc.* shifts the absorption maximum of the main band considerably towards the ultraviolet. This is usually explained as an increase in the pure electronic transition energy due to a greater reduction of the resonance energy in the excited state than in the ground state. The present spectrum, however, shows rudimentary vibrational structure with the peaks not far from the positions in the all-*trans*-isomer (Fig. 6). The observed shift of the maximum, also in the completely structureless bands of *cis*-isomers of stilbene, diphenylbutadiene, *etc.*, must therefore be due mainly to a larger change in bond order upon excitation, so that according to the Franck-Condon principle more vibrational quanta are co-excited, and the maximum in the intensity distribution shifted towards the ultraviolet.

Similar spectral evidence is also available from Karrer's hindered *cis*-isomers of lycopene¹⁸ and diphenyl-tetramethyl-octadecanonaene¹⁹. It is here quite clear that the pure electronic transition energy is only increased from that of the all-*trans*-compound by the same small amount as for the un-hindered *cis*-isomers²⁰, but the transition probability maximum is shifted to much higher vibrational levels, and a greater band width results.

EXPERIMENTAL

The spectra were recorded in a Beckman DK-1 instrument using hexane as a solvent except when otherwise noted. In the lowest wave length region 2 mm silica cells were used. The sparingly soluble compounds were also measured in 5 cm cells.

Biphenyl, *m*-terphenyl, styrene, stilbene, 1,4-diphenylbutadiene, and diphenylacetylene (tolan) were purified commercial samples. Professor L'Ecuyer, Québec, most kindly provided samples of *m*-distyrylbenzene, *p*-distyrylbenzene and *p*-(phenylbutadienyl)-stilbene prepared by the Meerwein reaction¹⁰.

p-Distyrylbenzene could also be prepared in good yield from *p*-dibromobenzene and phenylacetaldehyde in a Grignard reaction. The intermediate diol was dehydrated by boiling with toluenesulfonic acid. M. p. 265 °C.

p,p'-Distyrylstilbene. *p,p'*-Dinitrostilbene, prepared according to Walden and Kernbaum²¹, was reduced with stannous chloride²² to *p,p'*-diaminostilbene, m. p. 228 °C. 1.05 g of this compound (0.005 moles) was dissolved in 2.2 ml of 25 % HCl, and, after cooling and addition of 2.2 g of ice, diazotized with 0.37 g of NaNO₂ in 0.75 ml of water. The solution of the diazonium salt was poured into a cooled mixture (0 °C) of cinnamic acid (0.74 g), acetone (7.5 ml), anhydrous sodium acetate (0.8 g), and cupric chloride (0.23 g). The mixture was stirred vigorously and allowed to warm up slowly until the gas evolution started. The reaction mixture was steam-distilled, the water decanted off while hot, and the dry residue successively extracted in a Soxhlet apparatus with ethanol, acetone, hexane and chloroform. The earlier fractions contained *p,p'*-dichlorostilbene, m. p. 170 °C (Sandmeyer reaction), and a yellow substance which proved to be *p*-chloro-*p'*-styryl-stilbene, m. p. 238–40°, λ_{\max} in hexane 353 m μ ; this product is to be expected in a combination of the Meerwein and Sandmeyer reactions. The boiling chloroform deposited orange-yellow crystals of *p,p'*-distyrylstilbene already during the extraction. These were redissolved in chlorobenzene and precipitated with hexane. The very fine crystals were centrifuged, washed several times with hexane and finally sublimed *in vacuo*. The substance decomposes without melting at 310 °C, and is so extremely insoluble in the solvents commonly used for ultraviolet spectroscopy that even with chloroform quantitative extinction values could not be obtained.

Attempts to prepare o-distyrylbenzene. In a Grignard reaction between α,α' -dibromo-*o*-xylene and benzaldehyde no crystalline material was obtained. In a Grignard reaction between benzyl bromide and *o*-phthalaldehyde the only crystalline product was bibenzyl. In a Meerwein reaction between the diazonium salt of *o*-aminostilbene and cinnamic acid, following the prescription of L'Ecuyer and Turcotte¹⁰, only stilbene and *o*-chlorostilbene could be isolated as crystalline materials. Furthermore, a sample of the compound described by these authors as *o*-distyrylbenzene, m. p. 120–22 °C, and kindly put at my disposal by professor L'Ecuyer, was examined spectroscopically both in the U.V. and the I.R. and proved to be stilbene, which melts at 124 °C when pure, admixed with some yellow impurity.

Attempt to prepare o,o'-distyrylstilbene. *o,o'*-Dinitrostilbene was prepared according to Bischoff²³ and reduced with stannous chloride²² to *o,o'*-diaminostilbene, m. p. 174–75 °C. An attempted Meerwein reaction gave as the only crystalline material a good yield of the Sandmeyer product *o,o'*-dichlorostilbene, m. p. 98 °C.

Attempt to prepare o,p'-distyrylstilbene. *o,p'*-Dinitrostilbene was made in a cross-reaction between *o*- and *p*-nitrobenzylchloride. In order to keep the less reactive *o*-compound in excess during the reaction, the procedure was as follows: A solution of 17 g of *o*-nitrobenzylchloride and 2 g of *p*-nitrobenzylchloride in 72 ml of ethanol was placed in a three-necked flask equipped with a stirrer and two dropping funnels. A solution of 15 g of

p-nitrobenzylechloride in 56 ml of warm ethanol in one of the funnels and a solution of 11.5 g of KOH in 140 ml of ethanol in the other funnel were allowed to run slowly into the flask over the same period of time. After cooling, the crystal mass was filtered off and boiled with benzene. The insoluble residue was recrystallized from acetone; it consisted of *p,p'*-dinitrostilbene. Upon cooling the benzene solution, white-yellowish needles of *o,o'*-dinitrostilbene deposited. On further cooling, yellow needles of *o,p'*-dinitrostilbene started growing from the bottom of the vessel. The reaction products could also be resolved by chromatography of the benzene solution on alumina; the *o,o'*-compound is adsorbed less strongly than the *o,p'*-compound. After recrystallization, *o,p'*-dinitrostilbene melts at 143 °C, as compared with 138–140 °C reported for a sample made by a different method²⁴. *o,p'*-Diaminostilbene was obtained by reduction with stannous chloride, and melted at 125 °C. A Meerwein reaction of its diazonium salt with cinnamic acid gave as the only crystalline products, *o,p'*-dichlorostilbene, m. p. 71 °C, and a good yield of a yellow substance which proved to be *o*-chloro-*p'*-styrylstilbene, m. p. 200 °C, λ_{\max} in hexane 350 μ .

Isomerization of p-distyrylbenzene. A solution of *p*-distyrylbenzene in benzene was exposed to daylight for several weeks. Extensive destruction took place. The benzene was distilled off and the residue dissolved in hexane and chromatographed on alumina with benzene/hexane as developer. The first few fractions that were collected were empty. Then came the only fraction containing more than traces of substance; it yielded a compound melting at about 95 °C, which must be the mono-*cis*-isomer. Upon illumination in the presence of catalytic amounts of iodine the spectrum changed towards the characteristic spectrum of the all-*trans*-isomer, but the rearrangement was apparently accompanied by much destruction.

Isomerization of p-(phenylbutadienyl)stilbene. The illumination and the separation of the mixture was performed as for *p*-distyrylbenzene (see above). The only fraction containing any quantity of substance was collected quite early. The substance did not crystallize and may be one or more of the three possible mono-*cis*-isomers. In view of the intense *cis*-peak in the U.V. spectrum the *cis*-bond is most probably centrally located. Upon illumination in the presence of iodine the spectrum reverted very quickly to the characteristic spectrum of the all-*trans*-isomer.

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