# The Spatial Configurations and the Ultraviolet Absorption Spectra of the Stilbene Derivatives(1)

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The ultraviolet absorption spectrum of *trans*-stilbene has a maximum at λ 2940 A., which is shifted progressively toward shorter wave lengths as one, and then two methyl groups are introduced into the $\alpha$- and $\alpha'$-positions of the molecule.(2) These hypsochromic shifts have been explained as being due to the steric interferences of the substituents which prevent the molecule from assuming a planar configuration.

On the other hand, *cis*-stilbene has an absorption maximum at shorter wave lengths than the trans isomer. This has been also explained by the inference that in this compound the two phenyl groups can not be simultaneously coplanar with the central ethylenic linkage owing to the steric necessities. For the same reason, it is inferred that the resonance energy is less in the cis isomer than in the trans isomer. This provides a reasonable explanation for the fact the cis isomer is more labile and is easily converted to the trans isomer by the action of heat or of various reagents.(3)

Similar hypsochromic effects have been observed also in other cases; for examples, *ortho*-substituted biphenyls,(4) *N*, *N*-dimethylanilines,(5) and acetophenones,(4,a) and have been explained in a similar manner by the steric interferences by the substituents.

These prevailing explanations are based on the rather vague assumption that the spectrum is related to resonance and hence to the planar configuration of the molecule, and that the destruction of the planar configuration may cause a change in the spectrum. But how the spectrum changes when the planar configuration is prevented to any extent is not satisfactorily accounted for by these explanations.

Jones(6) has divided several stilbene derivatives into three groups: compounds which have spectra similar to that of styrene, compounds which have spectra similar to that of *trans*-stilbene, and compounds which have spectra intermediate between these two extremes. In triphenylethylene and tetraphenylethylene, all the phenyl groups cannot be accommodated in a strainless planar structure, so that one, or two, phenyl groups are turned out from the plane, leaving the two remaining *trans*-related phenyl groups in the plane of the central ethylenic linkage, hence these compounds have the spectra similar to that of *trans*-stilbene; that is, these compounds have the structures containing a "stilbene chromophore". Also, a close similarity of the spectra between 1, 1-diphenylethylene and styrene has been explained by assuming a rotation of one of the phenyl groups of the former compound out of the plane of the ethylenic linkage, giving rise to a molecule containing a "styrene chromophore". In a similar manner, the fact that *trans*-$\alpha$, $\alpha'$-dimethylstilbene has a spectrum similar to that of styrene has been explained by the assumption that only one phenyl group is turned out, leaving a structure containing a "styrene chromophore".

But such considerations can not explain the "intermediate" spectra of *cis*-stilbene and $\alpha$-methylstilbene. Further, the two phenyl groups in $\alpha, \alpha'$-dimethylstilbene are in equivalent positions with regard to the molecular structure, so that; even when one of these is turned out from the plane, the steric strain cannot be relieved. Rather, both should be considered as turned out to the same extent from the plane of the central ethylenic linkage. According to this assumption, the so-called "stilbene chromophore" or "styrene chromophore" must be absent in $\alpha, \alpha'$-dimethylstilbene. But it may be rather reasonable to think that the deviation of both phenyl groups to some extent from the plane of the ethylenic linkage does result not in the notable deformation or the simple destruction of the

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(2) (a) H. Ley and F. Rinke, *Ber.*, **56**, 771 (1923).
(b) B. Arends, *Ber.*, **64**, 1936 (1931).

(3) G. Egloff, G. Hulla, and V. I. Komarewsky, "Isomerization of Pure Hydrocarbons" Reinhold, 1942, p. 164-167.

(4) (a) W. H. Rodebush, *et al.*, *J. Am. Chem. Soc.*, **62**, 2906 (1940); **63**, 3018 (1941); **68**, 896 (1946).
(b) D. W. Sherwood and M Calvin, *J. Am. Chem. Soc.*, **64**, 1350 (1942).

(5) Remington, *J. Am. Chem. Soc.* **67**, 1838 (1945).

(6) R. N. Jones, *J. Am. Chem. Soc.*, **65**, 1818 (1943).

spectrum characteristic of stilbene, but only in the shift of the absorption maximum toward shorter wave lengths, with the result that the spectrum of $\alpha, \alpha'$-dimethylstilbene happens to resemble that of styrene. This assumption implies that the perfect coplanarity is not prerequisite to the appearance of a spectrum characteristic of such a conjugated system as stilbene or biphenyl but that the necessity of coplanarity is a question of degree.

From such a view point, and generally, in order to obtain a clearer understanding of the relationship between the resonance and the absorption spectrum which is frequently apt to be misunderstood, the present author has carried out new measurements of the absorption spectra of several stilbene derivatives and has performed calculations to assess the quantitative relations between the degree of the deviation from the coplanarity and the absorption spectrum as well as the resonance energy for the stilbene derivatives.

## Calculations

The calculations have been performed according to the usual molecular orbital method(7) and therefore require no detailed description. Since, for this treatment, the stilbene molecule can be considered as belonging to the symmetry group $D_2$, the secular equation for the determination of the fourteen approximate molecular orbitals as linear combinations of $2p\pi$ atomic orbitals is factorized into the following four equations:

$$A_1,\ x^5+\gamma x^4-(5+\alpha^2)x^3-5\gamma x^2+(4+3\alpha^2)x+4\gamma=0,$$

$$B_2,\ x^5-\gamma x^4-(5+\alpha^2)x^3+5\gamma x^2+(4+3\alpha^2)x-4\gamma=0,$$

$$B_1,\ x^2-1=0,$$

$$B_3,\ x^2-1=0,$$

where $x=W/\beta=(Q-E)/\beta$, $Q$, $E$, and $\beta$ having their usual meanings. By parameters $\alpha$ and $\gamma$ allowances are made for the situation that the $1-2$, $1'-2'$ and $1-1'$ bonds have lengths different from those in the phenyl group, $\alpha\beta$ and $\gamma\beta$ denoting the exchange integral for the $1-2$ or $1'-2'$ and the $1-1'$ bond respectively. (See Fig. 1.)

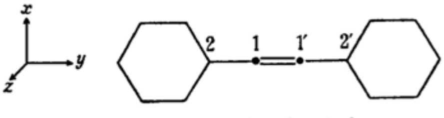

Fig. 1.—Stilbene molecule skeleton.

Now, since the exchange integral can be taken to be approximately proportional to the overlap integral $S$,(8) the overlap integal for some $\pi-\pi$ bond divided by that for the $\pi-\pi$ bond in benzene whose length is 1.39 A., namely $S/S$ (1.39 A.), represents the coefficient of $\beta$ in the exchange integral for this $\pi-\pi$ bond. The relation between the $\pi-\pi$ bond length and the corresponding overlap integral can be obtained from Mullikens' Tables.(9) Thus, using the value of 1.34 A. for the length of the $1-1'$ bond which is assumed to be not varied to any important extent by resonance,(10) $\gamma$ is estimated to be 1.08.

According to the results of X-ray diffraction measurement reported by Robertson and Woodward,(10) stilbene has a planar configuration and the length of the bonds joining the phenyl groups to ethylenic carbon atoms, namely the $1-2$ and $1'-2'$ bonds, is 1.45 A.. With this value, $\alpha$ is estimated to be 0.900 for stilbene. This value of $\alpha$ must become smaller as the phenyl groups are turned out from the plane of the central ethylenic linkage. Thus we can see how the energy levels change as the phenyl groups are twisted gradually from the plane, by taking decreasing values such as 0.9, 0.8, 0.7,......, 0.1, 0, in turn for $\alpha$ in the above equations and solving them.

The results of such calculations are shown in Fig. 2, where the values of $W$ are plotted against $\alpha$. The solid lines represent the energy levels belonging to $A_1$ and the broken lines the energy levels belonging to $B_2$. In addition to these levels, there are two two-fold degenerate levels at $-\beta g$ and $+\beta$ belonging to $B_1$ and $B_3$, whose energies do not vary with the value of $\alpha$. In the lower part of Fig. 2, the calculated extra-resonance energy, R. E., is plotted against $\alpha$.

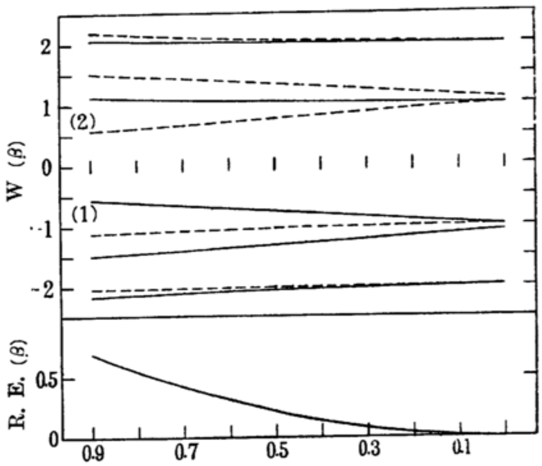

Fig. 2.—The energy levels and the resonance energy as functions of $\alpha$ for stilbenes.

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(7) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry", John Wiley & Sons, Inc., 1944, p. 255.

(8) (a) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).
(b) J. Van Dranen and J. A. A. Ketelaar, *J. Chem. Phys.*, **17**, 1338 (1949).

(9) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(10) J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* (London), **A 162**, 568 (1937).

In the ground state, the levels lower than zero are all occupied by pairs of electrons, and the levels higher than zero are all vacant. According to the group theory, the transition from $A_1$ to $B_2$ is allowed by the absorption of the light polarized in the y-direction. Therefore, since the present calculations apply to vertical excitation, that is, to electron jumps without change in nuclear configuration, the absorption band characteristic of stilbene derivatives is assumed to correspond to the energy difference between the (1)- and (2)-levels in Fig. 2, which is denoted by $\Delta E$. From Fig. 2, it can be seen that the value of $\Delta E$, which is $1.150\,\beta$ when $\alpha=0.900$, that is, for stilbene itself, increases with the decrease of the value of $\alpha$, and simultaneously, the resonance energy decreases. Thus, the present calculations indicate clearly that the absorption maximum is shifted progressively toward shorter wave lengths, and simultaneously, the resonance energy decreases, as the departure from the planar configuration becomes gradually larger. When $\alpha=0$, the energy levels reduce to those of benzene and ethylene, and the value of $\Delta E$ becomes $2\beta$. In Table 1, the values of $\Delta E$ and R. E. for various values of $\alpha$ are recorded.

Table 1

| $\alpha$ | 0.9 | 0.8 | 0.7 | 0.6 | 0.5 | 0.4 | 0.3 | 0.2 | 0.1 | 0 |
|---|---|---|---|---|---|---|---|---|---|---|
| $\Delta E(\beta)$ | 1.150 | 1.236 | 1.326 | 1.422 | 1.522 | 1.624 | 1.730 | 1.838 | 1.940 | 2 |
| R. E. ($\beta$) | 0.690 | 0.548 | 0.418 | 0.312 | 0.216 | 0.134 | 0.076 | 0.032 | 0.009 | 0 |

According to Platt,(11) in the absorption spectrum of benzene, the "center-of-gravity of singlets", 48,000 cm.$^{-1}$ in wave number, *i. e.* the average of the energies of the three singlet levels measured in solution, corresponds to the energy difference of $2\beta$ calculated by the molecular orbital method of the same order of approximation as the present treatment. On the other hand, the wave number 34,014 cm.$^{-1}$ of the observed absorption maximum of stilbene corresponds to the calculated energy difference $\Delta E$ of $1.150\,\beta$. Therefore, in order to correlate the position of the absorption maximum with the calculated energy difference $\Delta E$, it is assumed that the former expressed in wave number changes linearly with respect to the change in the latter from 34,014 cm.$^{-1}$ corresponding to $\Delta E=1.150\,\beta$ to 48,000 cm.$^{-1}$ corresponding to $\Delta E=2\beta$.

The next problem to be settled is in what manner the value of $\alpha$ varies as the phenyl groups are gradually turned out. Denoting by $\theta$ the angle through which the axis of the $2p\pi$-orbital on C atom 2 or 2′ is twisted about the 1−2 or 1′−2′ bond axis against the axis of the $2p\pi$-orbital on C atom 1 or 1′ which lies perpendicular to the plane of ethylenic linkage, it is easily verified that the overlap integral $S(\theta)$ in the case where the angle of twist is $\theta$ is equal to the overlap integral $S(0)$ when $\theta$ is zero, multiplied by $\cos\theta$. If it is assumed that the exchange integral is approximately proportional to the overlap integral in such a case also, and further that the bond length $R$ is maintained constant even when the phenyl groups are turned out to any extent, $\alpha$ would be $S(R)\cos\theta/S(1.39\text{ A.})$. But any deviation from the planar configuration must inevitably inhibit the $\pi-\pi$ interaction to the corresponding extent, and consequently must be accompanied by change in the bond length. Therefore, we need to take into consideration the variation of $\alpha$ due to the change in the bond length resulting from the twist. This problem may be very complicated, but we can proceed approximately as follows.

The length $R$ of the 1−2 bond was tentatively assumed to vary with $\theta$ according to the relation

$$\{S(R)-S(1.54\text{ A.})\}/\{S(1.45\text{ A.})-S(1.54\text{ A.})\}=S(\theta)/S(0)=\cos\theta,$$

since $R$ will vary from 1.45 A. for stilbene to 1.54 A., the length of the normal $C-C$ single bond, as $\theta$ varies from 0° to 90°. When the angle of twist $\theta$ is given, the corresponding value of $S(R)$ is easily obtained, and then the value of $\alpha$ is given by $S(R)\cos\theta/S(1.39\text{ A.})$. Thus the position of absorption maximum for a stilbene derivative in which the phenyl groups are twisted from the coplanar position to any extent is inferred by estimating the $\Delta E$ by means of Fig. 2 for an appropriate value of $\alpha$ and then the corresponding wave number by means of the linear relationship assumed above between the absorption maximum and $\Delta E$.

Conversely, when the position of the absorption maximum is known experimentally for some stilbene derivative, the values of $\Delta E$, $\alpha$, $\theta$, $R$, and R. E. can be successively estimated by reversing the above procedure.

A few examples of the results of such estimations are shown in Table 2. In the calculations of the extra-resonance energies, the value of 21.74 kcal. was used for $\beta$, which was deduced from the calculated value $0.690\,\beta$ and the observed value 15 Kcal.(12) for the extra-resonance energy for stilbene itself. In $\alpha$-methylstilbene, the positions of the two phenyl groups are not equivalent, and therefore, their angles of twist may not be equal. But they were assumed to be so in deducing the above values.

The difference in resonance energy between the trans and the cis isomers of stilbene as calculated above is 3.9 kcal./mol in satisfactory agreement with the experimental value of 3 kcal./mol estimated from the results of the thermal isomerization by Kistiakowsky and Smith(13) and by Taylor

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(11) J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

(12) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1933).

(13) G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, **56**, 638 (1934).

Table 2

| | λ(A.)obs. | ΔE(β) | α | R. E. | | θ | R(A.) |
|---|---|---|---|---|---|---|---|
| *cis*-Stilbene | 2780 | 1.268 | 0.765 | 0.51 β | 11.1 kcal. | 29° | 1.462 |
| *trans*-α-Methylstibene | 2720 | 1.318 | 0.709 | 0.43 | 9.3 | 36° | 1.467 |
| *trans*-α, α′-Dimethylstilbene | 2435 | 1.578 | 0.445 | 0.17 | 3.7 | 58° | 1.492 |
| *trans*-α, α′-Diethylstilbene | 2400 | 1.616 | 0.408 | 0.14 | 3.0 | 60° | 1.496 |

Table 3

The Absorption Maxima of the Stilbene Derivatives

| | *Trans* | λ(A) | ε×10⁻⁴ | *Cis* | λ(A.) | ε×10⁻⁴ |
|---|---|---|---|---|---|---|
| Stilbene | (1) m. p. 123–4° | 2940 | 2.76 | (1′) b. p. 136–7°/10 mm. | 2780 | 0.98 |
| α-Methylstilbene | (2) m. p. 83.0–83.5° | 2720 | 2.10 | (2′) b. p. 151–5°/14 mm. | 2670 | 0.934 |
| α, α′-Dimethylstilbene | (3) m. p. 107° | 2435 | 1.226 | (3′) m. p. 67° | 2520 | 0.878 |
| α-Methyl-α′-ethylstilbene | (4) m. p. 47–8° | 2400 | 1.195 | | | |
| α, α′-Diethylstilbene | (5) m. p. 77–8° | 2375 | 1.102 | (5′) b. p. 177–8°/22 mm. | 2440 | 0.774 |
| Methyltriphenylethylene | m. p. 88–9° | 2750<br>2260 | 0.986<br>1.372 | | | |

and Murray.(14)

Regarding the angle of twist, there is no available experimental evidence such as X-ray diffraction measurement. But these values may be guessed from purely geometrical considerations. Thus, according as we assume a twisted structure for *trans*-α, α′-dimethylstilbene in which the ortho hydrogen atom of a phenyl group just touches the methyl group attached to the same ethylenic carbon atom as the phenyl group or a structure in which that hydrogen atom just touches the other methyl group, the angle of twist is calculated to be 60° or 56°, the following values for distances and angles being used: C=C, 1.34 A.; $C-CH_3$, 1.54 A.; $C_6H_5-C$, 1.49 A.; C−C in $C_6H_5$, 1.39 A.; $C_6H_5-H$, 1.08 A.; angles $C=C-CH_3$ and $C=C-C_6H_5$, 124°20′(15); $CH_3$-radius, 2.0 A.; H-radius, 0.9 A. (the "Wirkungsradius" of Stuart(6)) (Fig. 3.).

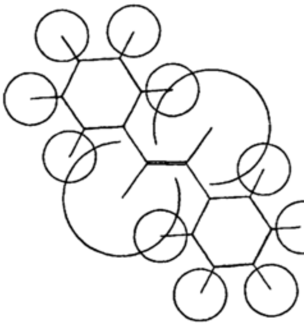

Fig. 3.—Scale drawing of *trans*-α, α′-dimethylstilbene.

For *cis*-stilbene, using the same values except for $C_6H_5$-C, for which the length is assumed to be 1.46 A., the angle of twist of both phenyl groups out of the plane of the ethylenic linkage is calculated to be about 25°. These values for the angles of twist are in fair agreement with the values calculated above from the absorption spectra. Although to these agreements too much significance should, perhaps, not be attached mainly because of uncertainties in the values for bond lengths, bond angles, and interference radii, it may be supposed that the quantitative relation between the angle of twist and the absorption spectrum has been satisfactorily assessed here.

## Results of Measurements of Spectra

The results of the measurements of the absorption spectra are shown in Fig. 4 and in Table 3.

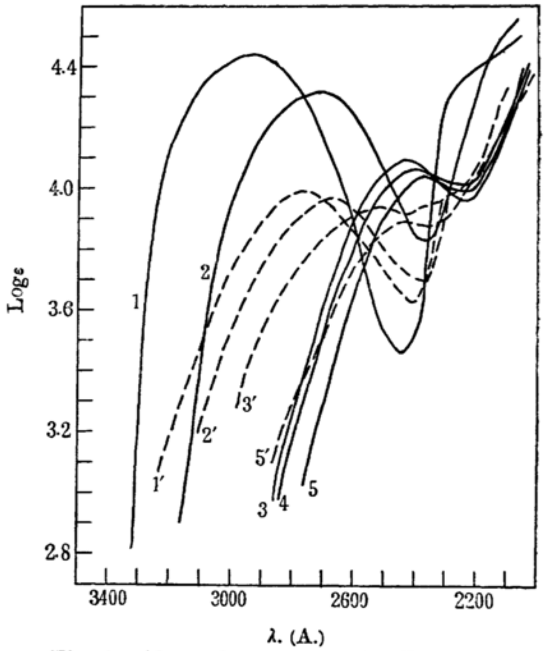

Fig. 4.—Absorption spectra of stilbene derivatives. The solid lines are those for *trans* compounds and the broken-lines those for *cis* compounds listed in Table 3.

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(14) T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

(15) L. Zechmeister and A. L. LeRosen, *J. Am. Chem. Soc.* **64**, 2755 (1942).

It can be seen that the absorption maximum is shifted progressively toward shorter wave lengths and decreases in intensity gradually, as a larger substituent is introduced into the $\alpha$- and $\alpha'$-positions of *trans*- or *cis*-stilbene. In addition it may be noticed that the absorption spectra for the trans and those for the cis isomers form two groups quite distinct from each other in that the former shows a larger molecular extinction coefficient than the latter. This fact may be explained on the basis of the theory advanced by Mulliken(16) and applied to the interpretation of the spectra of carotenoids(17) that the longer the conjugated system in the direction of the electric vector of the light wave responsible for an absorption band, the greater is the intensity of the absorption maximum. On account of this fact, it is believed that the present measurements make it possible to make assignment of trans or cis configuration to these compounds, even when the difference in the position of the absorption maximum between the trans and the cis isomers is very small as compared with that between the two isomers of stilbene, or even when the maximum of a trans isomer is at shorter wave lengths than that of the corresponding cis isomer as in the case of dimethylstilbene. Thus, the geometrical configuration has now been determined as shown in Table 3 for diethylstilbene, methylstilbene and methylethylstilbene for which either only one of the possible geometrical isomers is known or, when both isomers are known, the geometrical configuration has not been unambiguously established.

The cis isomer of $\alpha,\alpha'$-dimethylstilbene has the absorption maximum at longer wave lengths than the trans isomer. Therefore, it would be anticipated from the above arguments that the former is more stable than the latter. Actually, it was reported by Lamart-Lucas and coworker(18) that the isomerization of the trans isomer to the cis isomer took place by heat whereas the reverse isomerization did not. But the results of the experiments by the present author were contrary to this theory. The isomerization by heat at 210°C. in the presence of traces of sulfuric acid gave an equilibrium mixture, in which the ratio of the amounts of the cis and the trans isomers was about 45:55, whether the starting material was the trans or the cis isomer. From this result, the difference in the stability between the two isomers of dimetylstilbene is concluded to be very small, the trans isomer to be slightly more stable. This conclusion is contrary to the anticipation from the absorption spectra alone. But a more careful examination of the stereochemistry of dimethylstilbenes shows that such may actually be the case, because, while in the trans isomer the steric repulsion between the large substituents may be almost completely relieved by the rotation of the two phenyl groups out of the plane of the molecule, in the cis isomer on the other hand, the steric repulsion between the two methyl groups can not be reduced by the rotation of the phenyl groups, the steric strain still remaining causing the cis isomer to be the less stable one.

Methyltriphenylethylene has the two absorption maxima at 2750 A. and 2260 A., and the absorption curve near the maximum at longer wave lengths coincides almost perfectly with that of *cis*-stilbene. On the other hand, the absorption spectrum of tetraphenylethylene resembles that of *trans*-stilbene. These facts may be thought to indicate that the two *trans*-related phenyl groups in tetraphenylethylene, if rotated out of the plane, permit the other *trans*-related phenyl groups to assume the configuration coplanar with the ethylenic linkage, and that, if one of the rotated phenyl groups is replaced by a methyl groud, even the *trans*-related phenyl groups cannot assume the coplanar configuration.

A similar relation may be found on comparison of the spectrum of *trans*-$\alpha$-methylstilbene with that of triphenylethylene.

## Experimental

**The measurements of the spectra.**—The absorption spectra were determined with a Beckman Quartz Spectrophotometer Model DU. 95% Ethanol was used as the solvent. The concentrations of the solutions were approximately $10^{-4}$ mole per liter in all the cases.

**Materials.**— $\alpha$, $\alpha'$-Dimethylstilbene was prepared by dehydration of 2, 2-diphenylbutanol-(3), which was obtained by the action of methylmagnesium iodide on methyldiphenylcarbinal.(19) The trans and the cis isomers were separated by fractionational crystallization from petroleum ether.

Other compounds were prepared by analogous methods.

**Isomerization of $\alpha,\alpha'$-dimethylstilbene.**—About 0.8 g. of *cis*-or *trans*-$\alpha,\alpha'$-dimethylstibene and pumice impregnated with concentrated sulfuric acid were placed in a sealed tube, and heated in boiling nitrobenzene for about 20 hours. The composition of the products were determined by comparing the melting-points with those of the standard mixtures prepared from known amounts of the two isomers.

## Summary

(1) With certain simple assumptions, calculations based on the molecular orbital method have been performed to assess the quantitative relations between the degree of the deviation from the coplanarity of the molecular configuration and the ultraviolet absorption spectrum as well as the resonance energy for the stilbene derivatives.

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(16) R. S. Mulliken, *J. Chem. Phys.*, **7**, 364 (1939).

(17) L. Zechmeister, *Chem. Rev.*, **34**, 207 (1944).

(18) Ramart-Lucas and M. E. Salmon-Legagneur, *Bull. soc. chim. France*, [4] **45**, 718 (1929).

(19) E. Ott, *Ber.*, **61**, 2135 (1928).

(2) New measurements of the spectra of the several stilbene derivatives have been carried out.

(3) By these calculations and the measurements of the spectra, it has been clarified that the absorption maximum is shifted progressively toward shorter wave lengths with the increasing angle of twist of the phenyl groups out of the plane of the ethylenic linkage.

(4) Further, from the results of these calculations and the observed position of the absorption maximum, it is possible to deduce the adequate values of the angle of twist and the resonance energy for any stilbene derivative.

(5) It has been shown that the absorption spectra for the trans isomers and those for the cis isomers of the stilbene derivatives form two groups quite distinct from each other in hat the former shows a larger molecular t extinction coefficient than the latter. On the basis of this fact, the assignments of the geometrical configurations have been determined for some stilbene derivatives.

(6) The experiments on the geometrical isomerization of $\alpha, \alpha'$-dimethylstilbene by heat have been carried out and the results have been interpreted, based on a consideration of the spatial configurations of the two isomers.

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