Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. VI. Triphenylethylene, Tetraphenylethylene and Tolan

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The method developed in the preceding part[1] of this series is applied to triphenylethylene, tetraphenylethylene and tolan, and the relation between the ultraviolet absorption spectra and the spatial configurations of these compounds is discussed.

Triphenylethylene and Tetraphenylethylene

Spectra. — The ultraviolet absorption spectra of tri- and tetraphenylethylene in chloroform were formerly measured by Arends[2]. According to the results, the spectra differ only slightly from the spectrum of *trans*-stilbene. Jones[3] explained this spectral similarity as follows. "The three phenyl groups of triphenylethylene and the four phenyl groups of tetraphenyl ethylene can not be accommodated in a strainless planar structure; the strain can be eased either by a small rotation of all of the phenyl groups along their 1, 4-axes, or by a larger displacement of one of the phenyl groups of triphenylethylene or two of the *trans*-related phenyl groups of tetraphenylethylene, leaving two remaining *trans*-phenyl groups in the plane of the ethylenic bond. This second hypothesis leaves the molecule of tetraphenylethylene with a *trans*-stilbene chromophoric system together with two *insulated* phenyl groups, the absorption of which is too feeble to affect the spectrum".

The spectra of these compounds in *n*-heptane and in benzene have been newly measured by the present author. The results are shown in Table I and Fig. 1, in which the spectra of *trans*-stilbene[1] are included for comparison.

The A-band (conjugation band) of triphenylethylene as well as that of tetraphenylethylene has no distinct fine structure in contrast to that of *trans*-stilbene. The B-band, on the other hand, of triphenylethylene has a pattern of fine

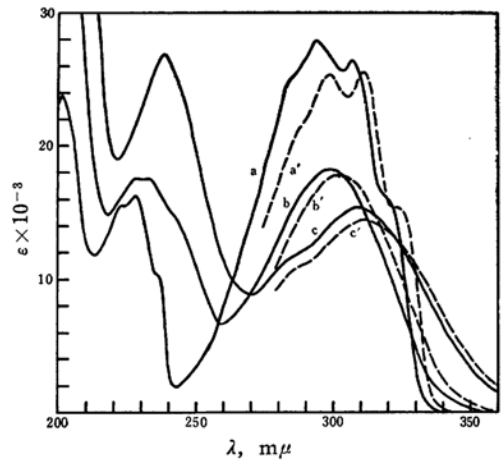

Fig. 1. Ultraviolet absorption spectra of *trans*-stilbene (a, in *n*-heptane; a', in benzene), triphenylethylene (b, in *n*-heptane; *b'*, in benzene), and tetraphenylethylene (c, in *n*-heptane; *c'*, in benzene) (cf. Table I).

structure closely similar to that of *trans*-stilbene.

Assuming that the maxima of the A-bands in the spectra of tri- and tetraphenylethylene in *n*-heptane are to be compared with the most intense maximum, viz. the γ-band, of fine structure of the A-band of *trans*-stilbene in the same solvent, the position of the maximum of the conjugation band is progressively shifted toward longer wavelengths as the number of phenyl groups in a molecule increases. The B-band is also shifted toward longer wavelengths in the same sequence. On the other hand, while the molecular extinction coefficient of the A-band decreases in the sequence, that of the B-band as well as that of the C-band increases markedly in the sequence.

Calculation and Discussion. — When it is assumed that triphenylethylene as well as tetraphenylethylene has a configuration in which the two *trans*-related phenyl groups are coplanar with the plane of the ethylenic bond according to Jones' second

1) H. Suzuki, This Bulletin, **33**, 379 (1960).
2) B. Arends, *Ber.*, **64**, 1936 (1931).
3) R. N. Jones, *J. Am. Chem. Soc.*, **65**, 1818 (1943).

TABLE I. ULTRAVIOLET ABSORPTION SPECTRA OF *trans*-STILBENE, TRIPHENYLETHYLENE AND TETRAPHENYLETHYLENE

Compound		A-band		B-band		C-band	
Solvent		λ_{max}, mμ	ε	λ_{max}, mμ	ε	λ_{max}, mμ	ε
trans-Stilbene							
n-Heptane	α	(320.5)	16000	(236)	10400	201.5	23900
	β	306.9	26500	228.5	16200		
	γ	294.1	27950	(222)	15500		
Benzene	α	(324.5)	15400				
	β	311.2	25600				
	γ	298.8	25340				
Triphenylethylene							
n-Heptane		298.5	18220	(242.5)	14570	(200)	40200
				232.0	17580		
				(228)	17540		
Benzene		301.8	17700				
Tetraphenylethylene							
n-Heptane		308.7	15300	238.5	26800	(203)	62500
		(285.8)	11700				
Benzene		311.2	14350				
		(288)	10900				

Wavelengths in parentheses denote inflections.

TABLE II. RESULTS OF CALCULATIONS

	trans-Stilbene		*Triphenylethylene*		*Tetraphenylethylene*	
	(γ)	(β)	(γ)	(β)	(γ)	(β)
λ_{max}, mμ	294.1	306.9	298.5		308.7	
$\Delta E_A(-\beta)$	1.1423		1.112	1.193	1.044	1.132
ρ	0.9084		0.946	0.849	1.032	0.922
ρ'	—		0.669	0.529	0.730	0.652
θ°	0		40	52	34.5	42
R, Å	1.445		1.467	1.481	1.462	1.469
$R.\ E.\ (-\beta)$	0.704		0.764	0.610	0.906	0.720
$p_{\alpha-\alpha'}$	0.8555		0.845	0.873	0.820	0.852
$p_{\alpha-1}$	0.384		(ρ) 0.400	0.359	0.310	0.277
			(ρ') 0.285	0.225		
$\Delta E_B(-\beta)$	1.571		1.556	1.597	1.522	1.566

hypothesis, it is evident that calculations quite similar to the one for stilbene described in the preceding part of this series can be applied to these compounds.

Alternatively, when it is assumed that in tetraphenylethylene all of the phenyl groups are rotated out of the plane of the ethylenic bond to the same extent as each other according to Jones' first hypothesis, the secular equation for the determination of the molecular orbitals as linear combinations of $2p\pi$ atomic orbitals is factorized into one equation identical in form with the one for stilbene and two equations for benzene, when ρ' is $1/\sqrt{2}\times\rho$, $\rho'\beta$ representing the $\pi-\pi$ resonance integral for each bond connecting a phenyl group to a ethylenic carbon atom.

Similarly, when it is assumed that ρ' is equal to $1/\sqrt{2}\times\rho$ also in triphenylethylene, in which the $\pi-\pi$ exchange integral for each of the bonds connecting two phenyl groups to the same ethylenic carbon atom and that for the bond connecting the other phenyl group to the other ethylenic carbon atom are denoted by $\rho'\beta$ and $\rho\beta$, respectively, the secular equation for this molecule can be factorized into an equation identical in form with the one for stilbene and the equation for benzene.

Therefore, whichever the configurations may be, the calculation based on the same equation as the one for stilbene can be applied to these compounds. Thus, after the procedure described in the preceding part of this series, the values of ρ can be computed from the observed positions of the A-bands.

Since the A-bands of these compounds

are at longer wavelengths than the A-γ-band of *trans*-stilbene as the reference, the values of ρ for the former compounds should be larger than that for the latter. If the models according to Jones' second hypothesis are chosen, the large values of ρ for tri- and tetraphenylethylene relative to the value for *trans*-stilbene must be explained only by the assumption that the lengths of the bonds linking the coplanar *trans*-related phenyl groups to the ethylenic carbon atoms in tri- and tetraphenylethylene were shorter than the corresponding one in *trans*-stilbene, since the most probable configuration of *trans*-stilbene is considered to be already planar. This is undoubtedly implausible.

The inference that Jones' second hypothesis is implausible seems to be supported also by the following consideration. Thus, as is seen in Table I and Fig. 1, the molecular extinction coefficient of the A-band decreases markedly in the order *trans*-stilbene > triphenylethylene > tetraphenylethylene. If there were any *trans*-stilbene chromophore in these compounds, all these compounds would show the almost identical molecular extinction coefficient at least approximately.

Now, when the alternative models according to Jones' first hypothesis are assumed for the most probable configurations of tri- and tetraphenylethylene, the values of ρ' are obtained from the values of ρ, and then, from the values of ρ' the values of θ, R and $p_{\alpha-1}$ can be obtained by the procedure analogous to the one for stilbene in the preceding part of this series. The results of calculations are shown in Table II, in which those for *trans*-stilbene are included for comparison. (The symbols have the same significance as in the preceding part.)

The fact that the calculated value of θ in triphenylethylene is apparently greater than that in tetraphenylethylene is, needless to say, due to the probably unreal starting assumption that one of the phenyl groups in triphenylethylene is coplanar with the plane of the ethylenic bond. The most probable configuration of triphenylethylene is presumed to be the one in which all of the phenyl groups are rotated out of the plane of the ethylenic bond to certain extents. Therefore, no reliance is to be placed on the values of θ, R and $p_{\alpha-1}$ for this compound, while the values of $R.E.$, $p_{\alpha-\alpha'}$ and ΔE_B can probably be considered as rough approximations.

The above mentioned calculations are based on the assumption that the maxima of the A-bands of tri- and tetraphenylethylene are to be compared with the γ-band in the A-band of *trans*-stilbene. However, as is seen in Table I and Fig. 1, while the maxima in the spectra of tri- and tetraphenylethylene in benzene are considered to correspond to the maxima in *n*-heptane, the most intense maximum in the spectrum of *trans*-stilbene in benzene is the β-band and not the γ-band as in *n*-heptane. Accordingly the possibility that the β-band instead of the γ-band is to be taken as the reference can not perhaps be ruled out. In Table II, the results of the calculations carried out by taking the β-band as the reference are also shown, being denoted by symbol β, in addition to those mentioned already, which are denoted by symbol γ. However, in view of the correlations of these results with some properties of the compounds, results γ seems more adequate, and hence subsequently the results of the calculations refer solely to results γ.

The B-bands are probably due to the allowed transitions from the highest occupied orbitals to the vacant orbitals with the energy of $-\beta$, or from the occupied orbitals with the energy of $+\beta$ to the lowest vacant orbitals, similarly to the case of stilbene. The C-bands are probably due to the allowed transitions from the orbitals with the energy of $+\beta$ to the orbitals with the energy of $-\beta$.

The B-band as well as the C-band increases the intensity in the order *trans*-stilbene < triphenylethylene < tetraphenylethylene, with an increasing number of benzene nuclei. It is interesting that the ratio of the molecular extinction coefficients of the C-bands of these compounds are roughly 1:2:3, in accordance with the ratio of the numbers of the orbitals which are considered to participate in these transitions.

In addition, it is of interest that the magnitude of the red-shift of the conjugation band associated with the change of solvent from *n*-heptane to benzene is appreciably smaller in the cases of tri- and tetraphenylethylene than in the case of *trans*-stilbene as well as some para-substituted *trans*-stilbenes which are presumed to be planar. If the presumption in the preceding part of this series that the shift is due to the special interaction between the π-orbitals of benzene and

those of the solute molecule is correct, this fact may be related to the nonplanarity of the configurations of tri- and tetraphenylethylene. This subject will be discussed more fully in a later part of this series.

Correlations between the Spatial Configurations and Some Properties of the Compounds.—The melting point of tetraphenylethylene is 223~224°C, and is considerably lower than that of its positional isomer, *p*,*p'*-diphenyl-*trans*-stilbene (about 300°C). In addition, the solubilities of the former compound in usual organic solvents are much greater than those of the latter. These facts are probably due to the nonplanarity of the configuration of tetraphenylethylene. The melting point of triphenylethylene is 68~69°C and markedly lower than that of its positional isomer, *p*-phenyl-*trans*-stilbene (about 220°C), and even than that of *trans*-stilbene (125°C). This fact is probably due to the nonplanarity and the unsymmetrical nature of the configuration of triphenylethylene.

According to Everard and others[4], the exaltation of the molecular refraction ($E[R]_D$) of *trans*-stilbene is +6.6, and that of triphenylethylene is about the same as, or only 0.1 at most less than, that of *trans*-stilbene. This fact may be considered to indicate that the extent of conjugation in triphenylethylene is almost equal to that in *trans*-stilbene, almost in complete accordance with the present conclusion deduced from the ultraviolet absorption spectra.

Next, the relations between the spatial configurations and the reactivities of these compounds will be discussed. In general, steric effects in reactions of olefinic compounds may be divided into the two main types: the steric hindrance to the approach of the reagent to the reaction site and the steric hindrance to resonance. The former may be illustrated by the fact that the rate of bromination of neopentylethylene is smaller than that of *t*-butylethylene[5]. That is, the steric effect of this type retards the reactions in most cases.

Tetraphenylethylene does not add bromine[6,7]. This is probably due to the steric effect of the first type mentioned above. That is, it seems that the phenyl groups rotated out of the plane of the central ethylenic bond inhibit the approach of the reagent to the bond.

According to Leavitt and others[8], the "methyl affinity" is 205 for *trans*-stilbene, 85 for triphenylethylene, and less than 25 for tetraphenylethylene. The "methyl affinity" is considered as a measure of reactivity of compounds to the methyl radical, although it is not clear which atoms of the compounds are attacked. The order of the "methyl affinity" mentioned above appears to be well explained in terms of the steric effect of the first type.

The reaction of olefins with perbenzoic acid in nonpolar solvents gives excellent yields of the corresponding epoxides. It has been presumed that in this reaction perbenzoic acid acts as a "double-bond reagent". According to Lynch and Pausacker[9], the reactivity of the series of phenyl-substituted ethylenes toward perbenzoic acid follows the double-bond orders of the olefinic links calculated by Coulson and Jacobs[10] (i.e. styrene>*trans*-stilbene > triphenylethylene> tetraphenylethylene). However, the calculations by Coulson and Jacobs are unacceptable because they are based on unreal planar molecular models even in the cases of tri- and tetraphenylethylene.

In spite of this, the sequence of the π-bond orders calculated by Coulson and Jacobs agrees qualitatively with the sequence of the π-bond orders as well as that of the extra-resonance energies (i.e. the bond localization energies of the ethylenic bonds) calculated here by taking the spatial configurations into account. (The π-bond orders of the ethylenic bonds calculated by Coulson and Jacobs are: *trans*-stilbene, 0.820; triphenylethylene, 0.752; tetraphenylethylene, 0.685. On the other hand, those calculated by the present author are 0.8555, 0.845 and 0.820, respectively.) Therefore, the sequence of the bond order and hence the sequence of the bond localization energy are presumed to determine at least partly the sequence of the reactivity. However, judging from the fact that the differences of the bond order and of the bond localization energy among these compounds are small, the steric effect of the first type may also be a contributory factor to the reactivity. This subject will be discussed in somewhat

4) K. B. Everard, L. Kumar and L. E. Sutton, *J. Chem. Soc.*, **1951**, 2807.
5) P. W. Robertson, J. K. Heyes and B. E. Swedlund, ibid., **1952**, 1014.
6) H. Bauer, *Ber.*, **37**, 3317 (1904).
7) J. Meisenheimer, *Ann.*, **456**, 139 (1927).
8) F. Leavitt, M. Levy, M. Szwarc and V. Stannett, *J. Am. Chem. Soc.*, **77**, 5493 (1955).
9) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, **1955**, 1525.
10) C. A. Coulson and J. Jacobs, ibid., **1949**, 2805.

TABLE III. ULTRAVIOLET ABSORPTION SPECTRA OF TOLAN

Solution in n-heptane

	A-band		B-band		C-band	
	λ_{max}, mμ	ε	λ_{max}, mμ	ε	λ_{max}, mμ	ε
α	297.2	27500	237.2	6930	196.5	38000
β	288.5	20800	232.2	6520		
γ	279.9	30800	222.0	16500		
δ	272.7	22400	217.2	18500		
ε	265.3	20600	(212)	19000		

Crystals (pressed KCl-disk)

	A-band				B-band			
	λ_{max}, mμ	$\Delta\lambda$	A	ε	λ_{max}, mμ	$\Delta\lambda$	A	ε
α	301.6	+4.4	0.282	1920	(239.0)	+1.8	0.100	680
β	292.4	+3.9	0.247	1680				
γ	283.3	+3.4	0.350	2380	(223.5)	+1.5	0.227	1540
δ	(275.8)	+3.1	0.288	1960	(218.5)	+1.3	0.264	1790
ε	268.0	+2.7	0.259	1760				

Wavelengths in parentheses denote inflections.

$\Delta\lambda$ denotes the magnitude of the wavelength displacement (in mμ) of each band relative to the corresponding band in the spectrum in *n*-heptane.

A denotes the absorbance (optical density).

greater detail in the succeeding part of this series.

In the reactions discussed so far, the reactivity decreases in the order *trans*-stilbene > triphenylethylene > tetraphenylethylene. This order coincides not only with the order in which the steric hindrance to the approach of the reagent to the ethylenic bond increases, but also with the order in which the π-bond order decreases and hence the bond localization energy increases. Both the factors, steric and electronic, will contribute to the reactivity in the same direction.

On the other hand, in the polarographic reduction the effect of conjugation operates in the opposite direction. Thus, the reduction takes place more easily with an increasing extent of conjugation, and the isolated double bond is not reducible. Maccoll[11] has found that there exists a linear relationship between the reduction potential and the energy required to place one or two electrons in the lowest vacant orbital of the molecule, that is, the energy (in $-\beta$) of the lowest vacant orbital, which is evidently half of $\Delta E_A(-\beta)$ in the present treatment. That is, the reduction potential should be related directly to the transition energy corresponding to the conjugation band. According to Laitinen and Wawzonek[12], in the series of phenylated ethylenes the ease of electro-reduction increases with increasing substitution in the order styrene < 1,1-diphenylethylene < *trans*-stilbene < triphenylethylene < tetraphenylethylene. The mean value of the reduction potential E (in V.) is -2.1425 for *trans*-stilbene, -2.1155 for triphenylethylene, and -2.046 for tetraphenylethylene. On the other hand, the energies of the lowest vacant orbitals (in $-\beta$) of these compounds are calculated to be 0.5712, 0.5558 and 0.5219, respectively. There exists a linear relationship between the reduction potential and the energy of the lowest vacant orbital at least in so far as these compounds are concerned. Tolan has a slightly more negative reduction potential (-2.195 V.) than *trans*-stilbene. This fact corresponds only qualitatively to the fact that the conjugation band of tolan is at shorter wavelengths than that of *trans*-stilbene as will be shown in the succeeding section (the energy of the lowest vacant orbital of tolan is calculated to be $-0.635\ \beta$).

trans-Stilbene forms a colored complex with 1,3,5-trinitrobenzene. According to the qualitative study by Ley and Rinke[13], when an aromatic compound is mixed with 1,3,5-trinitrobenzene in chloroform (both concentrations, 0.02 mol./l.), the solution colors as follows: *trans*-stilbene, intense yellow; triphenylethylene, yellow; tetraphenylethylene, very feeble yellow; (tetraphenylethane, colorless). The extent of coloration is considered to indicate

11) A. Maccoll, *Nature*, **163**, 178 (1949).
12) H. A. Laitinen and S. Wawzonek, *J. Am. Chem. Soc.*, **64**, 1765 (1942).
13) H. Ley and F. Rinke, *Ber.*, **56**, 771 (1923).

qualitatively the extent of the complex formation. Thus, the extent of the complex formation decreases with an increasing number of phenyl groups in the series of phenylated ethylenes, and accordingly may be related to the spatial configurations of these compounds.

Tolan

Spectra. — The ultraviolet absorption spectra of tolan (diphenylacetylene) are shown in Table III and Fig. 2. The spectra exhibit the conjugation band with well-resolved fine structure at considerably shorter wavelengths than the conjugation band of *trans*-stilbene. The spectrum of tolan in the crystalline state measured

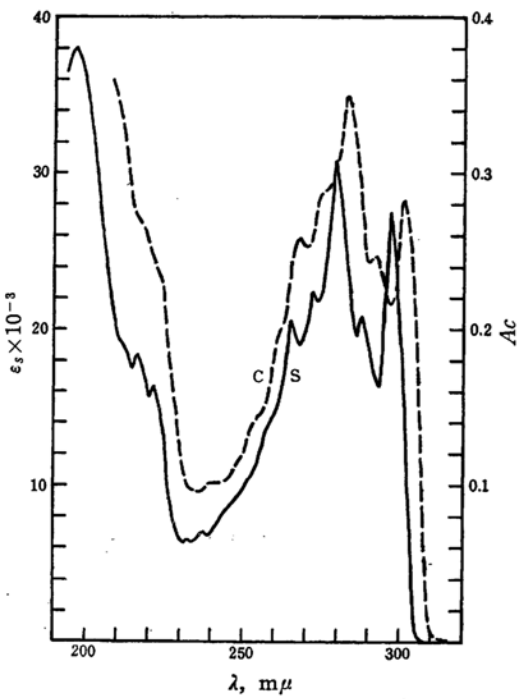

Fig. 2. Ultraviolet absorption spectra of tolan in solution in *n*-heptane (S) and in the crystalline state (the pressed KCl-disk) (C). Note separate ordinates for solution and crystals (cf. Table III).

by the pressed KCl-disk technique resembles the solution spectrum on the whole.

The red-shift of each band associated with the change of the state from the *n*-heptane solution to the crystalline state is seen to increase with almost complete regularity with the wavelength of the band from about 1.3 mμ at 217.2 mμ to about 4.4 mμ at 297.2 mμ, although these shifts are considerably smaller than the values determined by Dale[14] for naphthalene and anthracene (about 2 mμ at 220 mμ to 8 mμ at 300 mμ).

As seen already in the case of *trans*-stilbene in the preceding part of this series, also in the case of tolan, the apparent molecular extinction coefficients in the KCl-disk spectrum are much smaller than the corresponding molecular extinction coefficients in the solution spectrum, the former ones being only about 1/13 of the latter ones.

Calculation. — The notation used is as follows: the carbon atoms of the central triple bond, α and α'; the carbon atoms attached to α and α', 1 and 1'; the $2p\pi$ atomic orbitals at 1 and 1', ϕ_1 and $\phi_{1'}$; the two π-bonds in the triple bond, $(\alpha-\alpha')_x$ and $(\alpha-\alpha')_z$; the corresponding $2p\pi$ atomic orbitals, ϕ_x, $\phi_{x'}$, ϕ_z, and $\phi_{z'}$; the $\pi-\pi$ resonance integral for each of $(\alpha-\alpha')_x$ and $(\alpha-\alpha')_z$, $\eta\beta$; the $\pi-\pi$ resonance integral between ϕ_1 and ϕ_x as well as that between $\phi_{1'}$ and $\phi_{x'}$, $\rho_x\beta$; that between ϕ_1 and ϕ_z as well as that between $\phi_{1'}$ and $\phi_{z'}$, $\rho_z\beta$.

The secular equation for the determination of the molecular orbitals of tolan as linear combinations of the $2p\pi$ atomic orbitals can be factorized into the stilbene-type equation and the equation for an isolated π-bond, either when one of the parameters ρ_x and ρ_z is zero and the other is replaced by ρ, or when the parameters are equal to each other and both are replaced by $1/\sqrt{2}\times\rho$. The former requirement means that the two phenyl groups are in conjugation solely with one of the two π-bonds in the triple bond, leaving the other insulated. The alternative requirement means, needless to say, that the axes of ϕ_1 and $\phi_{1'}$ form an angle of 45° with the axes of ϕ_x and $\phi_{x'}$ as well as the axes of ϕ_z and $\phi_{z'}$.

According to the X-ray crystal analysis by Robertson and Woodward[15], tolan in the crystalline state has a planar configuration in which the lengths of the $\alpha-\alpha'$ bond and of the $\alpha-1$ as well as the $\alpha'-1'$ bond are 1.19±0.02 and 1.40±0.02 Å, respectively. The most probable configuration in solution is thought not to differ significantly from the configuration in the crystalline state, in view of the close similarity of the spectra in the two states. From the values of the bond lengths the values of the parameters η and ρ are

14) J. Dale, *Acta Chem. Scand.*, **11**, 650 (1957). See also Ref. 1 and Part I of this series: This Bulletin, **32**, 1340 (1959).

15) J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* (*London*), **A164**, 436 (1938).

calculated to be 1.378 and 0.983, respectively, by the usual procedure based on the proportionality between the $\pi-\pi$ resonance integral and the $\pi-\pi$ overlap integral. By solving the secular equation, the following values are obtained: $\Delta E_A(-\beta)$, 1.270; $\Delta E_A(-\gamma)$, 1.303; *R. E.* $(-\beta)$, 0.732; *R. E.* $(-\gamma)$, 0.221; $p_{\alpha-\alpha'}$, 1.868; $p_{\alpha-1}=p_{\alpha'-1'}$, 0.372; $\Delta E_B(-\beta)$, 1.635. (The symbols have the same significance as in the preceding part of this series.)

Whereas the length of the $\alpha-1$ "single" bond in tolan is shorter than the length of the corresponding "single" bond (1.44± 0.02 or 1.45±0.02 Å) in *trans*-stilbene, the π-bond order of the former is smaller than that of the latter (0.384). This fact is perhaps attributed to the difference of the hybridization of the σ-orbital at the α carbon atom in these two compounds (tolan, sp; stilbene, sp^2). Berthier and Pullman[16] reported somewhat different values for the π-bond orders of these compounds (tolan: $\alpha-\alpha'$, 1.909; $\alpha-1$, 0.307; *trans*-stilbene: $\alpha-\alpha'$, 0.879; $\alpha-1$, 0.352), but the relationship among the values is similar.

By using the linear relation between ΔE_A and ν_A postulated for the stilbene-type compounds in the precending part of this series (the longer-wavelength-side reference is the γ-band in the spectrum of *trans*-stilbene in *n*-heptane and the shorter-wavelength-side reference is the center of gravity of singlets of benzene), the wave number ν_A corresponding to the value of $\Delta E_A(-\beta)$ for tolan is calculated to be 36086 cm^{-1} (277.1 mμ). This is in good agreement with the observed position (279.9 mμ) of the γ-band of tolan in *n*-heptane, which is the most intense maximum of fine structure of the conjugation band. In addition, when the α-band or the β-band in the spectrum of *trans*-stilbene in *n*-heptane is taken as the longer-wavelength-side reference, the value of ν_A is computed to be 33702 cm^{-1} (296.7 mμ) or 34879 cm^{-1} (286.7 mμ), correspondingly, in agreement with the observed positions of the α-band (297.2 mμ) and the β-band (288.5 mμ) in the spectrum of tolan in *n*-heptane. The good agreement between the calculated wavelengths and the observed ones of the bands seems to justify the postulation of the linear relation between ΔE_A and ν_A.

16) G. Berthier and B. Pullman, *Compt. rend.*, **228**, 397 (1949).

Experimental

Measurements of Spectra.—All the spectra were measured with a Cary recording spectrophotometer Model 14 M-50.

The crystal spectrum of tolan was measured by the pressed KCl-disk technique quite analogously to the case of *trans*-stilbene in the preceding part of this series. About 3 mg. of tolan was thoroughly ground with about 200 mg. of potassium chloride and then about 10 mg. of the mixture was ground with about 350 mg. of potassium chloride and pressed. The disk used weighed 84.7 mg. (the thickness, about 0.321 mm.).

Materials.—Triphenylethylene was prepared by dehydration of 1,1,2-triphenylethanol obtained by the reaction of benzophenone with benzyl magnesium chloride[17]. From 27.3 g. (0.15 mol.) of benzophenone, 24.3 g. (0.095 mol.) of triphenylethylene, white crystals melting at 68~69°C, were obtained after recrystallization from 95% ethanol (63.3% of the theoretical amount).

Tetraphenylethylene was prepared by heating diphenyldichloromethane (benzophenone dichloride) with powdered copper in anhydrous benzene[18]. Diphenyldichloromethane was prepared from benzophenone and phosphorus pentachloride[19]. From 9.1 g. (0.05 mol.) of benzophenone, 4.7 g. (0.014 mol., 56.5% of the theoretical amount) of tetraphenylethylene, almost colorless crystals melting at 223~224°C, were obtained after recrystallization from a 1 : 1 by volume mixture of absolute ethanol and benzene.

Tolan was prepared, according to the directions of Schlenk and Bergmann[20], by oxidizing benzil dihydrazone with mercuric oxide. Benzil was prepared by oxidation of benzoin with nitric acid[21]. The yield of pure tolan, colorless crystals melting at 62°C, from 47 g. (0.219 mol.) of benzil was 16.4 g. (0.092 mol., 42% of the theoretical amount) after repeated recrystallization from ethanol.

Summary

The most probable configuration of triphenylethylene as well as that of tetraphenylethylene has been inferred to be the one in which all of the phenyl groups are rotated out of the plane of the ethylenic bond, on the basis of the analysis of the ultraviolet absorption spectra by application of the method based on the simple LCAO molecular orbital method described in the preceding part of this series. Some physical and chemical properties of these compounds have been

17) L. F. Fieser (Editor-in-Chief), "Organic Syntheses", Vol. XVII, John Wiley & Sons, Inc., New York (1937), p. 89.
18) R. S. Schreiber (Editor-in-Chief), ibid., Vol. 31 (1951), p. 104.
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discussed with reference to the spatial configurations.

The method has been applied also to tolan (diphenylacetylene), and it has been shown that the calculated wavelengths of the bands agree fairly well with the observed ones.

In addition, it has been shown that the spectrum of tolan in the crystalline state measured by the pressed KCl-disk technique resembles the spectrum of the solution in *n*-heptane on the whole, and that the red-shift of each band associated with the change of the state from the *n*-heptane solution to the crystalline state increases with almost complete regularity with the wavelength of the band from about 1.3 mμ at 217.2 mμ to about 4.4 mμ at 297.2 mμ, the shifts observed here being appreciably smaller than the analogous shifts observed by Dale in the spectra of naphthalene and anthracene.

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