Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. IV. Polyphenyls

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In this part of the series, the electronic absorption spectra and the spatial configurations of polyphenyls are briefly surveyed, and the relation between them is discussed especially for *o*- and *p*-terphenyls, the method applied being analogous to the one for the treatment of biphenyl presented in Part I[1] of this series.

***p*-Polyphenyls.**—It is well known that the first intense band in *p*-polyphenyl is shifted progressively toward longer wavelengths and increases in its intensity as the number of benzene rings is increased, no limit having been reached with the first six members which have been studied experimentally[2]. The band is regarded as the conjugation band, and the bathochromic shift and the intensification of this band with the increasing number of benzene rings may be attributed to the increasing extent of conjugation due to the elongation of the conjugated system. It may be stated in this connection that the first four members have been proved to be planar in the crystalline states[3].

The relation between the position of the conjugation band and the number of benzene rings in *p*-polyphenyl has been discussed by several workers on various grounds. Thus, for example, Davydov[4] has treated this problem quantum-mechanically, and derived the following equation:

$$\Delta E_{\min}=A-2|M|\,|\cos[\pi/(n+1)]|$$

where $\Delta E_{\min}$ is the transition energy corresponding to the conjugation band, M is the matrix element of the interaction between neighboring benzene rings, and n is the number of benzene rings in the molecule. Hence, with increasing n, the band should shift toward longer wavelengths, and the magnitude of the shift should decrease. From the experimental data of Gillam and Hey[2] for biphenyl and for sexiphenyl, the values of A and of M have been estimated at 50060 cm^{-1} and at 10300 cm^{-1}, respectively, in chloroform, and at 50900 cm^{-1} and at 10200 cm^{-1}, respectively, in hexane. Accordingly, when n is ∞, the band should be expected to be at about 339 mμ in chloroform and at about 328 mμ in hexane. A somewhat similar equation has been derived empirically by Hirayama[5].

Further, Dewar[6] has calculated the wavelengths of the conjugation bands of *p*-polyphenyls by his NBMO method, and obtained values which are in excellent agreement with the experiment.

***m*-Polyphenyls.** — The spectra of linear *m*-polyphenyls form a system quite different from that of *p*-polyphenyls. In the meta-series there is virtually no change in the position of the first intense band after biphenyl up to the highest member of the series yet prepared, in which the number of benzene rings is 16, in marked contrast to the para-series. On the other hand, the intensity of the band increases as the series ascends, being roughly proportional to the number of benzene rings in the molecule[2].

The different characteristics of the spectra of the two series have been ascribed to the presence of conjugation which covers the whole molecule in the para- but not in the meta-series. Thus Dewar[6] has considered the *m*-polyphenyls as the cross-conjugated systems according to his definition, and stated that the largest non-cross-conjugated unit present in them is biphenyl. In addition, Dale[7] has described it in line with Dewar's theory as follows; in *m*-terphenyl, one orbital of each of two sets of doubly degenerate π-orbitals in the central benzene ring will interact mainly with the orbitals in one of the benzene rings

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[1] H. Suzuki, This Bulletin, **32**, 1340 (1959).
[2] A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, **1939**, 1170.
[3] L. W. Pickett, *Nature*, **131**, 513 (1933).
[4] A. S. Davydov, *Zhur. Ekspt1. Teoret. Fiz.* (*J. Exptl. Theoret. Phys.*), **18**, 515 (1948); *Chem. Abstr.*, **43**, 3714 (1949).
[5] K. Hirayama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 682 (1954).
[6] M. J. S. Dewar, *J. Chem. Soc.*, **1952**, 3544.
[7] J. Dale, *Acta Chem. Scand.*, **11**, 971 (1957).

attached to the parent benzene ring, while the other orbital interacts mainly with the orbitals in another benzene ring. These explanations seem considerably satisfactory.

In spite of this, however, Murrell and Longuet-Higgins[8] have proposed a different explanation. They have attempted to account for the main features of the spectra of *m*- and *p*-polyphenyls by electron interaction between the chromophores in these series, and stated that the different characteristics of the spectra of the two series can be interpreted without reference to conjugation between the aromatic rings.

While data of the spatial configurations of linear *m*-polyphenyls appear to have not been available yet, it is of great interest that 1, 3, 5-triphenylbenzene has been found to be non-planar not only in the vapor state but also in the crystalline state. According to Bastiansen[9], the angle between two adjacent benzene ring planes in this compound in the vapor phase is 46±5°, which is almost completely identical with the value found for biphenyl in the vapor phase[10]. 1, 3, 5-Triphenylbenzene has been found to have the non-planar configuration even in the crystalline state, in which the interplanar angles are about 25° according to Lonsdale[11] or +34°, −27° and +24° according to Farag[12], in striking contrast to biphenyl which is known to be planar in the crystalline state[13].

***o*-Polyphenyls.**—While *p*-polyphenyls have been proved to be planar in the crystalline states, *o*-polyphenyls can not be planar owing to the steric necessities. Actually it has been found that *o*-terphenyl is non-planar in the crystalline state[14]. Consequently, *o*-terphenyl should be less conjugated than the *p*-isomer, and hence the electronic absorption spectrum of the former should be appreciably different from that of the latter. In fact, this has been shown to be the case[15].

***o*-Terphenyl, *p*-Terpheny and Some Related Compounds.**—Now, the relation between the spectra and the most probable spatial configurations of *o*- and *p*-terphenyls and of some related compounds will be discussed below by application of a method analogous to the one used in the treatment of the similar problem of biphenyl in Part I of this series.

The $\pi-\pi$ resonance integral for each of the co-annular bonds in *o*- and *p*-terphenyls is denoted by $\mu\beta$, and by the parameter μ an allowance is made for a change of the resonance integral associated with changes of the interplanar angle and of the bond length, quite similarly to the case of biphenyl.

o-Terphenyl is considered to belong to the symmetry group C_2. Seven of nine orbitals belonging to each of the representations A and B vary with μ, and the other two orbitals of each set do not vary with μ (one of which has energy of $+\beta$, and the other $-\beta$). The highest occupied orbital belongs to B, and the lowest vacant one to A. The transition between these two orbitals is allowed. On the other hand, *p*-terphenyl is considered to belong to D_2. To each of the representations B_1 and B_3, there belong five orbitals which vary with μ and one orbital which does not vary with μ (B_1, $+\beta$; B_3, $-\beta$). In addition, to each of A_1 and B_2, three orbitals whose energies do not vary with μ (A_1 $+\beta$, $-\beta$, $-\beta$: B_2; $+\beta$, $+\beta$, $-\beta$) belong. The highest occupied orbital belongs to B_3, and the lowest vacant one to B_1. The transition between these two orbitals is allowed.

The transition between the highest occupied orbital and the lowest vacant one in each compound is considered to correspond to the conjugation band in the spectrum of each compound, and the corresponding transition energy ΔE_A can be evaluated as a function of μ by the simple LCAO molecular orbital method. The results of calculations are shown in Table I, in which the data for biphenyl reported previously[1] are included for comparison.

It is evident that the value of ΔE_A increases in each of the systems as the value of μ decreases, indicating that the conjugation band should be shifted toward shorter wavelengths with decreasing μ. When μ is 0, ΔE_A in each system is $2(-\beta)$, and coincides with the value for benzene.

The difference between the value of ΔE_A for *o*-terphenyl and that for *p*-terphenyl at the same value of μ is much smaller than the difference between the

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[8] J. N. Murrell and H. C. Longuet-Higgins, *J. Chem. Soc.*, **1955**, 2552.

[9] O. Bastiansen, *Acta Chem. Scand.*, **6**, 205 (1952).

[10] O. Bastiansen, ibid., **3**, 408 (1949).

[11] K. Lonsdale, *Z. Kryst.*, **97**, 91 (1937); *Chem. Abstr.*, **31**, 8302 (1937).

[12] M. S. Farag, *Acta Cryst.*, **7**, 117 (1954).

[13] (a) J. Dhar, *Indian J. Phys.*, **7**, 43 (1932); *Chem. Abstr.*, **26**, 4517 (1932). (b) Idem., *Proc. Natl. Inst. Sci. India*, **15**, 11 (1949); *Chem. Abstr.*, **43**, 4655 (1949).

[14] C. J. B. Clews and K. Lonsdale, *Proc. Roy. Soc. (London)*, **A161**, 493 (1937).

[15] J. Dale, *Acta Chem. Scand.*, **11**, 650 (1957).

TABLE I

μ	$\Delta E_A(-\beta)$ p-T	$\Delta E_A(-\beta)$ o-T	$\Delta E_A(-\beta)$ B
1	1.1853	1.2206	1.4092
0.9	1.2527	1.2894	1.4596
0.8	1.3234	1.3611	1.5120
0.7	1.3976	1.4354	1.5666
0.6	1.4750	1.5120	1.6232
0.5	1.5556	1.5908	1.6820
0.4	1.6393	1.6713	1.7424
0.3	1.7258	1.7529	1.8048
0.2	1.8150	1.8353	1.8686
0.1	1.9065	1.9179	1.9338
0	2	2	2

Symbols p-T, o-T and B represent p-terphenyl, o-terphenyl, and biphenyl, respectively.

value for biphenyl and that for o- or p-terphenyl. This fact seems to give some support to the assumption in the treatment of o-alkyl- and of o,o'-dialkylbiphenyls in the earlier part[16] of this series that the normal electronic bathochromic effect of an o-alkyl substituent and that of the corresponding p-substituent are approximately of the same magnitude.

According to Dale[15], the ultraviolet absorption spectra of p- and of o-terphenyls in the crystalline states measured by the pressed KCl-disk technique do not significantly differ from the respectively corresponding solution spectra. Only a normal, or slightly larger than normal, red-shift is observed for each compound. This fact is considered to indicate that the interplanar angles in each compound in solution are not much larger than in the crystalline state. Thus, the spectrum of p-terphenyl in hexane shows an intense absorption band without fine structure at 276 mμ (ε=32100), which is considered to be the conjugation band. (According to the present measurement[17] λ_{max} is 276.5 mμ and ε is 31800 in n-heptane. According to Gillam and Hey[2], λ_{max} is 276 mμ and ε is 35000 in hexane, and λ_{max} is 280 mμ and ε is 25000 in chloroform.) On the other hand, the spectrum of the crystalline p-terphenyl shows an intense band at 284 mμ. The spectrum of o-terphenyl in hexane exhibits a maximum at 232 mμ (ε=26900), and the spectrum of the crystal at 237 mμ. In addition, the spectra of o-terphenyl in both the states show a diffuse maximum or inflection at about 250～260 mμ (in the hexane solution, λ_{max} is about 252 mμ and ε is about 11400). Dale has regarded this vestigial band as the λ_1-band, namely, the "main band" which covers the full chromophore, and the band at 232 mμ or 237 as the λ_2-band, namely, the "overtone" or "minor" band.

It is undertaken by applying the author's method to infer the most probable spatial configurations of o-terphenyl and of p-terphenyl in solution from their spectra. In that case, p-terphenyl in the crystalline state is taken as the longer-wavelength-side reference compound, because it has been known to have the planar configuration with the co-annular bond length (R) of 1.48 Å [18]. This value of R is equal to that in biphenyl in the crystalline state[13]. Therefore, the value of μ for the planar p-terphenyl molecule is 0.858. This is quite similar to the case of the planar biphenyl[1], and the correspnding value of ΔE_A is estimated at 1.282($-\beta$), which is referred to as ΔE_L as usual. The peak wave number of the conjugation band in the spectrum of p-terphenyl in the crystalline state measured by the pressed KCl-disk technique, corrected for the normal red-shift[1,15], is taken as the value of the wave number corresponding to ΔE_L (viz. ν_L). The magnitude of the normal red-shift may be estimated to be about 6 mμ at 284 mμ according to the regular relation between the position of the band and the magnitude of the corresponding normal red-shift determined by Dale[15]. Accordingly, the value of ν_L may be assumed to be 35971 cm^{-1} (278 mμ).

On the other hand, benzene is taken as the shorter-wavelength-side reference compound, similarly to the case of biphenyl. That is, the value of ΔE_A when μ is 0 is 2($-\beta$) (viz. ΔE_S), and the corresponding value of ν (viz. ν_S) is assumed to be 48000 cm^{-1} (the center of gravity of singlets of benzene).

From the positions of the conjugation bands of o-terphenyl and of p-terphenyl in solution, the respectively corresponding values of ΔE_A are obtained by the usual procedure (cf. Ref. 1, Eq. 8). (As the conjugation band of o-terphenyl the inflection at about 252 mμ is taken, accepting

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[16] H. Suzuki, This Bulletin, **32**, 1350 (1959).

[17] p-Terphenyl was prepared by the reaction of bis-nitrosoacetyl-1,4-phenylenediamine with benzene as described in "Organic Reactions", edited by R. Adams et al., Vol. II, John Wiley & Sons, Inc., New York (1944), p. 252, and purified by sublimation succeeded by repeated recrystallizations from ethanol. The spectrum was measured with a Cary recording spectrophotometer Model 14 M-50.

[18] L. W. Pickett, *Proc. Roy. Soc.* (*London*), **A142**, 333 (1933).

TABLE II

Compound	$\lambda_{\rm max}$, mμ	$\Delta E_{\rm A}(-\beta)$	μ	θ°	R, Å
p-Terphenyl (p)	278	(a) 1.282	0.858	0	1.48
		(b) 1.247	0.908	0	1.445
p-Terphenyl (s)	276.5	(a) 1.294	0.842	11	1.481
		(b) 1.259	0.891	9.5	1.447
	276	(a) 1.298	0.836	12.5	1.482
		(b) 1.263	0.885	11.5	1.447
o-Terphenyl (s)	(252)	(a) 1.504	0.611	43	1.496
		(b) 1.479	0.643	42.5	1.470

Symbols p and s represent the "isolated" planar molecule and the molecule in solution, respectively. Wavelength in parentheses denotes an inflection.

the assignment by Dale, although this would appear to be open to question.) From these values of $\Delta E_{\rm A}$ the corresponding values of μ are estimated according to the relations shown in Table I between μ and $\Delta E_{\rm A}$ for o-terphenyl and for p-terphenyl. Then, the corresponding values of θ (the interplanar angle) and of R are computed according to the relation between μ and θ as well as R postulated in Part I of this series (cf. Eqs. 1—7 in Ref. 1). The results of calculations are shown in Table II, being denoted by symbol a.

The fact that the length of the co-annular bonds in the planar molecule of p-terphenyl is equal to that in biphenyl would appear to be rather surprising, for it would be expected that the length of the "single" bond might be contracted with the increasing extent of conjugation. This problem will be discussed later. Here, it is tentatively assumed that the co-annular bond length in planar p-terphenyl were equal to the "single" bond length, 1.445 Å, in planar *trans*-stilbene, considering that terphenyl as well as stilbene can be regarded as a "tri-conjugated system"[19]. The results of calculation carried out on the basis of this assumption are also shown in Table II, being denoted by symbol b. It is to be noted that the change of the value of the length of the pivot bond of the reference compound from 1.48 to 1.445 Å does not significantly affect the calculated values of the interplanar angles.

According to the result of the X-ray crystal analysis[14], the configuration of o-terphenyl in the crystalline state is the one in which the planes of the two outer phenyl groups are turned approximately 50° or less (probably 45~50°) out of the plane of the parent nucleus. Since the interplanar angle in the molecule in solution is considered to be not significantly different from that in the crystalline state in view of the spectral similarity between both the states, it may be said that the calculated value is in considerably good agreement with the experimental value. The interplanar angle in o-terphenyl in the vapor phase has been very roughly determined by the electron diffraction method to be about 90°[20].

The most probable configuration of p-terphenyl in solution has been inferred to be slightly non-planar, in accordance with the infrared spectroscopic evidence by Dale[21]. It may be noteworthy that the calculated value of the interplanar angle in p-terphenyl in solution is considerably smaller than the corresponding one in biphenyl in solution (about 20°)[1]. Furthermore, the value in p,p'-quaterphenyl is inferred to be still smaller than that in p-terphenyl. According to Dale[15], the position of the conjugation band in the pressed KCl-disk spectrum and that in the hexane solution spectrum (in parentheses) are as follows (wavelengths are in mμ): biphenyl, 253 (246); p-terphenyl, 284 (276); p,p'-quaterphenyl, 303 (294). On the other hand, the magnitude of the normal red-shift may be estimated to be about 3.5 mμ at 253 mμ, about 6 mμ at 284 mμ, and about 8 mμ at 303 mμ. Accordingly, the position of the conjugation band of the "isolated planar molecule" may be presumed to be 249.5 mμ for biphenyl, 278 mμ for p-terphenyl, and 295 mμ for p,p'-quaterphenyl, and consequently the differences between the positions of the conjugation bands of the assumed isolated planar molecules and those of the corresponding molecules in solutions are 3.5, 2 and 1 mμ, respectively. This fact may be considered to indicate

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[19] E. A. Braude and E. S. Waight, "Progress in Stereochemistry", Vol. 1, edited by W. Klyne, Butterworths, Scientific Publications, London (1954), p. 126.

[20] I. L. Karle and L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 1974 (1944).

[21] J. Dale, *Acta Chem. Scand.*, **11**, 640 (1957).

that the degree of the deviation of the most probable configuration of the molecule in solution from the planarity decreases in the order biphenyl >*p*-terphenyl >*p,p'*-quaterphenyl, although it may be somewhat doubtful whether much significance can be attached to the numerical values of these differences themselves mainly because of inevitable uncertainty in the estimation of the magnitude of the normal red-shift.

o,p'-Quaterphenyl has two bands at 284 mμ and at 255 mμ in the pressed KCl-disk spectrum, and at 276 mμ and at 248 mμ in the solution spectrum. Dale has interpreted these two bands as λ_1- and as λ_2-bands, respectively, on the basis of his concept of the "overtone" band. At any rate, it is of interest that the band at 284 mμ (276 mμ) appears to correspond to the conjugation band of *p*-terphenyl and the band at 255 mμ (248 mμ) to the conjugation band of biphenyl.

On the Bond Length.—Lastly, the length of the "single" bond in conjugated systems is briefly discussed. It is noteworthy that the length of the co-annular bond has been proved to be 1.48 Å in each of biphenyl, *p*-terphenyl, and *p,p'*-quaterphenyl[22)] in the crystalline state. This fact appears to be in contrast to the expectation that the length of the "single" bond might be contracted with the increasing extent of conjugation, or in other words, with the increasing elongation of the conjugated system, and would be considered to support the striking hypothesis proposed recently by Dewar and coworker[23)] that when the distinctions between the bond radius and the energy of bond formation of an sp^3 carbon atom and those of an sp^2 carbon atom are made it appears that bond lengths and heats of formation can be predicted without considering resonance at all. According to Platt[24)], one of the important evidence contributory to Dewar's hypothesis is that the length of the "single" bond 1.48 Å in butadiene represents no shortening of Dewar's sp^2–sp^2 single bond distance. Butadiene in the vapor phase has been found probably to have almost exclusively the planar *trans*-configuration in which the length of the 2—3 bond is 1.483±0.01 Å [25)].

On the other hand, *trans*-stilbene is known to have the planar or nearly planar configuration in which the length of the α–1 "single" bond is 1.44±0.02 Å or 1.45± 0.02 Å in the crystalline state[26)]. That is, the further shortening of the sp^2–sp^2 bond occurs in *trans*-stilbene as compared with those in polyphenyls and in butadiene. In addition, Cook[27)] has pointed out that the length of the sp^2–sp^2 "single" bond varies from about 1.44 to about 1.55 Å with the angle between the planar groups joined by such a bond, in accordance with the assumptions made previously by the present author[1,28)]. Therefore, in spite of Dewar's new hypothesis, it seems evident that the length of the "single" bond depends on the extent of conjugation, or in other words, on the extent of the π—π interaction across the bond. Hence, the bond length may be to be correlated with the π-bond order as usual after all.

When the actual bond lengths are taken into account, the value of the π-bond order is estimated at 0.319 for the co-annular bond of biphenyl[1)] and at 0.384 for the α–1 bond of *trans*-stilbene[29)]. On the other hand, when the π—π resonance integral is taken as β for all the bonds, the value of the π-bond order is 0.370 for the co-annular bond of biphenyl[1)], is 0.375 for that of *p*-terphenyl[30)], and is 0.431 for the α–1 bond of *trans*-stilbene[30)]. In view of these values it may not be surprising that the length of the co-annular bond of *p*-terphenyl as well as that of *p,p'*-quaterphenyl is not substantially different from that of biphenyl in spite of the elongation of the conjugated system, and that the length of the "singe" bond of *trans*-stilbene is considerably shorter than those of these polyphenyls. It may be of interest in this connection that Syrkin and Dyatkina[31)] have shown by calculations by the molecular orbital method that there is an increase of 0.38($-\beta$) in the resonance energy for each Ph–Ph bond in the formation of biphenyl, terphenyl, or quaterphenyl.

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[23)] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).
[24)] J. R. Platt, *Ann. Rev. Phys. Chem.*, **10**, 349 (1959).
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[26)] J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* (*London*), **A162**, 568 (1937).
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Summary

The ultraviolet absorption spectra and the spatial configurations of polyphenyls have been briefly surveyed, and then the most probable spatial configurations of *p*-terphenyl and of *o*-terphenyl have been inferred from the spectra by application of the method analogous to the one for biphenyl in the first part of this series, resulting in the interplanar angle of about 10° for *p*-terphenyl and in that of about 43° for the *o*-isomer. Some related compounds have also been discussed. Further, it has been shown that the length of the "single" sp^2-sp^2 bond of the conjugated system depends on the extent of the $\pi-\pi$ interaction across the bond, contrary to Dewar's recent hypothesis.

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