Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. I. Biphenyl

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A twist of a "single" bond in a conjugated system caused by steric effects affects the electronic absorption spectrum of the molecule. Since the interaction of the π-orbitals across the bond and hence the conjugation of the system are maximal when the system is planar, as is well known, any deviation from the planarity of the molecular configuration reduces the degree of conjugation to the corresponding extent, and consequently alters the spectral feature.

The relation between the spatial configuration and the electronic absorption spectrum of a conjugated system may conveniently be divided into the following three kinds; (A) that between the spatial configuration and the shape of the absorption curve (mainly an appearance of fine structure), (B) that between the spatial configuration and the intensity of the conjugation band, and (C) that between the spatial configuration and the position of the conjugation band.

Concerning the relation of A, Merkel and Wiegand[1] proposed the hypothesis that the appearance of fine structure depended on the planarity of the molecular configuration. Thus, the spectra of fluorene and of carbazole, for example, which are thought to be planar, and also that of biphenyl in the crystalline state exhibit fine structures. On the basis of this hypothesis, Merkel and Wiegand suggested that the lack of structure in the spectrum of biphenyl in solution might indicate the non-planarity of the molecule in solution. However, this hypothesis has been denied by Kortüm and Dreesen[2]. According to their opinion, the appearance of fine structure does not depend on planarity of the molecular configuration, but depends rather on its rigidity. However, whether there is an unconditional relation between the molecular configuration and the appearance of fine structure or not has not yet been clarified, since this problem is considerably complicated, and since an appearance of fine structure depends on techniques of measurement, on solvents, etc.

A change in spatial configuration about a "single" bond in a conjugated system has conventionally been thought to affect the position and the intensity of the conjugation band in any of the following three ways, depending on the degree of deviation from the coplanarity[3]: (1) No change in the position of the absorption maximum but a decrease in the intensity. This effect is caused by relatively small twists. (2) A shift of the absorption maximum to shorter wavelengths in addition to a decrease in the intensity. This effect is caused by larger twists than the first effect. (3) When the twist is large enough to eliminate almost completely the $\pi-\pi$ interaction across the twisted bond, the spectrum is similar to the sum of the spectra of the component parts of the molecule on either side of the bond.

On the basis of such a classification, Braude and his coworker[4] assumed the following relation between the angle of twist θ and the molar extinction coefficient ε of the absorption maximum of the conjugation band for the cases of type 1, namely the cases in which the steric effect changes the absorption intensity alone;

$$\varepsilon/\varepsilon_0 = \cos^2\theta$$

where ε_0 is the molar extinction coefficient of the corresponding absorption maximum of the planar reference compound. Braude and his coworkers applied this postulated relation to some sterically hindered derivatives of benzaldehyde[4], of acetophenone[4], of styrene[5], and of biphenyl[6],

1) (a) Chr. Wiegand and E. Merkel, *Ann.*, **557**, 242 (1947). (b) E. Merkel and Chr. Wiegand, *Naturwiss.*, **34**, 122 (1947). (c) E. Merkel and Chr. Wiegand, *Z. Naturforsch.*, **3b**, 93 (1948).

2) G. Kortüm and G. Dreesen, *Chem. Ber.*, **84**, 182 (1951).

3) See, for example: M. S. Newman, "Steric Effects in Organic Chemistry", John Wiley & Sons, Inc., New York (1956), p. 484.

4) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, **1955**, 3754.

5) E. A. Braude and F. Sondheimer, ibid., **1955**, 3773.

6) E. A. Braude and W. F. Forbes, ibid., **1955**, 3776.

and stated that the satisfactory value of the angle of twist θ was obtained for each of the compounds. However, it can not be recognized that only a change of the intensity of the conjugation band occurs without any significant displacement of the position in each of the systems of compounds cited by Braude and others, in spite of their assumption. And further, it seems that the derivation of their equation and its basic theory are open to considerable criticism.

However, independently from Braude and others' works, a relation bearing a close similarity to the one mentioned above has been proposed. Thus, Klevens and Platt[7] have stated that the oscillator strength of the conjugation band is linearly related to the van der Waals radius of the interfering group and to the $\cos^2$ of the calculated angle of the C–N bond twist in some ortho-substituted dimethylanilines. In addition, Beale and Roe[8] have found that the changes in oscillator strength of the conjugation band for substitution with methyl groups in stilbene are additive, and that the ortho-substitution reduces the oscillator strength.

Regarding the relation of C, that is, the relation between the spatial configuration of a molecule and the position of the conjugation band, the following examples may be cited: *trans*-Stilbene has the conjugation band at about 294 mμ, which is progressively shifted toward shorter wavelengths with the concurrent decreases in the intensity as one, and then two methyl groups are introduced into the α- and α'-positions of the molecule[9,10]. Biphenyl has the conjugation band at about 247 mμ, which is markedly shifted toward shorter wavelengths in the spectrum of o,o'-dimethylbiphenyl[11]. Further, bimesityl does not exhibit the characteristic conjugation band, but absorbs as two molecules of mesitylene[11,12]. These hypsochromic wavelength displacements are explained in terms of the steric interference of the substituents which prevents the molecule from assuming a coplanar configuration.

Although these phenomena had been known for a considerably long time as the references cited show, no theoretical explanation had been established satisfactorily, and consequently, the quantitative relation between the dimensions of the spatial configuration of the molecule, especially the angle of twist, and the position of the conjugation band had not been clarified[13]. Thus, the prevailing explanations were rather unsatisfactory or unreasonable ones such as, for example, the following: The appearance of the conjugation band is related to the conjugation, and therefore requires the coplanarity of the molecular configuration. On the basis of such an assumption, the hypsochromic shifts observed in, for example, the spectra of α- and α,α'-substituted stilbenes as well as in that of *cis*-stilbene as compared with that of *trans*-stilbene needed to be explained by a rather implausible hypothesis based on a concept of "partial chromophore"[14]. The alternative prevailing explanation was as follows: The extent of the contribution of the dipolar structure in the electronic excited state is larger than in the ground state. Since the dipolar structure requires a coplanarity of the molecular configuration, steric hindrance to such a configuration will raise the potential energy of the excited state more than that of the ground state, and hence, the transition energy will be increased[15].

Previously, the present author calculated the quantitative relations between the degree of deviation from coplanarity of the molecular configuration and the position of the conjugation band as well as the extent of conjugation for stilbenes[16] and also for biphenyls[17,18], by the method based on the simple LCAO molecular orbital method. By the results of the calculations he clarified the fact that the perfect coplanarity is not prerequisite to the occurrence of conjugation and to the appearance of the characteristic conjugation band, and that the conjugation band is gradually shifted toward shorter wavelengths as the degree of deviation from the coplanarity increases. Further he showed that the values of the angle of

7) H. B. Klevens and J. R. Platt, *J. Am. Chem. Soc.*, **71**, 1714 (1949).
8) R. N. Beale and E. M. F. Roe, ibid., **74**, 2302 (1952).
9) (a) H. Ley and F. Rinke, *Ber.*, **56**, 771 (1923). (b) B. Arends, ibid., **64**, 1936 (1931).
10) R. N. Jones, *J. Am. Chem. Soc.*, **65**, 1818 (1943).
11) M. T. O'Shaughnessy and W. H. Rodebush. ibid., **62**, 2906 (1940).
12) L. W. Pickett, G. F. Walter and H. France, ibid., **58**, 2296 (1936).
13) See, for example: (a) R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, **1953**, 2755. (b) W. Klyne, "Progress in Stereochemistry", Vol. 1, Butterworths Scientific Publications, London (1954), p. 142.
14) See, for example: E. A. Braude, *J. Chem. Soc.*, **1949**, 1902. See also Ref. 10.
15) For examples: W. R. Remington, *J. Am. Chem. Soc.*, **67**, 1838 (1945). And also: Refs. 6, and 13b, p. 131.
16) H. Suzuki. This Bulletin, **25**, 145 (1952).
17) H. Suzuki, ibid., **27**, 597 (1954).
18) H. Suzuki, ibid., **29**, 945 (1956).

twist as well as the effective resonance energy can be satisfactorily computed from the observed position of the conjugation band.

Although these previous treatments seem fairly satisfactory in principle, it was found afterwards that they included an inadequate assumption. Thus, the choice of the absorption maximum corresponding to the planar molecule of biphenyl in the previous paper[17] was found to be probably inadequate. In addition, it seems that there are some aspects which were not given adequate consideration in the previous papers. Thus, first, the spectrum of *trans*-stilbene in solution was assumed to be that of the planar molecule of the compound without sufficient consideration. Strictly speaking, there is no evidence to indicate that *trans*-stilbene in the solution state has the planar configuration. Secondly, the electronic bathochromic effects of substituents such as methyl groups were ignored, and this ignoring seems to be an over-simplification. These electronic effects of substituents should not be ignored particularly when the substituents are on the benzene nuclei. Lastly, the position of absorption maximum varies more or less with the solvent, so the solvent effect should also be taken into account.

In this series of papers, the erroneous assumption mentioned above being corrected, and the aspects which were not given sufficient consideration being re-examined, a method similar to the previous one is applied to the greater range of conjugated compounds, and the relation between the spatial configuration of the molecule and the electronic absorption spectrum, especially the position of the conjugation band, is discussed more comprehensively and more fully. The relation of the intensity of the band and that of the appearance of fine structure to the spatial configuration of the molecule will also be referred to at suitable places in this series.

The present series is concerned mainly with the spatial configurations and the electronic states of the molecules in solution. This subject is certain to be very important in studying the relations between molecular structures and reactivities of organic compounds. In this connection, it seems that there is no precise and direct means to determine the spatial configurations of molecules in solution, such as the X-ray analysis for the crystalline states or the electron diffraction analysis for the vapor states. Therefore, information from the analysis of the electonic absorption spectra is conceivably important and useful in this respect. From this point of view, in this series the spatial configurations of the compounds inferred from the electronic absorption spectra are correlated as much as possible with the other properties, especially the reactivities of the compounds.

In this part of series, the ultraviolet absorption spectra of biphenyl in the various states, i.e. the crystalline, the solution, and the vapor state, and their relations to the spatial configurations of the molecule are discussed in detail as the basis of the present treatment.

Calculation

Although the procedures of calculation were already outlined in the previous papers[16,17], those for biphenyl are shown below in somewhat more refined form.

(1) Correlation of a Parameter for the Resonance Integral for the Pivot Bond with the Bond Length and the Interplanar Angle. — The π—π resonance integral for the 1-1′ bond, namely the co-annular or pivot bond, is denoted by $\mu\beta$, in which β is the π—π resonance integral for the C-C bond in the benzene ring and μ is a parameter by which allowance is made for changes of the resonance integral with the bond length and the angle of twist, i.e. the angle between the planes of the two benzene rings, which is subsequently referred to also as the interplanar angle. (The symbol α in the previous papers was replaced by μ.)

The π—π resonance integral for C-C bond can be taken to be approximately proportional to the π—π overlap integral[19], and, as easily verified, the π—π overlap integral $S(R, \theta)$ in the case where the bond length is R and the angle of twist is θ is equal to the overlap integral $S(R, 0°)$ in the case where the bond length is R and the angle of twist is 0°, multiplied by $\cos\theta$. Accordingly, the parameter μ can approximately be expressed by the following equation;

$$\mu = S(R, 0°) \cos\theta / S(1.39, 0°) \qquad (1)$$

where $S(1.39, 0°)$ represents the π—π overlap integral for the C-C bond in the benzene ring, the length of which is 1.39 Å.

The relation between the bond length R and the corresponding overlap integral $S(R, 0°)$ can be obtained from Mulliken's Tables[20]. According to results of calculation based on the tables, the values of $S(R, 0°)$ and hence of $S(R, 0°)/S(1.39, 0°)$ vary linearly with R, at least in the range of R

19) (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).

20) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, ibid., **17**, 1248 (1949).

between 1.44 and 1.54 Å, and the relations can approximately be expressed as follows:

$$S(R,0°)=0.1920+(1.54-R)\times 0.36 \quad (2)$$

$$S(R,0°)/S(1.39,0°)=0.77108+(1.54-R)\times 1.4458 \quad (3)$$

where the value of $S(1.39,0°)$ is 0.249.

According to the result of X-ray crystal analysis by Dhar[21], R is 1.48 Å and θ is 0° in biphenyl in the crystalline state. Consequently, the corresponding value of μ is evaluated at 0.858.

Any deviation from the coplanar configuration must inevitably reduce the π—π interaction across the co-annular bond to the corresponding extent, and consequently must be accompanied by change in the bond length. Thus, the value of R will vary from 1.48 Å in the planar biphenyl molecule to 1.54 Å, i. e. the length of the normal C-C single bond, as θ varies from 0° to 90°. Therefore, the following relation may tentatively be assumed between R and θ:

$$\{S(R,0°)-S(1.54,0°)\}/\{S(1.48,0°)-S(1.54,0°)\}=S(R,\theta)/S(R,0°)=\cos\theta \quad (4)$$

Hence, evidently from Eq. 2,

$$R=1.54-(1.54-1.48)\times\cos\theta \quad (5)$$

Then, from Eqs. 1 and 4 one obtains;

$$\mu=\cos\theta\times S(1.54,0°)/S(1.39,0°)+\cos^2\theta\times\{S(1.48,0°)/S(1.39,0°)-S(1.54,0°)/S(1.39,0°)\} \quad (6)$$

And further, from Eqs. 3 and 6

$$\mu=\cos\theta\times 0.77108+\cos^2\theta\times(1.54-1.48)\times 1.4458 \quad (7)$$

It is evident that the value of μ becomes gradually smaller as the value of θ becomes larger and that μ becomes 0 when θ is 90°.

(2) Solution of the Secular Equation for the Determination of the Molecular Orbitals. — By solving the secular equation for the determination of the molecular orbitals as linear combinations of $2p\pi$ atomic orbitals, one can obtain the values of energies of the molecular orbital corresponding to the value of the parameter μ. Consequently, the values of the extra-resonance energy (subsequently referred to as *R.E.*), of the coefficients of the $2p\pi$ atomic orbitals in the molecular orbital functions, and of the quantities such as the π-bond orders corresponding to the molecular configuration prescribed by the value of μ can also be obtained by the usual procedures[22].

The biphenyl molecule can be considered as belonging to the symmetry group D_2. Then, the highest occupied π-orbital (π_1) in the biphenyl molecule belongs to the representation B_3, and coincides with the φ_1 orbital in benzene when μ is 0. On the other hand, the lowest vacant π-orbital (π_1^*) belongs to A_1, and coincides with the φ_2 orbital in benzene when μ is 0. (The notation for orbitals in benzene is according to Sklar[23].) Transitions from orbitals belonging to B_2 to those belonging to A_1 are allowed by absorption of light polarized along the direction of the long-axis of the molecule. Accordingly, the energy difference (referred to as ΔE_A) between the lowest vacant orbital π_1^* and the highest occupied orbital π_1 is considered to be the transition energy corresponding to the conjugation band (the A-band) in the spectrum of biphenyl.

In addition to the eight orbitals belonging to B_1 and B_3, energies of which vary with μ, there are two sets of doubly degenerate orbitals belonging to A_1 and B_2, energies of which do not vary with μ. These orbitals may be considered as ones localized in the benzene rings. Thus, the two of these orbitals whose energy is $+\beta$ (φ) correspond to the φ_{-1} orbital in benzene, and another two whose energy is $-\beta$ (φ^*) correspond to the φ_{-2} orbital in benzene. In other words, it can be considered that one orbital of each of the two sets of doubly degenerate orbitals in each benzene ring interacts with the neighboring π-orbitals to give whole-molecular orbitals when two benzene rings are linked with each other, whereas the other orbital of each set remains isolated. The intense bands observed at about 200 mμ in the spectra of biphenyl and its related compounds are presumably due to transitions between the orbitals localized in the benzene rings.

The results of calculations are shown in Table I. In this table, $\Delta E_A(-\beta)$ and $R.E.(-\beta)$ are values obtained by ignoring the π—π overlap integral, and $\Delta E_A(-\gamma)$ and $R.E.(-\gamma)$ are values obtained by taking the overlap integral into account, assuming the value of the overlap integral for the C-C bond in benzene as 0.25. The symbol $p_{1-1'}$ represents the π-bond order of the 1-1′ bond.

It is evident that the values of ΔE_A increase as the value of μ decreases, and agree with the values for benzene when μ is 0. This means that the conjugation band is gradually shifted toward shorter wavelengths as the value of μ decreases, and therefore as the value of θ increases, and that the band will coincide with that of benzene when μ is 0 and therefore θ is 90°.

It appears that there is no simple quantitative relation between μ and ΔE_A, or between ΔE_A and *R.E.* On the other hand, examination of the data in Table I reveals that *R.E.* $(-\beta)$ is almost completely proportional to μ^2 and can approximately be expressed as $0.385\times\mu^2$, a fact which coincides with the qualitative generalization by Dewar[24]. In addition, $p_{1-1'}$ is roughly proportional to μ and can roughly be expressed as

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

22) See, for example: H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry", John Wiley & Sons, Inc., New York (1944), p. 254 ff. See also: C. A. Coulson, "Valence", Clarendon Press, Oxford (1952), p. 250 ff.

23) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

24) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3345 (1952). (*Theorem 14*).

TABLE I

μ	1.1	1.0	0.9	0.8	0.7	0.6
$\Delta E_A(-\beta)$	1.3610	1.4092	1.4596	1.5120	1.5666	1.6232
$\Delta E_A(-\gamma)$	1.4016	1.4544	1.5099	1.5680	1.6290	1.6929
$R.E.(-\beta)$	0.4606	0.3832	0.3128	0.2484	0.1914	0.1414
$R.E.(-\gamma)$	0.1416	0.1184	0.0972	0.0774	0.0600	0.0446
$p_{1-1'}$		0.370	0.334	0.298	0.264	0.228
μ	0.5	0.4	0.3	0.2	0.1	0
$\Delta E_A(-\beta)$	1.6820	1.7424	1.8048	1.8686	1.9338	2
$\Delta E_A(-\gamma)$	1.7598	1.8292	1.9016	1.9764	2.0538	2.1333
$R.E.(-\beta)$	0.0988	0.0632	0.0358	0.0160	0.0040	0
$R.E.(-\gamma)$	0.0312	0.0200	0.0114	0.0052	0.0014	0
$p_{1-1'}$	0.193	0.156	0.118	0.079	0.040	0

$0.375\times\mu$. The value of $p_{1-1'}$ is 0.319 when μ is 0.858.

(3) Correlation of the Calculated Transition Energy with the Observed Position of the Conjugation Band. — The present calculations are concerned with the vertical excitations according to the Franck-Condon principle, namely, to electron jumps without change in the configuration of the molecular skeleton.

In general, the most probable spatial configuration of a conjugated compound and its stability are believed to be determined mainly by the combined effect of the resonance stabilization and the steric repulsion. The steric repulsion will raise the potential energy of the molecule in the ground state. Accordingly, in the problem which is concerned with, for example, the difference of stability between the geometrical isomers, the steric repulsion energy must be taken into account in principle.

On the other hand, since the spatial configuration of the molecule is assumed not to change between in the ground state and in the electronic excited state, the magnitudes of the steric repulsion energies involved in both the states may be the same at least approximately, and therefore, it seems that the electronic transition energy must not contain any significant contribution of the steric repulsion energy itself, and must be determined as a function of the spatial configuration of the molecule alone. That is, the values of ΔE_A shown in Table I may be correlated directly with the observed wave numbers of the absorption maxima of the conjugation bands. (In this connection, the interpretations by Braude and others on the relation between the steric effect and the position of the conjugation band are highly questionable. This will be referred to in detail in later parts of this series.)

The correlation of the calculated transition energy ΔE_A with the observed position ν_A (in wave number) of the conjugation band is accomplished as follows. When there are two compounds whose spatial configurations are already known and whose corresponding electronic absorption spectra are already observed, the linear relation of ΔE_A to ν_A is assumed between the two points prescribed by the two reference compounds.

As one of the two reference compounds, the planar compound is chosen in most cases. This is subsequently referred to as the longer-wavelength-side reference compound. The corresponding ΔE_A and ν_A are denoted by ΔE_L and ν_L, respectively. On the other hand, as the shorter-wavelength-side reference compound the one which corresponds to the value 0 of the parameter μ or the analogous one is chosen in most cases. The corresponding ΔE_A and ν_A are denoted by ΔE_S and ν_S, respectively. Then, the value of ΔE_A for a given compound of the type under consideration is obtained from the observed value of ν_A by the following equation:

$$\Delta E_A = \Delta E_S - (\Delta E_S - \Delta E_L)(\nu_S - \nu_A)/(\nu_S - \nu_L) \quad (8)$$

Consequently, the corresponding value of μ and then the values of θ, R, $R.E.$, etc. can be calculated in turn.

In the case of biphenyl, biphenyl in the crystalline state is chosen as the longer-wavelength-side reference compound. In this molecule, θ is 0°, and R is 1.48 Å as mentioned already, and consequently, the corresponding values of μ and of ΔE_A (i.e. ΔE_L) are computed to be 0.858 and $1.482(-\beta)$, respectively. On the other hand, as the shorter-wavelength-side reference compound, benzene is chosen, which corresponds to the case where the values of μ and of ΔE_A (i.e. ΔE_S) are 0 and $2(-\beta)$, respectively. However, it requires sufficient consideration to determine what values of ν are to be taken as ν_L and ν_S, corresponding to ΔE_L and ΔE_S, respectively. Therefore, these choices of the references are discussed in detail in the next sections.

The Shorter-wavelength-side Reference

When the value of the parameter μ is 0, the energy levels in biphenyl coincide with those in benzene, and the value of ΔE_A (i.e. ΔE_S) is $2(-\beta)$. According to Platt[25], the "center of gravity of singlets", 48000 cm^{-1} in the absorption spectrum of benzene, that is, the weighted mean of the energies of the three singlet-singlet transitions at 48000 cm^{-1} (208.3 mμ, B_{1u}), at 38200 cm^{-1} (261.8 mμ, B_{2u}), and at 53000 cm^{-1} (188.7 mμ, E_{1u}) measured in solution[26], corresponds to the energy

25) J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).
26) H. B. Klevens and J. R. Platt, ibid., **17**, 470 (1949).

difference of $2(-\beta)$ calculated by the molecular orbital method of the same order of approximation as the present treatment. Therefore, the value of 48000 cm^{-1} was taken as ν_S in the previous papers.

The same assumption is used also in the present treatment, since this assumption seems to be supported by the following facts. First, Dewar[27] has used the value of 208 mμ for the wavelength of the band of benzene in his application of the NBMO method to spectra of catacondensed aromatic compounds. Secondly, Dale[28] has used a value of about 205 mμ for benzene in his attempt to correlate the wavelength positions of the main bands of linear polyphenyls with the numbers of linked chain benzene nuclei. Furthermore, according to Wenzel[29], the intense conjugation band at about 250 mμ in the spectrum of biphenyl corresponds to the band at about 210 mμ of benzene. All these values for benzene are closely similar to the "center of gravity of singlets" mentioned above.

The Longer-wavelength-side Reference

Spectra of Biphenyl in the Crystalline State.— The value of ΔE_A (i. e. ΔE_L), $1.482(-\beta)$, calculated by using the values of the dimensions of the spatial configuration of biphenyl in the crystalline state is to correspond to the wave number of the absorption maximum of the conjugation band of the "isolated" planar molecule of biphenyl. The spectrum of biphenyl in solution has the conjugation band at about 247 mμ, but this band should not be taken as the band corresponding to ΔE_L, because there is no evidence to indicate that the molecule of biphenyl in solution would have the same spatial configuration as in the crystalline state. In the earlier paper[17], the wave number 36306 cm^{-1} of the first absorption maximum in the spectrum of biphenyl in the crystalline state measured by Deb[30] was taken as ν_L, i. e. the wave number corresponding to ΔE_L. According to Deb, the characteristic (conjugation) band in the spectrum of biphenyl in the liquid state is split up into two broad bands at 36306 cm^{-1} (2754 Å) and at 37386 cm^{-1} (2675 Å) in the spectrum of the solid at 30°C, and the band at 36306 cm^{-1} was presumed to be the intrinsic band. This assignment of the band is evidently inadequate, in view of the studies by Wenzel[29] and by Dale[28].

Wenzel[29] has proposed the hypothesis that the intense transition at about 250 mμ in biphenyl in solution is interpreted as a superposition of a strong and a weak transition corresponding to the 210 mμ and the 260 mμ transition in benzene, respectively. According to her, the weak transition is hidden by the strong one in the spectrum of biphenyl in solution. From comparison of spectra of some 3- and 3,3'-substituted biphenyl derivatives with pairs of spectra of benzene and the correspondingly substituted benzene derivatives and with pairs of spectra of naphthalene and its correspondingly substituted derivatives, she has inferred that the "hidden transition" of biphenyl may be located at about 275 mμ or at about 271 mμ, and that the intensity of this transition may be of the same order as the weak transitions in benzene and naphthalene.

The existence of the hidden transition in biphenyl has experimentally been corroborated by Dale[28]. He has measured the spectrum of biphenyl in the crystalline state by the pressed KCl-disk technique, and found that the spectrum is very similar to the solution spectrum. Thus, the spectrum of the solid showed an intense, structureless band with a maximum at 253 mμ, which is to be compared with the band at about 246 mμ in the solution spectrum. On the other hand, the spectra measured on thin films of solidified melt, on those by evaporation of a thin layer of solution, and on those of sublimed crystals of biphenyl revealed a band showing fine structure with a maximum at about 275 mμ. The molar extinction coefficient of the absorption maximum has been very roughly estimated to be about 1000~2000. In addition, whereas the spectra of *p*-terphenyl and of *p,p'*-quaterphenyl either in solution or in the crystalline states measured by the pressed KCl-disk technique showed the intense bands without structure at considerably longer wavelengths than that of biphenyl, the spectra of solidified melts or sublimed crystals of these compounds showed bands with structure at about 275 mμ, similarly to the corresponding one of biphenyl. These weak bands at about 275 mμ are probably due to the transversely polarized transitions normally hidden by the stronger conjugation bands. This revelation of the hidden transitions in biphenyl and *p*-polyphenyls has been interpreted as follows. Since the incident light is almost parallel to the long molecular axes in the thin films of crystals prepared by solidification of melts, by evaporation of solutions, or by sublimation, owing to the orientation of molecules in these samples, the conjugation bands due to transitions polarized along the long molecular axes are so reduced that the weak hidden transitions are revealed.

In view of the evidences mentioned above, the band at about 275 mμ in the spectrum of the solid biphenyl measured by Deb[30] is probably the "hidden transition". In this connection, Merkel and Wiegand[1] reported that the spectrum of biphenyl in the crystalline state exhibited a band showing fine structure in sharp contrast with that in the solution, and assumed this fact as one of the bases for their hypothesis concerning the relation between the appearance of fine structure and the coplanarity of the molecular configuration. Probably they compared impertinently the "hidden transition" revealed in the solid spectrum with the conjugation band in the solution spectrum.

Besides the bands at about 275 mμ and at 267 mμ mentioned above, Deb[30] found a very feeble band at about 290 mμ with structure in spectra

27) M. J. S. Dewar, *J. Chem. Soc.*, **1952**, 3532.
28) J. Dale, *Acta Chem. Scand.*, **11**, 650 (1957).
29) A. Wenzel, *J. Chem. Phys.*, **21**, 403 (1953).
30) A. R. Deb, *Indian. J. Phys.*, **27**, 305 (1953).

of biphenyl measured on the liquid films and on the solid films of larger thickness. This feeble band was resolved as sharp absorption peaks when the temperature of the solid film was reduced to −180°C. Deb has assumed that this feeble band at about 290 mμ belongs to a system different from the one to which the bands at 275 mμ and at 267 mμ belong, and that this feeble system is due to the transition in one of the two benzene rings in biphenyl when the second one is in the excited state. Perhaps the same feeble band at about 290 mμ was recently found by Coffman and McClure[31] and by Broude and his collaborators[32] in the spectrum of a single crystal of biphenyl at 20°K with polarized light, and also by Kanda[33] in the spectrum of the solution at low temperature. In addition, biphenyl appears to have a very feeble band at longer wavelengths than 300 mμ. Although the assignments of these feeble bands have not yet been established with certainty, it may be safe to say that these bands are to be excluded from the present consideration.

Although it may be somewhat open to criticism that the state of biphenyl in the pressed KCl-disk is the same as that in the crystal, it is assumed to be so. Then, from the above considerations, the intense band detected by the pressed KCl-disk technique may be taken as the conjugation band of the planar molecule of biphenyl in the crystalline state. Consequently, one would assume that the wave number 39526 cm^{-1} (253 mμ) of the position of the maximum might be ν_L, corresponding to the calculated transition energy $1.482(-\beta)$, ΔE_L, for the planar molecule of biphenyl. However, there is the possibility that interactions between the molecules in the crystal may affect the energy levels in the molecule and consequently the absorption spectrum of the compound. Accordingly, although such intermolecular interactions are supposed to be weak in nonpolar aromatic crystals[34], it is necessary to make allowances for this effect in the choice of the references for the correlation between ν_A and ΔE_A.

Normal Red-shift.—According to the results of measurements by Dale[28], the absorption maximum in the spectrum measured by the pressed KCl-disk technique is always at longer wavelengths than the corresponding one in the spectrum of the solution. The magnitude of the wavelength displacement of a band of a rigid molecule due to the change of the state from the solution in hexane to the solid state, which was referred to as the "normal red-shift", was found to vary regularly with the wavelength of the corresponding band, by measuring the spectra of naphthalene and of anthracene in both the states. Thus, the normal red-shift increases regularly from about 2 mμ at 220 mμ to 8 mμ at 300 mμ, and to 19 mμ at 400 mμ, with increasing wavelength of the position of the band. This normal red-shift is supposed to be due to the effect of interactions between the molecules in the crystals. From the analogy of the solvent effect[35] and of the Davydov effect[36-41] in a single crystal, it would be expected that the magnitude of the normal red-shift might be related to the intensity of the band. But, in fact, it is not so. The band cited by Dale includes the bands of considerably different intensity from each other, and no regularity between the magnitude of the normal red-shift and the intensity of the band can be found. Thus, the logarithms of the molar extinction coefficients of the bands of naphthalene at about 275 mμ and at about 221 mμ are 3.82 and 5.02, respectively[42], and the oscillator strengths of these bands are 0.11 and 1.7, respectively[41]. The logarithms of the molar extinction coefficients of the bands of anthracene at about 376 mμ and at about 252 mμ are 3.88 and 5.25, respectively[42], and the oscillator strengths of these bands are 0.1 and 2.3, respectively[37]. And further, according to Craig and others, the band of naphthalene[41] at about 275 mμ and that of anthracene[37-39] at about 380 mμ are assigned as "short-axis transitions", and that of naphthalene at about 220 mμ and that of anthracene at about 250 mμ are assigned as "long-axis transitions". From these considerations, the regular relation between the magnitude of the normal red-shift and the wavelength of the position of the absorption band seems to hold regardless of kinds of compounds, of characters of bands, and of intensities of bands. Accordingly, by application of this relation, the magnitude of the normal red-shift corresponding to the wavelength 253 mμ of the maximum of the conjugation band in the spectrum of biphenyl in the crystalline state (measured by the pressed KCl-disk technique) may be estimated to be about 3.5 mμ. (The oscillator strength of the conjugation band of biphenyl is 0.411 in solution, according to Almasy and Laemmel[43].)

On the other hand, according to the results of the measurements by the present author, which will be reported in detail in Part V of this series, the intense bands at 294.1 mμ and at 306.9 mμ in the spectrum of *trans*-stilbene in *n*-heptane are shifted toward longer wavelengths by about 4.5 mμ and by about 5.5 mμ, respectively, in the spectrum measured by the pressed KCl-disk

31) R. Coffman and D. S. McClure, *Can. J. Chem.*, **36**, 48 (1958); D. S. McClure, ibid., **36**, 59 (1958).
32) V. L. Broude, E. A. Izrailevich, A. L. Liberman, M. I. Onoprienko, O. S. Pakhomova, A. F. Prikhot'ko and A. I. Shatenshtein, *Optika i Spektroskopiya*, **5**, 113 (1958).
33) Yoshiya Kanda (Kyushu Univ.), a personal communication.
34) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).
35) N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).
36) (a) A. S. Davydov, *Zhur. Eksptl. Teoret. Fiz.* (*J. Exptl. Theoret. Phys.*), **18**, 210 (1948). (Translated by M. Kasha.) (b) V. L. Broude, V. S. Medvedev and A. F. Prikhot'ko, ibid., **21**, 665 (1951). (c) A. S. Davydov, ibid., **21**, 673 (1951).
37) D. P. Craig and P. C. Hobbins, *J. Chem. Soc.*, **1955**, 539.
38) D. P. Craig, ibid., **1955**, 2302.
39) D. P. Craig and P. C. Hobbins, ibid., **1955**, 2309.
40) D. P. Craig and J. R. Walsh, *J. Chem. Phys.*, **25**, 588 (1956).
41) D. P. Craig and J. R Walsh, *J. Chem. Soc.*, **1958**, 1613.
42) E. Clar, *Spectrochim. Acta*, **4**, 116 (1950).
43) F. Almasy and H. Laemmel, *Helv. Chim. Acta*, **33**, 2092 (1950).

TABLE II. ULTRAVIOLET ABSORPTION SPECTRA OF BIPHENYL IN VARIOUS SOLVENTS

Solvent	A-band		B-band		C-band	
	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
n-Heptane	247.0	16450	(205.0)	41400	200.5	45100
Methanol	247.2	17300	—		—	
95% Ethanol	247.7	18050	(204.5)	42000	201.5	43000
Chloroform	249.5	16700	—		—	
Carbon tetrachloride	256.5	16450	—		—	

Wavelengths (mμ) in parentheses denote inflections.

technique. (The oscillator strength of the conjugation band in the spectrum of *trans*-stilbene in solution is 0.745, according to Beale and Roe[8].) These values, probably corresponding to the normal red-shifts of the conjugation band of *trans*-stilbene, are considerably smaller than those (about 8 and 9 mμ) anticipated from the relation mentioned above between the shift and the position of the band.

The crystals of naphthalene[41], anthracene[37], biphenyl[44], and *trans*-stilbene[44,45] all belong to the monoclinic space group C_{2h}^5, and bear a certain similarity to each other. However, whereas in each of these compounds except for the last the number of molecules in a unit cell is 2, in the crystal of *trans*-stilbene the number of molecules in a unit cell is 4. On the other hand, the molecular structure of biphenyl may be said to have greater similarity to that of *trans*-stilbene than to those of naphthalene and anthracene. From such considerations, it seems that there may be a possibility that the magnitude of the normal red-shift of the conjugation band of biphenyl is smaller than the value estimated above and is probably about 2 mμ, on the analogy of the case of *trans*-stilbene.

Since the estimation of the magnitude of the normal red-shift of the conjugation band of the "planar" molecule of biphenyl, at any rate, includes inevitable uncertainty, the alternative values of 3.5 and 2 mμ are assumed in the present calculation. After being corrected for the normal red-shift by these values, the position of the absorption maximum of the conjugation band of the "isolated" planar biphenyl molecule is assumed to be 249.5 mμ (a) or alternatively 251 mμ (b), and the corresponding wave numbers, (a) 40080 cm^{-1} and (b) 39841 cm^{-1}, are assumed to be ν_L.

The difference between the above assumed position of the conjugation band of the "isolated" planar biphenyl molecule, 249.5 or 251 mμ, and the corresponding one of biphenyl in solution, 247 mμ (in *n*-heptane, the present work) or 246 mμ (in hexane[28]), is assumed to be due to the difference in the most probable spatial configuration of the molecule between in the solution state and in the crystalline state.

44) J. Hengstenberg and H. Mark, *Z. Kristallogr. Kristallgeometr., Kristallphysik, Kristallchem.*, **70**, 283 (1929); *Chem. Zentr.*, **CI**, 3668 (1930).
45) (a) J. M. Robertson, M. Prasad and I. Woodward, *Proc. Roy. Soc.* (London), **A154**, 187 (1936). (b) J. M. Robertson and I. Woodward, ibid., **A162**, 568 (1937).

Spectra of Biphenyl in Solution

The ultraviolet absorption spectra of biphenyl in various solvents measured by the present author on a Cary recording spectrophotometer Model 14 M-50 are shown in Table II and Fig. 1. In Fig. 1, the spectra of biphenyl in the crystalline state and in the vapor state found in the literature are also shown for comparison.

The band represented as A-band in Table II is the conjugation band (the so-called K-band). The C-band is the one presumably due to transitions between the orbitals localized on each of the benzene rings, as already mentioned. The B-band (inflection) is probably the vestigial band due to transitions from the highest

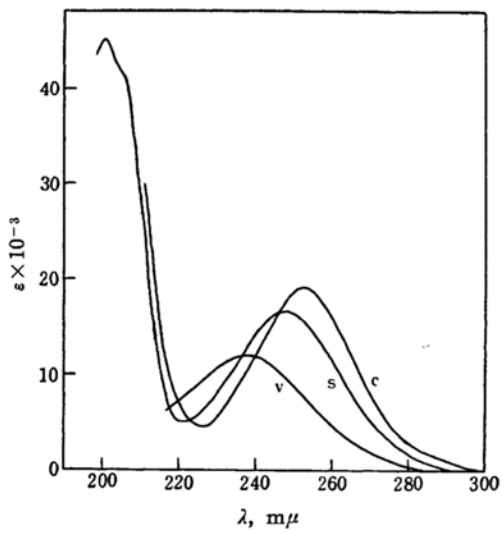

Fig. 1. Ultraviolet absorption spectra of biphenyl in various states.
c. The crystal spectrum measured by Dale[28] by the pressed KCl-disk technique. (The extinction scale is arbitrary for the reliable absolute extinction value could not be obtained.)
s. The solution spectrum (solvent: *n*-heptane).
v. The vapor spectrum measured by Almasy and Laemmel[43] at 170°C.

occupied orbital $\pi_1(B_2)$ to the orbitals φ^* belonging to A_1 or B_2 whose energy is $-\beta$, or from the orbitals φ belonging to A_1 or B_2 whose energy is $+\beta$ to the lowest vacant orbital $\pi_1^*(B_1)$.

It is seen that the spectrum is affected more or less by the solvents. Thus, the conjugation band at 247 mμ in the spectrum of the solution in *n*-heptane is shifted more or less toward longer wavelengths in the spectra in other solvents. The magnitude of the bathochromic shift by the solvent effect is small in methanol and in ethanol, is considerably larger in chloroform, and is extraordinarily large in carbon tetrachloride. In view of these solvent effects, data of spectra in the same solvent should in principle be compared at least in each of the systems of compounds in the treatment. In this part, the data of the spectra in non-polar hydrocarbon solvents being taken as the basis for comparison, and being corrected for the wavelength displacements of the band resulting from changes in phase (i. e. the normal red-shift mentioned above for the crystalline state and the solvent effect for the vapor state which will be mentioned later), the data of the spectra of biphenyl in the various states are compared.

Since the difference of the solvent effect between that of *n*-heptane and of *n*-hexane is supposed to be very small, the difference between the result of the measurement by the present author using *n*-heptane as solvent and that by Dale[28] using *n*-hexane as solvent may be ascribed to experimental errors. At any rate, the position of the maximum of the conjugation band in the spectra of biphenyl in the non-polar hydrocarbon solvents is located at slightly shorter wavelengths than that assumed above for the "isolated" planar molecule of biphenyl. This fact may be supposed to indicate that the most probable conformation of the molecule of biphenyl in solution is slightly non-planar, agreeing with the inference by Dale[46] from comparison of the results of measurements of the infrared absorption spectra of biphenyl in the solutions and in the pressed KBr-disk.

Spectra of Biphenyl in Vapor State

The spectra of biphenyl in the vapor state were studied thoroughly by Almasy and Laemmel[43]. They measured the spectra of biphenyl vapor at the various temperatures from 170 to 520°C and investigated also effects of various foreign gases.

It is noteworthy that the spectrum of pure biphenyl vapor is not largely affected by temperature at least in the range mentioned above, and that whereas the intensity ε of the absorption maximum of the conjugation band decreases gradually from 12050 at 170°C to 9400 at 520°C when the temperature is raised, the oscillator strength of the band is maintained almost constant regardless of the temperature. (The oscillator strength at 170°C is 0.316. The average of the values at 170, 260, 360 and 520°C is 0.311 ± 0.0035.)

The position of the absorption maximum is gradually shifted toward longer wavelengths from 42000 cm^{-1} at 170°C to 41750 cm^{-1} at 520°C, as the temperature is raised. From these results, the position of the maximum at 20°C was inferred by extrapolation as 42100 cm^{-1} (ε, 19000).

Whereas these spectra of the vapor, showing no fine structure, resemble in shape the spectra of the solutions and that of the crystal by the pressed KCl-disk technique, the absorption maximum is considerably shifted toward shorter wavelengths in the vapor spectra than in the solution spectra, and further than the assumed position of the maximum for the "isolated" planar molecule. This fact is supposed to indicate that the degree of deviation from the planarity of the molecular configuration is larger in the vapor state than in the solution state.

Correction for Solvent Effect.—In order to compare the position of the absorption maximum in the vapour spectrum with that in the solution spectrum and with that for the "isolated" planar molecule, the solvent effect must be taken into account.

According to Bayliss[35], the magnitude of the displacement $\Delta\nu$ (in cm^{-1}) of the absorption maximum of a nonpolar molecule to lower frequencies by a nonpolar solvent is related to the refractivity of the solvent, and is expressed as the following equation:

$$\Delta\nu=\frac{3e^2}{8\pi^2c^2m}\cdot\frac{f}{\nu a^3}\cdot\frac{n^2-1}{2n^2+1}$$

$$=10.71\times10^9\frac{f}{\nu a^3}\cdot\frac{n^2-1}{2n^2+1}$$

where n is the refractive index of the solvent at the frequency concerned, f is

46) J. Dale, *Acta Chem. Scand.*, **11**, 640 (1957).

TABLE III. RESULTS OF CALCULATIONS FOR BIPHENYL IN VARIOUS STATES

State	λ_{max}, mμ	ν_{max}, cm^{-1}	ΔE_A, $-\beta$	μ	$\theta°$	R, Å	$R.E.$, $-\beta$
Crystal	a) 249.5*	40080	1.482	0.858	0	1.48	0.286
	b) 251*	39841	〃	〃	〃	〃	〃
Solution	247.0	40486	a) 1.509	0.807	19	1.484	0.253
	(n-heptane)		b) 1.523	0.780	23	1.485	0.237
	246	40650	a) 1.519	0.787	22	1.485	0.241
	(n-hexane)		b) 1.533	0.762	26	1.486	0.227
Vapor	238.8**	41866	a) 1.599	0.643	40	1.494	0.163
	(170°C)		b) 1.611	0.621	42	1.495	0.152
	238.3**	41966	a) 1.605	0.631	41	1.495	0.157
	(20°C)		b) 1.617	0.611	43	1.496	0.147

* Values corrected for the normal red-shift.

** Values corrected for the solvent effect.

the oscillator strength of the band, ν is the wave number of the position of the absorption maximum, and a is the radius of the (spherical) solute molecule. This relation was experimentally verified by Coggeshal and Pozefsky[47] in their study on the spectra of naphthacene and some other cata-condensed aromatic hydrocarbons. By application of this equation, the magnitude of the shift toward lower frequencies of the maximum of the conjugation band of biphenyl resulting from change in the state from the vapor to the solution in n-hexane is computed to be about 134 cm^{-1}, the following values being used; f=0.316 (the value at 170°C); ν=42000 cm^{-1} (the absorption maximum at 170°C); n=1.438 (the refractive index of n-hexane[48] at 42000 cm^{-1}); a=5 Å (as the radius a of the molecule, the round value of the half length of the long molecular axis of biphenyl along which the transition is polarized was provisionally taken by consulting the study by Lippert[49] on p,p'-disubstituted stilbenes, although this evaluation is inevitably still somewhat arbitrary).

This calculated value of $\Delta\nu$ may approximately apply to the inferred position of the maximum at 20°C and also to the case where the solvent is n-heptane instead of n-hexane. Accordingly, being corrected for this solvent effect, the wave number of the position of the maximum of the conjugation band of biphenyl in the vapor state, which is to be compared with the corresponding ones in the spectra of the solutions of biphenyl in n-hexane and in n-heptane, is evaluated to be 41866 cm^{-1} (at 170°C) or 41966 cm^{-1} (at 20°C).

Application of Calculation

On the basis of the above considerations, from the observed positions of the absorption maxima in the solution spectra and the positions in the vapor spectra corrected for the solvent effect, the respectively corresponding values of ΔE_A can be evaluated according to the assumption that ΔE_A varies linearly with μ_A from ΔE_L [1.482$(-\beta)$] for ν_L (40080 or 39841 cm^{-1}) to ΔE_S [2$(-\beta)$] for ν_S (48000 cm^{-1}). Consequently, the corresponding values of μ, θ, R and $R.E.$ can be evaluated in turn. The results are summarized in Table III.

It is shown that the values calculated for the interplanar angles in the most probable conformations of biphenyl in the solution state and in the vapor state are about 20° and about 40~43°, respectively. These values coincide fairly well with those estimated by other workers on different grounds. Thus, Bastiansen[50] deduced the value of 45±10° for the angle in the vapor state from the result of his study by the electron diffraction sector method. This value agrees almost completely with the present one. On the other hand, Samoilov and Dyatkina[51] inferred the value to be about 30° from calculations of resonance energy and steric repulsion energy between the nearest hydrogen atoms by the molecular orbital method. Recently, Adrian[52] concluded, from calculations somewhat similar to those by Samoilov and Dyatkina, that the angle is probably between 20° and 30°. In addition, calculations by Coulson and Longuet-Higgins[53] are said to indicate that

47) N. D. Coggeshall and A. Pozefsky, *J. Chem. Phys.*, **19**, 980 (1951).
43) J. L. Lauer, ibid., **16**, 612 (1948).
49) E. Lippert, *Z. Naturforsch.*, **10a**, 541 (1955).
50) O. Bastiansen, *Acta Chem. Scand.*, **4**, 926 (1950).
51) S. Samoilov and M. Dyatkina, *Zhur. Fiz. Khim.*, **22**, 1294 (1948); *Chem. Abstr.*, **43**, 2606 (1949).
52) F. J. Adrian, *J. Chem., Phys.*, **28**, 608 (1958).
53) C. A. Coulson, presented at a Conference on Quantum-Mechanical Methods in Valence Theory, Washington, 1951. (According to Refs. 6 and 52.)

the decrease in repulsion energy between the ortho-hydrogen atoms and the decrease in resonance energy resulting from non-planarity are practically balanced for interplanar angles of up to about 20°. All these values are compatible with the values calculated here for the solution state.

Summary

1) The ultraviolet absorption spectra of biphenyl in the crystalline state, in the solution state, and in the vapor state have been discussed in detail.

2) The relation between the position of conjugation band in the spectra of biphenyl and the spatial configuration of the molecule has been clarified by calculations based on the simple LCAO molecular orbital method.

3) By using the results of the calculations, it has been inferred from the analysis of the absorption spectra that the angles between the planes of the two benzene rings in the most probable conformations of biphenyl in the solution state and in the vapor state are about 20° and about 40~43°, respectively. These values coincide fairly well with the values estimated by other workers on different grounds.

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