The Spatial Configurations and the Ultraviolet Absorption Spectra of Biphenyl and Some Related Compounds

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It is well-known that atrop-isomerism occurs when two or more of the ortho hydrogen atoms in biphenyl are replaced by larger atoms or groups. This phenomenon is explained as due to steric hindrance which prevents rotation about the central 1-1′ bond in the biphenyl derivatives. These molecules therefore must have a non-coplanar configuration.

Regarding the spatial configuration of biphenyl itself, on the other hand, there appear to be several conflicting evidences. Thus, the results of X-ray crystal analyses of biphenyl showed the molecule to have a completely planar configuration,[1] while electron diffraction investigations suggested a non-coplanar configuration in which the two benzene rings are perpendicular[2] or at an angle of about 45°[3] to each other. When it is assumed that the molecule of biphenyl is coplanar, the distance between the two nearest ortho hydrogen atoms attached to different benzene rings is about 1.8Å, which is considerably shorter than the usual van der Waals distance 2.0Å; therefore, there should be considerable steric interference between them.

The ultraviolet absorption spectrum of biphenyl is quite different from that of benzene and has an intense characteristic band. This is supposed to be due to the conjugation between the two benzene rings, indicating consequently that the molecule of biphenyl is coplanar or nearly coplanar, since it is generally assumed that such conjugation requires the coplanarity of the two benzene rings. On the other hand, the spectra of the derivatives of biphenyl in which the four ortho positions are substituted, e.g., bimesityl, fail to exhibit the characteristic biphenyl band, and are essentially those of the two corresponding benzene compounds.[4] This is explained by the theory that in these compounds the two benzene rings cannot be coplanar owing to steric interference of the ortho substituents[5] and consequently the conjugation between the benzene rings is destroyed. The occurrence of the conjugation between the two benzene rings in biphenyl is also proved by the fact that the extra-resonance energy has been found to be about 8 kcal./mol.[6] or about 5 kcal./mol.[7] for biphenyl, and further suggested by the fact that in *p*-nitro-*p*′-aminobiphenyl the *p*-nitro group exercises a marked effect upon the basicity of the *p*′-amino group and this effect is diminished by ortho substitution by two methyl groups[8], and also by the fact that the dissociation constants of substituted *p*-biphenylcarboxylic acids are influenced by the substituents, the effect being transmitted through the biphenyl system.[9] Furthermore, on the basis of the assumption of the coplanar configuration, London[10] has computed the energy levels of the biphenyl molecule by the method of antisymmetrized products of molecular orbitals with considerably good agreement between the theoretical electronic transitions and the observed ultraviolet absorption spectrum. These seem to be favourable for the coplanar configuration.

It should, however, be here pointed out that the conjugation requires not necessarily the perfect coplanarity. The conjugation operates by the overlapping of the π-orbitals of the 1, 1′ carbon atoms, so it should operate in full at coplanarity. However, partial loss of coplanarity is not necessarily associated with complete loss of conjugation. That is, the

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

2) J. L. Karle and L. O. Brockway, ***J. Am. Chem. Soc.***, **66**, 1974 (1944).

3) O. Bastiansen, ***Acta Chem. Scand.***, **3**, 408 (1949).

4) (a) L. W. Pickett, G. F. Walter and H. France, ***J. Am. Chem. Soc.***, **58**, 2296 (1936); (b) M. T. O'Shaughnessy and W. H. Rodebush, ibid., **62**, 2906 (1940).

5) Concerning the effects of ortho substituents on the spectra of biphenyls, see also: (a) M. Pestemer and E. Mayer-Pitch, ***Monatsh.***, **70**, 104 (1937); (b) M. Calvin, ***J. Org. Chem.***, **4**, 256 (1939); (c) B. Williamson and W. H. Rodebush, ***J. Am. Chem. Soc.***, **63**, 3018 (1941); (d) D. W, Sherwood and M. Calvin, ibid., **64**, 1350 (1942); (e) W. H. Rodebush and I. Feldman, ibid., **68**, 896 (1946); (f) R. A. Friedel, M. Orchin, and L. Reggel, ibid., **70**, 199 (1948).

6) (a) L. Pauling and J. Sherman, ***J. Chem. Phys.***, **1**, 606 (1933); L. Pauling, "The Nature of the Chemical Bond", (1939), p. 129; (b) M. Szwarc, ***Nature***, **161**, 890 (1948).

7) F. Wm. Cagle and H. Eyring, ***J. Am. Chem. Soc.***, **73**, 5628 (1951).

8) D. W. Sherwood and M. Calvin, ***J. Am. Chem. Soc.***, **64**, 1350 (1942).

9) E. Berliner and E. A. Blommers, ***J. Am. Chem, Soc.***, **73**, 2479 (1951).

10) A. London, ***J. Chem. Phys.***, **13**, 396 (1945).

perfect coplanarity is not prerequisite to the occurrence of conjugation and consequently to the appearance of the spectrum characteristic of such a conjugated system.

On the basis of such considerations, the apparently conflicting evidences are most satisfactorily interpreted as indicating that biphenyl is non-coplanar in the liquid or gaseous state while in the crystalline state it is maintained in the coplanar configuration presumably by the lattice force which overcomes the steric interference between the ortho hydrogen atoms. Then, the spectrum of biphenyl in the crystalline state should be that of the molecule in the coplanar configuration and the spectrum of biphenyl in the liquid or gaseous state should be that of the molecule in then on-coplanar configuration. Actually, in accordance with expectation, the spectrum of the crystal[11,12] is considerably different from that of the liquid or solution, and the former has the characteristic band at considerably longer wave-lengths than the latter, while the spectrum of the vapor is similar to that of the liquid;[12] so, it may be possible to infer the spatial configurations of biphenyls from their absorption spectra.

Previously,[13] the present author has determined the quantitative relations between the degree of deviation from coplanarity of the molecular configuration and the wave-lengths of the absorption spectrum as well as the extent of conjugation for stilbenes, and showed that the absorption maximum is shifted toward shorter wave-lengths and that the resonance energy is reduced progressively with increasing angle of twist of the phenyl groups out of the plane of the ethylenic linkage. The subject of the present paper is to determine analogous relations for biphenyls and discuss the spatial configurations of biphenyl and some related compounds.

Calculations

The calculations follow a procedure quite similar to the previous one[13] for stilbenes, so only the outline is given. In the present case the exchange integral for the 1-1′ bond is denoted by $\alpha\beta$. The value of the parameter α should vary with the length of the 1-1′ bond and the degree of twist of the benzene rings from the coplanar position around the 1-1′ bond. Since the biphenyl molecule belongs to the symmetry group D_2, the secular equation for the determination of the twelve approximate molecular orbitals as linear combinations of $2p\pi$ atomic orbitals is factorized into the following four equations:

$$\begin{aligned} A_1,\ & x^4+\alpha x^3-5x^2-3\alpha x+4=0, \\ B_2,\ & x^4-\alpha x^3-5x^2+3\alpha x+4=0, \\ B_1,\ & x^2-1=0, \\ B_3,\ & x^2-1=0, \end{aligned}$$

where $x=W/\beta=(Q-E)/\beta, Q, E$, and β having their usual meanings[14]. The numerical values of x obtained by solving these equations for various values of α represent the heights of the energy levels in units of β of the molecule in the spatial configuration prescribed by the corresponding value of α. The levels belonging to A_1 and those to B_2 vary, and those to B_1 and those to B_3 do not vary with α. These are reduced to those of benzene when α is zero. The absorption band characteristic of biphenyls is ascribed to the electronic transition from the highest occupied level to the lowest vacant level. In Table I, the values of the energy difference ΔE between these two levels and values of the extra-resonance energy $R.E.$ for various values of α are recorded. It is seen that the value of ΔE becomes larger and that of $R.E.$ smaller with decreasing value of α.

Since the exchange integral can be taken to be approximately proportional to the overlap integral, the value of α is assumed to vary with the angle of twist and the lengh of the 1-1′ bond R according to the relation

$$\alpha=S(R)\cos\theta/S(1.39\text{Å}),$$

where $S(R)$ is the π-π overlap integral when the bond length is R, and 1.39Å is the bond length between the adjacent carbon atoms in benzene ring. The value of $S(R)$ can be obtained from Mulliken's Table.[15] The value of R is assumed to be determined for any value of θ by the relation

$$\begin{aligned} &\{S(R)-S(1.54\text{Å})\}/\{S(1.48\text{A})-S(1.54\text{Å})\} \\ &=S(\theta)/S(0^\circ)=\cos\theta, \end{aligned}$$

where $S(\theta)$ is the π-π overlap integral for the angle of twist of θ and $S(0^\circ)$ is that for the angle of twist of 0° at the constant bond length, since the molecule of biphenyl in the crystalline state is coplanar and the length of the 1-1′ bond is 1.48Å according to the X-ray analysis,[1] and since consequently R will vary from 1.48Å, to 1.54Å, the length of the normal C-C single bond, as θ varies from 0° to 90°. Thus, the value of θ being given, the corresponding value of α is easily obtained, and then those of ΔE and $R.E.$ are also obtained according to Table I. When θ is zero and R is 1.48Å, namely, for the coplanar

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[11] E. Merkel and C. Wiegand, *Z. Naturforsch.*, **36**, 93 (1948).

[12] A. R. Deb, *Ind. J. Phys.*, 305 (1953).

[13] H. Suzuki, This Bulletin, **25**, 145 (1952).

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

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

TABLE I

α	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0
$\Delta E(\beta)$	1.410	1.460	1.512	1.566	1.624	1.682	1.742	1.804	1.868	1.934	2
$R.E.(\beta)$	0.382	0.312	0.248	0.192	0.142	0.098	0.064	0.036	0.016	0.004	0

TABLE II

Compound	Solvent	$\lambda_{max.}$(Å)	$\varepsilon_{max.}$	$\Delta E(\beta)$	α	θ	R(Å)	$R.E.(\beta)$
Biphenyl (crystal)	——	2754[a]	——	1.482	0.858	0°	1.48	0.285
4,5-Methylene-9,10-dihydrophenanthrene	Ethanol	ca. 2720[b]	ca. 18500	1.502	0.819	16.5°	1.482	0.260
9,10-Dihydrophenanthrene	Hexane	2635[c]	18000	1.555	0.720	31.5°	1.489	0.203
2,7-Dihydro-3,4-5,6-dibenzoxepin	Hexane	2500[c]	16500	1.646	0.562	47°	1.499	0.125
2,7-Dihydro-3,4-5,6-dibenzazepinium-1-*spiro*-1'''-piperidinium bromide	Water	2480[c]	15000	1.660	0.538	49°	1.501	0.115
Biphenyl	Heptane	2475	19000	1.664	0.531	50°	1.501	0.112
o-Methylbiphenyl	Heptane	2350	10000	1.759	0.373	63°	1.513	0.056
o,o'-Dimethylbiphenyl	Ethanol	(ca. 2270)[d]	6800	1.825	0.267	70.5°	1.520	0.029

a, A.R. Deb, Reference (12). *b*, R.N. Jones, Reference (22).
c, G.H. Beaven et al., Reference (18). *d*, G.H. Beaven et al., Reference (23).

molecule of biphenyl in the crystalline state, α is 0.858 and ΔE is 1.482(β).

According to Deb,[12] the characteristic band in the spectrum of biphenyl in the liquid state is split up into two broad bands at 36306 cm^{-1} (2754 Å) and 37386 cm^{-1} (2675 Å) in the case of the solid at 30°C, and the band at 36306 cm^{-1} is presumed to be the intrinsic band (ν_0). Consequently, this band corresponds to ΔE of 1.482 β. On the other hand, the "center of gravity of singlets"[16] in the absorption spectrum of benzene, 48000 cm,$^{-1}$ corresponds to ΔE of 2β. Therefore, in order to correlate the position of the absorption maximum with the calculated energy difference ΔE, it is assumed that the former expressed in wave number changes linearly with respect to the change in the latter from 36306 cm^{-1} corresponding to $\Delta E = 1.482\beta$ to 48000 cm^{-1} corresponding to $\Delta E = 2\beta$. Thus, the position of the absorption maximum of the biphenyl-type compound in which the two benzene rings are twisted to any extent from the coplanar position is easily inferred. Conversely, when the position of the absorption maximum is known experimentally, the degree of deviation from coplanarity, θ, as well as the extent of conjugation, $R.E.$, can be computed.

In Table II, the results of such computations are summarized. It is, for simplification, assumed that the absorption spectrum depends solely on the spatial configuration of the biphenyl skeleton in the compounds, and other effects, for example, the comparatively small bathochromic effect of the alkyl substituent or of the alicyclic bridge, are ignored.

Discussion

As is seen from the Table II, the characteristic absorption maximum is shifted toward shorter wave-lengths and the extra-resonance energy is reduced progressively with an increasing angle of twist.

For biphenyl in solution, the angle between the two benzene rings has been computed to be 50°. According to the electron diffraction sector method study by Bastiansen,[3,17] the angle is found to be 45° ±10°, 52° ±10°, 54° ±5°, and 45° for biphenyl, 3, 3'-dichlorobenzidine, 3, 3'-dibromobiphenyl, and 3, 3', 5, 5'-tetrabromobiphenyl respectively. If the actual angle is assumed to be the same for all the non-ortho-substituted biphenyls, it can be given the value 50° ±5° on the average.[17] The agreement between the value obtained here and that found by Bastiansen is surprisingly good, although the former refers to the molecule in solution while the latter to the molecule in the gaseous state. In this connection, the cases of the 2, 2'-bridged biphenyls are of interest. In these compounds the molecule is maintained in the comparatively rigid configuration. According to the models, the angle between the two benzene rings of the biphenyl skeleton in 2, 7-dihydro-3, 4-5, 6-dibenzoxepin (I) and 2, 7-dihydro-3, 4-5, 6-dibenzazepinium-1-*spiro*-1'''-piperidinium bromide (II) in which the 2, 2'-positions of biphenyl are bridged by a 7-membered ring is about 50°, and it is

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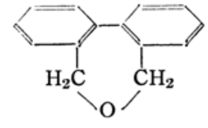
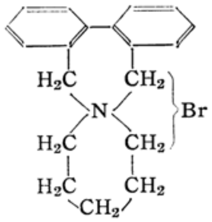
16) J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

17) O. Bastiansen, *Acta Chem. Scand.*, **4**, 926 (1950).



(I)



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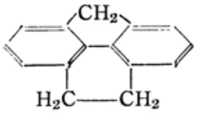

(III)

notable that these compounds show closely similar absorption spectra to that of biphenyl in solution,(18) and that the angle has been computed by the present method to be 47° and 49° respectively. This gives presumably some support to the above estimation of the angle of twist for the isolated molecule of biphenyl. Samoilov and Dyatkina,(19) in contrast to this, have deduced a value of about 30° for this angle in the isolated molecules of biphenyl and of terphenyl by calculations based on the molecular orbital method of the resonance energy and of the interaction between the nearest hydrogen atoms.

According to Beaven et al.,(18) the angle of twist in 9,10-dihydrophenanthrene in which the 2,2′-positions of biphenyl are bridged by a 6-membered ring is estimated to be about 20° from the model, while fluorene in which the 2,2′-positions of biphenyl is bridged by a 5-membered ring is best regarded as a strained planar structure. However, the absorption spectra of these two compounds are similar with the exception that in the latter compound fine structures appear.(20) The X-ray data, according to Jones,(21) favor a nonplanar configuration for crystalline fluorene. On the other hand, in 4,5-methylene-9,10-dihydrophenanthrene (III), the conflicting steric requirements of the two bridges would appear to be most favorably compromised in an approximately planar configuration. The above estimations of the angle of twist seem to suggest that it is the case. Thus, this compound has the characteristic absorption band(22) at considerably longer wave-lengths than those of 9,10-dihydrophenanthrene and of fluorene and nearer to that of biphenyl in the crystalline state. This suggests presumably that the molecule of 4,5-methylene-9,10-dihydrophenanthrene is nearer to coplanar and that the molecule of fluorene as well as of 9,10-dihydrophenanthrene deviates from coplanarity to a larger extent as compared with 4,5-methylene-9,10-dihydrophenanthrene. It is doubtful, of course, whether much significance can be attached to the numerical values of the angle of twist shown in Table II especially for these 2,2′-bridged biphenyls, because the straining effects of the 2,2′-bridge linkages in these compounds would be too complicated to be treated by such a simple method. (The above assumption, for example, of the relation between R and θ may be not pertinent to these cases.)

The angle of twist for ortho-methylbiphenyl has been computed to be 63°, which is in best accord with the value 62° deduced from the model in which the length of the 1-1′ bond is 1.51 Å and an ortho hydrogen atom just touches the ortho methyl group.

It is notable that the spectrum of *o,o′*-dimethylbiphenyl is markedly different from that of *o*-methylbiphenyl. If the molecule of *o,o′*-dimethylbiphenyl assumed the trans form in which the ortho hydrogen atoms just contact with the ortho methyl groups, the configuration would be similar to that of *o*-methylbiphenyl, and consequently *o,o′*-dimethylbiphenyl would show a closely similar spectrum to that of *o*-methylbiphenyl. As a matter of fact, the spectrum of *o,o′*-dimethylbiphenyl has no distinct band; however, according to Beaven et al.,(23) it has the inflection at about 2270 Å, which is regarded as a vestigial conjugation band. When this value is taken as a basis for calculation, θ and R are computed to be 70.5° and 1.520 Å. These values are in good agreement with the corresponding values, 70.6° and 1.525 Å, found for 2,2′-dimethylbenzidine dihydrochloride by the X-ray crystal analysis.(24) Considering the fact that the value of the angle between the two benzen rings found for gaseous 2,2′-dichlorobiphenyl by the electron diffraction method,(17) 74°, and that found for crystalline

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18) G. H. Beaven, D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, **1952**, 854.

19) S. Samoilov and M. Dyatkina, ***Zhur. Fiz. Khim.***, **22**, 1294 (1948); ***Chem. Abst.***, **43**, 2606.

20) R. N. Jones, *J. Am. Chem. Soc.*, **67**, 2127 (1945).

21) Reference (22); Iball, *Z. Krist.*, **94**, 397 (1936); Cook and Iball, *Chemistry and Industry*, **55**, 467 (1936).

22) R. N. Jones, *J. Am. Chem. Soc.*, **63**, 1658 (1941).

23) G. H. Beaven, D. M. Hall, M. S. Lesslie, E. E. Turner, and (in part) G. R. Bird, *J. Chem. Soc.*, **1954**, 131.

24) F. Fowwether and A. Hargreaves, *Acta Cryst.*, **3**, 81 (1950); ***Chem. Abst.***, **44**, 7118; A. Hargreaves and W. H. Taylor, *J. Sci. Instruments*, **18**, 138 (1941); ***Chem. Abst.***, **35**, 7261.

2, 2′-dichlorobenzidine by the X-ray investigation,[25] 72°, are in fact the same within the limits of experimental errors, and that both these compounds have been found to have the structures more similar to the *cis* form than to the *trans* form, it may be not unreasonable to compare the values for 2, 2′-dimethylbiphenyl in solution with those for 2, 2′-dimethylbenzidine dihydrochloride in the crystalline state, and to infer that the preferred configuration of the former as revealed by its absorption spectrum is similar to the configuration of the latter, which has been found to have the two ortho methyl groups in the *cis*-disposition.[24] At any rate, it seems to be sure that the conjugation between the two benzene rings still occurs, though faintly, in spite of large deviation from the coplanarity of the molecule. In this connection, it is of interest that Theilacker and Ozegowski[26] have found that 2, 2′-dimethyl-4, 4′-bis-(diphenylmethyl)-biphenyl has properties as a true biradical, although their results do not seem to be entirely free from ambiguity. Theilacker[27] mentioned also that the angle of twist was 37°–48° in this compound. In view of the above results, this value is presumably too small.

Lastly, it should be mentioned that the values computed above do not necessarily refer to the rigid configurations of the molecules but to the average or most probable ones. The fairly good agreements of the values computed above with the available data obtained by other methods throughout the cases under discussion may be supposed to prove the validity of such approximate treatments, and further, it is believed that the quantitative relations between the spatial configuration and the absorption spectrum as well as the extent of conjugation for biphenyl-type compounds have been almost satisfactorily determined here.

Experimental

o-Methylbiphenyl was prepared after the Gomberg's procedure[28] by diazotizing *o*-toluidine in concentrated hydrochloric acid and adding the reaction mixture into a stirred mixture of sodium hydroxide solution and benzene. *o*, *o*′-Dimethylbiphenyl was prepared by the action of zinc dust on the diazotized *o*-toluidine in aqueous sulfuric acid solution to which ethanol was added, following the Gattermann's procedure[29] for preparation of biphenyl.

The measurements of the ultraviolet absorption spectra of biphenyl, *o*-methylbiphenyl, and *o*, *o*′-dimethylbiphenyl were carried out with a Beckman Quartz Spectrophotometer Model DU. As the solvent *n*-heptane was used. The concentration of the solutions was $1/3\times10^{-4}$ mole per liter for biphenyl and $1/2\times10^{-4}$ mole per liter for *o*-methylbiphenyl and for *o*, *o*′-dimethylbiphenyl.

Summary

The quantitative relations between the degree of deviation from coplanarity of the molecular configuration and the ultraviolet absorption spectrum as well as the extent of conjugation for the biphenyl-type compounds have been determined by calculations based on the molecular orbital method. On the basis of the results, the spatial configurations of biphenyl, *o*-methylbiphenyl, *o*, *o*′-dimethylbiphenyl, fluorene, 9, 10-dihydrophenanthrene, 4, 5-methylene-9, 10-dihydrophenanthrene, 2, 7-dihydro-3, 4-5, 6-dibenzoxepin, and 2, 7-dihydro-3, 4-5, 6-dibenzazepinium-1-*spiro*-1‴-piperidinium bromide have been discussed.

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[25] D. L. Smare, *Acta Cryst.*, **1**, 150 (1948); *Chem. Abst.*, **42**, 8045.

[26] W. Theilacker and W. Ozegowski, *Ber.*, **73**, 33 (1940).

[27] W. Theilacker, *Naturwiss.*, **31**, 505 (1943); *Chem. Abst.*, **38**, 3885.

[28] M. Gomberg and J. C. Pernert, *J. Am. Chem. Soc.*, **48**, 1372 (1926).

[29] L. Gattermann, *Ber.*, **23**, 1226 (1890).