# *Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. III. o, o'-Bridged Biphenyls*

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The method developed in the earlier parts1,2) of this series is applied to some *o, o'*-bridged biphenyls, and the relation between the ultraviolet absorption spectra and the spatial configurations of these compounds is discussed.

A collection of the data of the spectra of some *o, o'*-bridged biphenyls is assembled in Table I.

### *o, o'*-One-atom-bridged and Two-atom-bridged Biphenyls

The spectra of fluorene and of 9,10-dihydrophenanthrene exhibit besides the intense bands at about 260 mμ lower bands at about 300 mμ. The former bands are probably the conjugation bands characteristic of the biphenyl-type compounds. The

TALBE I. ULTRAVIOLET ABSORPTION SPECTRA OF *o, o'*-BRIDGED BIPHENYLS

| Entry No. | Compound | Solvent | Conjugation band | | Ref. |
|---|---|---|---|---|---|
| | | | $\lambda_{max}$, mμ | ε | |
| 1 | Fluorene | Hp | 261.5* | 18900 | a |
| | | E | ca. 260* | 19000 | 3) |
| 2 | 9, 10-Dihydrophenanthrene | Hx | 263.5 | 18000 | 4) |
| | | E | 264 | 17000 | 4) |
| 3 | 4, 5-Methylene-9, 10-dihydrophenanthrene | E | ca. 272 | ca. 18500 | 5) |
| *o, o'-Three-atom-bridged biphenyls* | | | | | |
| 4 | 2, 7-Dihydro-3, 4-5, 6-dibenzoxepin | Hx | 250 | 16500 | 4) |
| 5 | 3, 4-5, 6-Dibenzocyclohepta-3, 5-diene-1-carboxylic acid | E | 249 | 15300 | 6) |
| 6 | 6, 6-Dicarbethoxydibenzo-[a, c] [1, 3]-cycloheptadiene | E | 249 | 16980 | 7) |
| 7 | Methyl 3, 4-5, 6-dibenzocyclohepta-3, 5-diene-1-carboxylate | E | 248.5 | 15500 | 6) |
| 8 | 1-Hydroxymethyl-3, 4-5, 6-dibenzocyclohepta-3, 5-diene | E | 248.5 | 15400 | 6) |
| 9 | 2, 7-Dihydro-3, 4-5, 6-dibenzazepinium-1-*spiro*-1'''-piperidinium bromide | W | 248 | 15000 | 4) |
| *o, o'-Four-atom-bridged biphenyls* | | | | | |
| 10 | Ethyl 4, 5-6, 7-dibenzocycloocta-4, 6-diene-1, 1, 2, 2-tetracarboxylate | E | 239.5 | 13100 | 6) |
| 11 | Methyl 4, 5-6, 7-dibenzocycloocta-4, 6-diene-1, 2-dicarboxylate | E | 236.5 | 12700 | 6) |

Solvent: E, ethanol; Hp, *n*-heptane; Hx, *n*-hexane; W, water.

* The most intense maximum of fine structure.

Ref. a refers to the present work (cf. Table II and Fig. 1).

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1) H. Suzuki, This Bulletin, **32**, 1340 (1959).

2) H. Suzuki, ibid., **32**, 1350 (1959).

3) W. V. Mayneord and E. M. F. Roe, *Proc. Roy. Soc.* (*London*), **A158**, 634 (1937).

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

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

6) G. H. Beaven, G. R. Bird, D. M. Hall, E. A. Johnson, J. E. Ladburg, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, **1955**, 2708.

7) D. C. Iffland and H. Siegel, *J. Am. Chem. Soc.*, **80**, 1947 (1958).

latter, which are absent from biphenyl, are difficult to interpret. Braude[8,9] seems to have attempted to explain these feeble bands by means of an assumption of C–C hyperconjugative interaction of the two benzene rings through the methylene bridge. Perhaps these bands may be considered to correspond to the "hidden transition" in biphenyl[10].

The spectrum of fluorene and that of 9,10-dihydrophenanthrene resemble each other considerably on the whole[11]. However, while the latter shows no fine structure, the former shows a remarkably well-resolved fine structure (Table II and Fig. 1). This may be related to the fact that fluorene has probably a strained or forced coplanar or near-coplanar configuration.

TABLE II. THE ULTRAVIOLET ABSORPTION SPECTRUM OF FLUORENE IN $n$-HEPTANE MEASURED ON A CARY RECORDING SPECTROPHOTOMETER MODEL 14 M-50 (cf. Fig. 1)

| | | Conjugation band | | | |
|---|---|---|---|---|---|
| $\lambda_{\max}$, m$\mu$ | $\varepsilon$ | $\lambda_{\max}$, m$\mu$ | $\varepsilon$ | $\lambda_{\max}$, m$\mu$ | $\varepsilon$ |
| 300.3 | 10070 | (277.4) | 8350 | 226.5 | 5680 |
| 293.6 | 5020 | 272.2 | 13050 | 220.4 | 16250 |
| 288.9 | 6190 | 264.2 | 18720 | 208.5 | 42500 |
| | | 261.5 | 18900 | 204.3 | 44500 |
| | | (255.5) | 16630 | | |

Wavelengths in parentheses denote inflections.

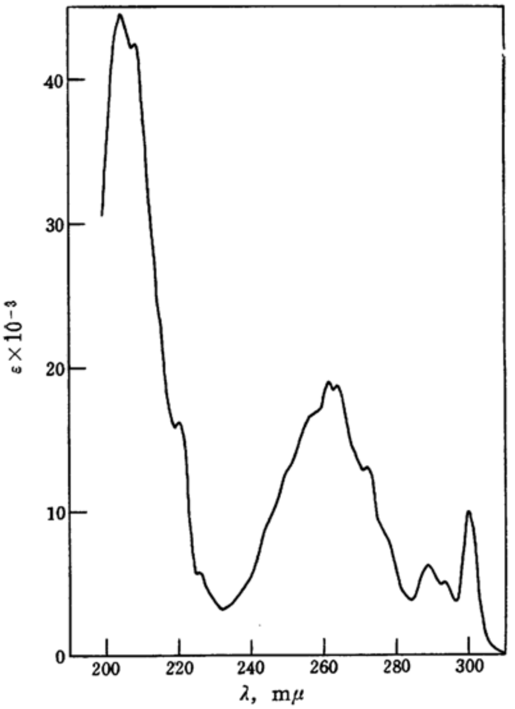

Fig. 1. The ultraviolet absorption spectrum of fluorene in $n$-heptane (cf. Table II).

The conjugation band of fluorene is at considerably longer wavelengths than that of biphenyl. This bathochromic shift of the band may be partly due to the forced coplanarity or near-coplanarity of the molecular configuration of fluorene, and partly to the hyperconjugation of the methylene group. When the relation postulated for biphenyl[1] between the calculated electronic transition energy $\Delta E_A$ and the observed position $\nu_A$ (in wave number) of the maximum of the conjugation band is provisionally applied without allowance for the bathochromic (hyperconjugation) effect of the substituent to fluorene, the value of the parameter $\mu$ in the $\pi-\pi$ resonance integral $\mu\beta$ for the co-annular bond in fluorene is estimated to be about 1.060 from the position 261.5 m$\mu$ (in $n$-heptane) of the most intense maximum of the conjugation band. This value is to be compared with the corresponding value 0.780 or 0.762 for biphenyl in solution, although this value for fluorene should be considered as a measure of the degree of "conjugation" in fluorene including hyperconjugation of the methylene group as well as intrinsic conjugation which depends on the spatial configuration of the biphenyl skeleton. The fact that the degree of conjugation in fluorene is considerably larger than in biphenyl may explain at least partly the extraordinarily larger reactivity of fluorene as compared with biphenyl in some kinds of reactions. A few examples are given below.

The reactivity of fluorene to nitration is much higher than that of biphenyl. Thus, while the "partial rate factor" (the rate constant of separate nuclear position of the compound relative to one nuclear position of benzene being taken as unity) at $p$-position and that at $o$-position in biphenyl are 38 and 41, respectively[12], or 11.0 and 18.5, respectively[13], the values at the corresponding positions (i. e. the 2- or 7- and the 4- or 5-positions) in fluorene are 2040 and 944, respectively[14].

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[8] E. A. Braude, *J. Chem. Soc.*, **1949**, 1902.

[9] E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods", Academic Press, Inc., New York (1955), p. 154 ff. (E. A. Braude).

[10] A. Wenzel, *J. Chem. Phys.*, **21**. 403 (1953). See also Ref. 1.

[11] R. N. Jones, *J. Am. Chem. Soc.* **67**, 2127 (1945).

[12] O. Simamura and Y. Mizuno, This Bulletin, **30**, 196 (1957).

[13] P. B. D. de la Mare and M. Hassan, *J. Chem. Soc.*, **1957**, 3004.

[14] M. J. S. Dewar and D. S. Urch, ibid., **1958**, 3079.

Berliner and Shieh[15] have correlated the rate constants of solvolysis of $\alpha$-arylethyl chlorides with the atom localization energies calculated by Dewar and others for the aryl radicals, and found that the reactivity of 2-fluorenyl compound is extraordinarily higher than expectation.

In addition, Sandin and coworkers[16] have compared the carcinogenic activities of 2-acetylaminofluorene, 4-acetylaminobiphenyl, and their related compounds, and found the fact that 2-acetylaminofluorene has a much higher activity as compared with 4-acetylaminobiphenyl and especially its *o*-methyl substituted derivatives. They have ascribed this fact to the greater planarity of the configuration of the biphenyl skeleton in 2-acetylaminofluorene than in the other compounds.

The interplanar angle in 9,10-dihydrophenanthrene has been estimated by Beaven and coworkers[4] to be about 20° by means of a model in which the saturated carbon atoms maintain their tetrahedral valency angle. Accordingly the bathochromic displacement of the conjugation band of this compound relative to that of biphenyl may be due mainly to the normal electronic substituent effect (probably hyperconjugation effect) of the alkyl group.

The maximum of the conjugation band of 4,5-methylene-9,10-dihydrophenanthrene is at even longer wavelengths than those of fluorene and 9,10-dihydrophenanthrene. In this compound the conflicting steric requirements of the two bridges would appear to be most favorably compromised in an approximately planar configuration. Accordingly the bathochromic shift of the conjugation band of this compound relative to those of fluorene and of 9,10-dihydrophenanthrene may be ascribed partly to the planarity or nearer-planarity of the configuration, and partly to the electronic substituent effect of the additional dimethylene or methylene bridge.

### *o, o′*-Three-atom-bridged and Four-atom-bridged Biphenyls

Each of the spectra of the compounds in which the *o,o′*-positions of biphenyl are bridged by a 7-membered ring (which are subsequently referred to as the *o,o′*-three-atom-bridged biphenyls) (entries 4—9, Table I) shows the conjugation band at considerably shorter wavelengths than those of fluorene and of 9,10-dihydrophenanthrene. The corresponding band of each of the compounds in which the *o,o′*-positions of biphenyl are bridged by an 8-membered ring (the *o,o′*-four-atom-bridged biphenyls, entries 10 and 11) is further shifted toward shorter wavelengths.

These *o,o′*-three-atom-bridged and four-atom-bridged biphenyls are considered to have non-planar configurations. Accordingly, the hypsochromic displacements of the conjugation band observed in these compounds with respect to fluorene or 9,10-dihydrophenanthrene are probably ascribed to the non-planarity of the configurations, and therefore, their configurations may be inferred from their spectra by application of the method described in the earlier parts of this series.

In application of the method to these compounds, 9,10-dihydrophenanthrene is taken as the longer-wavelength-side reference compound. The justification for taking this compound rather than fluorene as the reference compound is that this makes a pertinent allowance for the bathochromic effect of two methylene groups attached at the *o*- and the *o′*-positions of biphenyl, and further justification is found in the fact that the molecule of fluorene is presumed to contain a considerably large strain.

The previously assumed relation between the length of the co-annular bond $R$ and the interplanar angle $\theta$ (Eqs. 4 and 5 in Part I of this series) may not be pertinent to this case. However, a slight change in the value of $R$ does not substantially affect the calculated value of the interplanar angle $\theta$, as suggested by the results of calculations in the case of terphenyls which will be described in the next part of this series. Hence the relation is applied to the present case for simplification. Then, adopting the value (about 20°) estimated by Beaven and coworkers from the scale model for the interplanar angle in 9,10-dihydrophenanthrene, the corresponding value of $R$ is computed to be 1.4837 Å, and the parameter $\mu$ in the $\pi-\pi$ resonance integral $\mu\beta$ for the co-annular bond is evaluated to be 0.801. Consequently, the value of the calculated transition energy $1.5115(-\beta)$, viz. $\Delta E_L$, when $\mu$ is 0.801 is assumed to correspond to the wave number $37879\,\mathrm{cm}^{-1}$ ($264\,\mathrm{m}\mu$),

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[15] E. Berliner and N. Shieh, *J. Am. Chem. Soc.*, **79**, 3849 (1957).

[16] R. B. Sandin, R. Melley, A. S. Hay, R. N. Jones, E. C. Miller and J. A. Miller, ibid., **74**, 5073 (1952).

viz. $\nu_L$, of the position of the maximum of the conjugation band in the spectrum of 9,10-dihydrophenanthrene in ethanol. (In the present treatment the data of the spectra of the solutions in ethanol are compared in principle.)

As the shorter-wavelength-side reference, quite similarly to the previous treatment of *o*-alkyl- and *o,o'*-dialkylbiphenyls[2], the value of toluene, 46882 cm$^{-1}$ (213.3 m$\mu$), corresponding to the "center of gravity of singlets" of benzene is taken, because the effect of a methylene group upon the positions of the bands of benzene is considered to be approximately of the same magnitude as that of a methyl group (cf. Table II in Part II of this series). That is, the value of 46882 cm$^{-1}$ (viz. $\nu_S$) is assumed to correspond to the value of the calculated transition energy $2(-\beta)$ (viz. $\Delta E_S$) when $\mu$ is 0.

On the basis of the above assumptions, the value of $\Delta E_A$, $\mu$, $\theta$, $R$, etc. for each of the *o,o'*-three-atom-bridged and the *o,o'*-four-atom-bridged biphenyls can be computed by the usual procedure from the position of the conjugation band in its spectrum. The results of calculations are summarized in Table III.

TABLE III. RESULTS OF CALCULATION

*o,o'-Three-atom-bridged biphenyls*

| Compound | $\lambda_{max}$ m$\mu$ | $\nu_A$ cm$^{-1}$ | $\Delta E_A$ $-\beta$ | $\mu$ | $\theta$ | $R$ Å |
|---|---|---|---|---|---|---|
| 4 | 250 | 40000 | 1.627 | 0.594 | 44.5° | 1.497 |
| 5, 6 | 249 | 40161 | 1.635 | 0.579 | 46.0 | 1.498 |
| 7, 8 | 248.5 | 40241 | 1.640 | 0.572 | 46.7 | 1.499 |
| 9 | 248 | 40323 | 1.644 | 0.565 | 47.3 | 1.499 |
| (Average) | 249 | 40161 | 1.635 | 0.579 | 46.0 | 1.498 |
| *o,o'-Four-atom-bridged biphenyls* | | | | | | |
| 10 | 239.5 | 41754 | 1.722 | 0.434 | 58.0 | 1.508 |
| 11 | 236.5 | 42283 | 1.751 | 0.387 | 61.5 | 1.511 |
| (Average) | 238 | 42017 | 1.736 | 0.411 | 59.8 | 1.510 |

Compounds are represented by the entry numbers in Table I.

Beaven and coworkers have estimated the interplanar angle in *o,o'*-three-atom-bridged biphenyls as about 50°[4], and that in *o,o'*-four-atom-bridged biphenyls as about 60~65°[6] from models. The values have been computed here to be 44.5~47.3° average, 46°) and 58.0~61.5° (average, 59.8°), respectively, which agree fairly well with the values estimated from models.

From the close similarity between the spectrum of 2,7-dihydro-3,4-5,6-dibenzoxepin (entry 4,Table I)and that of biphenyl Beaven and others[4] have presumed that "in the oxepin the phenyl groups are no less conjugated and hence no less coplanar than in biphenyl", and concluded that "the biphenyl-type spectrum does not provide sure evidence for a coplanar configuration" "since the oxepin can not be coplanar". In addition, the present author considered in the previous paper[17] that the estimation of the value of the interplanar angle in biphenyl as about 50° was supported by this spectral similarity. A common flaw in these considerations is that the bathochromic effect of the substituents was not sufficiently taken into account.

On the other hand, Braude and Forbes[18] have estimated the interplanar angles in ortho-bridged biphenyls and their related compounds by applying the equation $\cos\theta = \varepsilon/\varepsilon_0$, assuming that $\varepsilon_0$ is equal to the molar extinction coefficient of the conjugation band of fluorene, and obtained the following values; 21° for 2,7-dihydro-3,4-5,6-dibenzoxepin (entry 4, Table I), 41° for its *o,o'*-dimethyl derivative, 47° for its *o,o'*-dimethoxy-derivative, and 27° for 2,7-dihydro-3,4-5,6-dibenzazepinium-1-*spiro*-1'''-piperidinium bromide (entry 9).

Their equation mentioned above has been assumed to be true on the basis of the hypothesis of transitions from the non-planar ground state to the uniplanar or near-planar excited state, and the starting point of their theory is the assumption that the absorption intensity is determined by the transition probability which is in turn governed mainly by the probability in which the molecule in the ground state assumes the uniplanar or near-planar configuration[19]. However, this probability must be governed by the shape of the potential energy curve for the tortional vibration, and hence mainly by the energy difference between the uniplanar or near-planar configuration and the most probable configuration. In spite of the hypothesis by Braude and others, it seems to be very questionable whether or not there is any direct relation between this probability, namely, the height of the energy barrier to the rotation about the pivot bond and the interplanar angle in the most probable configuration.

Furthermore, according to its basic theory, the equation mentioned above

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[17] H. Suzuki, This Bulletin, **27**, 597 (1954).

[18] E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, **1955**, 3776.

[19] E. A. Braude and F. Sondheimer, ibid., **1955**, 3754.

should be applied only to the case in which the so-called steric effect of type 1 is exerted, that is, to the case in which a reduction in the intensity of the conjugation band occurs alone without any significant hypsochromic shift. Nevertheless, it is evident that in the spectra of the compounds cited by Braude and Forbes remarkable hypsochromic shifts are involved. The application of the equation to these compounds is, therefore, inconsistent with its basic theory itself.

The introduction of two *o*-methyl groups or of two *o*-methoxyl groups into dihydrodibenzoxepin (entry 4, Table I) causes a remarkable decrease in the intensity of the "biphenyl-type" conjugation band. Considering this effect as being mainly due to the steric effect, Braude and Forbes[18] have stated that the assumption by Beaven and others of an angle of 50° between the benzene rings in the parent oxepin is questionable. Thus, adopting the assumption of Beaven and others, since the benzene rings in this compound are already at an angle of about 50°, the introduction of the *o*-substituents should have no steric consequences. On the other hand, Beaven and others[4] have attempted to explain this effect of the substituents by electronic interaction between the substituents and the separate benzene rings to which they are attached.

However, in the preceding part of this series, the interplanar angle in *o*,*o*′-dimethylbiphenyl was estimated to be about 70°, and this compound was inferred to have the *cis*-configuration. This value of the interplanar angle is considerably larger than that for dihydrodibenzoxepin, 50°, estimated by Beaven et al., or 44.5°, by the present author. Therefore, even when the value, 50° or 44.5°, is adopted as the interplanar angle in dihydrodibenzoxepin, the introduction of the substituents into the ortho positions can evidently increase the interplanar angle, and hence a decrease in the intensity and the hypsochromic shift caused by the introduction of two *o*-methyl groups can be explained sufficiently, contrary to the opinion of Braude and others. A decrease in the intensity of the band caused by the introduction of two *o*-methoxyl groups may be similarly explained by steric effect, but the fact that the band of *o*,*o*′-dimethoxy-derivative is at, though slightly, longer wavelengths than that of the parent compound may be attributed to the electronic effect of the substituents.

Finally, in connection with the spatial configuration of the *o*,*o*′-bridged biphenyls, it is noteworthy that recently Iffland and Siegel[7] succeeded first in preparing an optically active biphenyl derivative whose optical activity is due to non-planarity of the biphenyl skeleton as a consequence of the requirement of a three-carbon-atom-bridge across the *o*,*o*′-positions. According to them, this compound, *d*-6,6-dicarbethoxy-dibenzo-[a, c] [1, 3]-cycloheptadiene (entry 6, Table I), is optically stable in the crystalline state, and loses half of its activity ($[\alpha]_D^{32.5}$ +2.25° in cyclohexane) in 80 min. in cyclohexane solution.

## Summary

The ultraviolet absorption spectra of some *o*,*o*′-bridged biphenyls and their relations to the spatial configurations have been discussed. The method developed in the earlier parts of this series has been applied to these compounds, especially *o*,*o*′-three-atom-bridged (*o*,*o*′-7-membered-ring-bridged) and *o*,*o*′-four-atom-bridged (*o*,*o*′-8-membered-ring-bridged) biphenyls, and the interplanar angles have been calculated to be about 44.5∼47.3° (average, 46°) for the former compounds and about 58.0∼61.5° (average, 59.8°) for the latter.

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