Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. II. o-Alkyl- and o, o′-Dialkylbiphenyls

By Hiroshi SUZUKI

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In the preceding part[1] of this series the relation between the ultraviolet absorption spectra and the most probable spatial configurations of biphenyl in the various states has been discussed in detail on the basis of the calculation carried out by the simple LCAO molecular orbital method. In the present part, the same method is applied to some ortho-alkyl substituted biphenyl derivatives, and the relation between the spectra and the most probable spatial configurations of these compounds is discussed.

It is well known that atrop-isomerism occurs when two or more, especially when all, of the four ortho hydrogen atoms in biphenyl are replaced by larger atoms or groups. This phenomenon is explained as being due to steric hindrance caused by the substituents which prevents rotation about the central 1—1′ bond, namely the co-annular bond, in the biphenyl derivatives. Therefore, the most probable configurations of these compounds must be non-coplanar.

This inference is supported by information from the electronic absorption spectroscopy. Thus, for example, the spectrum of bimesityl does not exhibit the conjugation band characteristic of biphenyl-type compounds, but is closely similar to the sum of the spectra of two mesitylene molecules[2]. This fact is considered to indicate that the twist of the co-annular bond is large enough to eliminate almost completely the $\pi-\pi$ interaction across the

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

[2] (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). (c) E. Marcus, W. M. Lauer and R. T. Arnold, ibid., **80**, 3742 (1958).

bond in this compound. That is, it is inferred that the two benzene rings in this compound are almost perpendicularly oriented, as suggested by Guy by means of calculations of the energy associated with the tortion about the central linkage in 2, 2′, 6, 6′-tetramethylbiphenyl[3].

In either *o*- or *o*, *o*′-substituted biphenyls, the substituents do not confer, unless they are exceptionally large, measurable optical stability on the rotational enantiomorphs at room temperature[4], but contrariwise, they affect markedly the spectral feature. Thus, for example, the conjugation band of *o*-methylbiphenyl is at a considerably shorter wavelength and of considerably lower intensity than that of biphenyl. This hypsochromic shift is believed to indicate that the interplanar angle θ, i. e. the angle of twist of the co-annular bond, in the most probable spatial configuration of *o*-methylbiphenyl is considerably larger than the corresponding one of biphenyl itself. Further, the spectrum of *o*, *o*′-dimethylbiphenyl exhibits no distinct maximum of the conjugation band, but exhibits only an inflection at a further shorter wavelength than the position of the conjugation band of *o*-methylbiphenyl (Fig. 1.).

It is to be noted here that the effect of the substituents upon the spectra of these biphenyl derivatives must include not only the hypsochromic effect due to steric interference of the substituents, but also the electronic (probably bathochromic) effect of the substituents. As is seen in Fig. 1, the absorption maximum of the conjugation band of *p*, *p*′-dimethylbiphenyl

TABLE I. ULTRAVIOLET ABSORPTION SPECTRA OF BIPHENYL AND ALKYLBIPHENYLS

Compound	Solvent	Conjugation band		Ref.
		λ_{max}	ε	
Biphenyl	E	247.7	18050	1)
	Hp	247.0	16450	1)
p-Methyl-	E	253	13300	5)
o-Methyl-	E	235	10500	6)
	E	ca. 237	9960	a
	E	ca. 235		8)
	Cy	ca. 235		8)
	Hp	235	10000	7)
o-Ethyl-	E	233	10500	6)
o-*n*-Propyl-	E	233	10000	6)
o-Isopropyl-	E	233	11000	6)
o-*n*-Butyl-	E	233	10500	6)
p, *p*′-Dimethyl-	E	255.6	20500	a
	E	ca. 260	20000	9)
	Hp	255.2	21200	a
	Hx	256	21400	10)
o, *o*′-Dimethyl-	E	(ca. 227)	6800	11)
	E	(228～229)	(6000～6500)	a
p, *p*′-Diethyl-	E	256.5	22500	12)
p, *p*′-Diisopropyl-	E	256.5	23500	12)
o, *o*′-Diethyl-	E	(ca. 277)	6000	12)
o, *o*′-Diisopropyl-	E	(ca. 277)	5500	12)
o, *o*′-Di-*tirt*-butyl-	E	No conjugation band		12)
Bimesityl		No conjugation band		2)

Solvent: E, ethanol; Hp, *n*-heptane; Cy, cyclohexane; Hx, *n*-hexane.
Wavelengths (mμ) in parentheses denote inflections.
Ref. a refers to the present work.

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[3] J. Guy, *J. chim. phys.*, **46**, 469 (1949).

[4] R. Adams and H. C. Yuan, *Chem. Revs.*, **12**, 261 (1933).

[5] The Chemical Society of Japan, "Jikken Kagaku Koza" Vol. 1, Maruzen Co., Ltd., Tokyo (1957), p. 191 (K. Hirayama).

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

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

[8] R. A. Friedel, M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, **70**, 199 (1948).

[9] B. Williamson and W. H. Rodebush, ibid., **63**, 3018 (1941).

[10] R. A. Friedel and M. Orchin, "Ultraviolet Absorption of Aromatic Compounds", John Wiley & Sons, Inc., New York (1951).

[11] G. H. Beaven, D. M. Hall, M. S. Lesslie, E. E. Turner and G. R. Bird, *J. Chem. Soc.*, **1954**, 131.

[12] P. M. Everitt, D. M. Hall and E. E. Turner, ibid., **1956**, 2286.

from which the steric interference of the substituents is absent is at a considerably longer wavelengths as compared with the corresponding one of biphenyl. This bathochromic displacement of the band is probably due to the hyperconjugation effect of methyl groups. The similar bathochromic effect due to hyperconjugation must operate also in the spectra of ortho-substituted biphenyl derivatives such as *o*-methyl- and *o, o*'-dimethylbiphenyl. Accordingly, in order to clarify the relation between the spectra and the spatial configurations of *o*-alkyl- and *o, o*-dialkylbiphenyls, it is necessary to make allowance for the electronic bathochromic effect of the substituents.

Spectra of Alkylbiphenyls

The data of the ultraviolet absorption spectra of some alkylbiphenyls are summarized in Table I, in which that of biphenyl is included for comparison. Of the spectra measured by the present author, those of biphenyl and of *p, p*'-dimethylbiphenyl were measured with a Cary recording spectrophotometer Model 14 and those of *o*-methyl- and of *o, o*'-dimethylbiphenyl with a Beckman quartz spectrophotometer Model DU. These spectra are shown also in Fig. 1[13].

***o*-Alkylbiphenyls.**—The absorption maximum of the conjugation band of *p*-methylbiphenyl is at 253 mμ. The bathochromic effect due to the hyperconjugation effect of a *p*-methyl group and that of an *o*-methyl group are considered to be approximately of the same magnitude, as supported by the comparison of the results of calculations of the energy levels in *p*-terphenyl and in *o*-terphenyl, which will be reported in Part IV of this series.

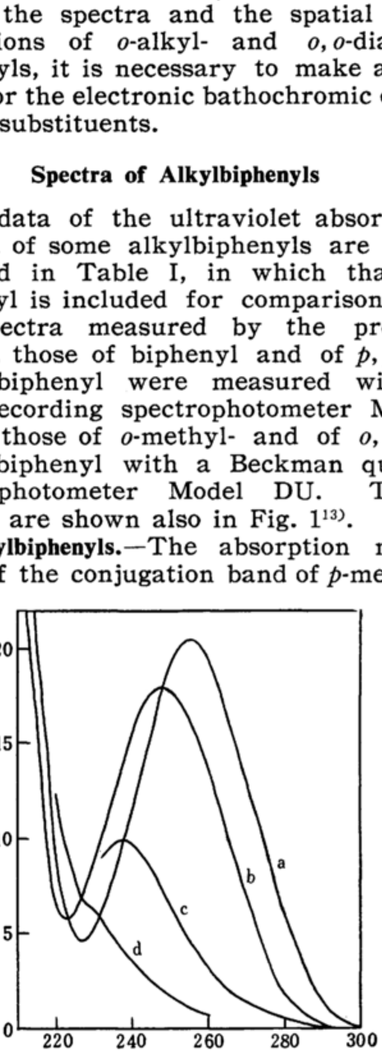

Fig. 1. The ultraviolet absorption spectra of biphenyl and of methylbipenyls in ethanol. a: *p, p*'-Dimethylbiphenyl. b: Biphenyl. c: *o*-Methylbiphenyl. *d*: *o, o*'-Dimethylbiphenyl.

Accordingly, if the steric effect of the ortho methyl substituent were absent, *o*-methylbiphenyl would exhibit the conjugation band at approximately the same position as that of the *p*-isomer. Hence *p*-methylbiphenyl may reasonably be taken as the longer-wavelength-side reference compound in this case.

It was reported in the preceding part that the value of the parameter μ in the $\pi-\pi$ resonance integral $\mu\beta$ for the $1-1'$ bond in biphenyl in solution is 0.780 and that the corresponding calculated transition energy ΔE_A is 1.523 $(-\beta)$ (cf. Table III in Ref. 1). From the above consideration, these values are assumed here to correspond approximately to the position of the maximum of the conjugation band of *p*-methylbiphenyl. That is, the values of ΔE_L and of ν_L in the present treatment of *o*-methylbiphenyl are assumed to be 1.523 $(-\beta)$ and 39526 cm^{-1} (253 mμ), respectively.

On the other hand, as the value of ν_S corresponding to ΔE_S $[2(-\beta)]$ when μ is 0, analogously to the choice of the "center of gravity of singlets" 48000 cm^{-1} of benzene[14] in the case of biphenyl itself[1], the corresponding value of toluene may be taken here.

In Table II, a collection of the relevant data of the spectra of benzene and of several alkylbenzenes is assembled. In this table also the data of *m*-xylene and of mesitylene which are not needed in the present part are conveniently included for the sake of reference in the later parts (probably VIII and XI) of this series.

It is seen in Table II that each of the bands of toluene is at a longer wavelength by about 5 mμ than the corresponding band of benzene. Therefore, as the value of toluene corresponding to the center of gravity of singlets 48000 cm^{-1} (208.3 mμ) of benzene, the value of 46882 cm^{-1} (213.3 mμ) may be taken. Accordingly, the value of ν_S is assumed here to be 46882 cm^{-1}.

In this manner, the allowance for the electronic bathochromic effect of the substituent is made by the choice of the

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[13] The author is indebted to Dr. Makoto Takahashi for a generous supply of the sample of *p, p*'-dimethylbiphenyl. Preparations of *o*-methyl- and of *o,o*'-dimethylbipheyl wer reported in Ref. 7.

[14] J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

TABLE II-1. ULTRAVIOLET ABSORPTION SPECTRA OF BENZENE AND ALKYLBENZENES (in n-heptane)[15]

Compound	Allowed transition			Forbidden transition		
	$\lambda_{\max}$, mμ	ε	f	$\lambda_{\max}$, mμ	ε	f
Benzene	183.5	46000	0.69	195.0	6900	0.10
Toluene	188.5	55000	0.97	200.0	8100	0.12
Ethylbenzene	189.0	57000	1.00	200.0	7400	0.11
m-Xylene	193.0	76000	1.28	203.0	10500	0.18

TABLE II-2. ULTRAVIOLET ABSORPTION SPECTRA OF BENZENE AND ALKYLBENZENES

Compound	Approx. center of band[16] (in n-hexane)		O-O band[17] (vapor)	O-O band[18]
	λ, mμ	ε	$\lambda_{\max}$, mμ	$\lambda_{\max}$, mμ
Benzene	255	230	262.54	262.46
Toluene	261	300	266.78	266.75
Ethylbenzene	261	220		266.43
n-Propylbenzene	261	245		266.52
Isopropylbenzene				265.87
n-Butylbenzene	260	235		266.63
m-Xylene	266	400		
Mesitylene	266	305	274.06	

references for correlation between the observed position of the conjugation band and the calculated transition energy. Thus, quite analogously to the treatment in the preceding part, the value of the transition energy ΔE_{A} corresponding to the wave number of the absorption maximum of the conjugation band of o-methylbiphenyl can be computed (cf. Eq. 8 in Ref. 1). In this case, it is assumed that ΔE_{A} varies linearly with ν_{A} in the range of ΔE_{L} $[1.523\,(-\beta)]$ to ΔE_{S} $[2(-\beta)]$. By the way, ΔE_{L} and ΔE_{S} correspond to ν_{L} (39526 cm^{-1}) and ν_{S} (46882 cm^{-1}), respectively. Then, one can obtain the corresponding values of μ, θ, R, etc. in turn according to the relation between ΔE_{A} and μ (cf. Table I in Ref. 1), and to the relation between μ and θ as well as R (the length of the $1-1'$ bond) (cf. Eqs. 1—7 in Ref. 1), which were postulated in the preceding part.

The absorption maxima of ethyl-, n-propyl- and n-butylbenzene are located at about the same wavelength, 260~261 mμ, as that of toluene. On the other hand, o-ethyl- o-n-propyl-, o-isopropyl-, and o-n-butylbiphenyl all exhibit the maxima of the conjugation bands at about the same wavelength, 233 mμ. Hence it is obvious that these o-alkylbiphenyls can be approximately treated also by application of the relation between ΔE_{A} and ν_{A} assumed above for the case of the o-methyl analogue.

o, o' - Dialkylbiphenyls. — The absorption spectra of o, o'-dimethyl-, o, o'-diethyl-, and o, o' - diisopropylbiphenyl are markedly different from those of the corresponding o-monoalkylbiphenyls. Each of the spectra of these o, o'-dialkylbiphenyls shows no distinct absorption maximum of the conjugation band, but merely an inflection at about 227 mμ, which is regarded as the vestigial or submerged conjugation band. According to Everitt and his coworkers[12], the spectra of these o, o'-dialkylbiphenyls exhibit feeble bands at about 263.5 mμ and at about 270~271 mμ (the molar extinction coefficients are lower than 1000) in addition to the vestigial conjugation band mentioned above. These feeble bands are believed to correspond to the "hidden transition" in biphenyl[19], and this revelation is probably due to the marked hypsochromic shift and the reduction in the intensity of the conjugation band caused by larger deviation from coplanarity of the configuration in these sterically hindered biphenyl derivatives, as compared with biphenyl itself.

In order to infer the most probable spatial configurations of these o, o'-dialkylbiphenyls by application of the present

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[15] J. R. Platt and H. B. Klevens, *Chem. Revs*, **41**, 301 (1947).

[16] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy", 2nd Ed., Edward Arnold Publishers, Ltd., London (1957), p. 134.

[17] K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947).

[18] W. West, "Chemical Applications of Spectroscopy" (Technique of Organic Chemistry IX), Interscience Publishers., Inc., New York (1956), p. 677 (F. A. Matsen).

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

TABLE III. RESULTS OF CALCULATION

Biphenyl derivative	$\lambda_{\max}$, mμ	ν_A, cm^{-1}	ΔE_A, $-\beta$	μ	θ	R, Å
o-Methyl-	235	42553	1.719	0.438	58°	1.508
o-Ethyl-, *o*-*n*-propyl, *o*-isopropyl-, *o*-*n*-butyl-	233	42918	1.743	0.399	60.7	1.5105
o, o'-Dimethyl-	(227)	44053	1.826	0.267	70	1.5193
o, o'-Diethyl-, *o, o'*-diisopropyl-	(227)	44053	1.829	0.262	70.3	1.5195

method, allowance for the electronic bathochromic effects of the substituents is made analogously to the case of *o*-monoalkylbiphenyls by choice of the references for correlation between the calculated transition energy and the observed position of the conjugation band. Thus, as ν_L corresponding to ΔE_L 1.523 ($-\beta$), the wave number 39124 cm^{-1} (255.6 mμ) of the maximum of the conjugation band of *p, p'*-dimethylbiphenyl is taken in the case of *o, o'*-dimethylbiphenyl, and the wave number 38986 cm^{-1} (256.5 mμ) of the maxima of the conjugation bands of *p, p'*-diethyl- and *p, p'*-diisopropylbiphenyl is taken in the case of the corresponding *o, o'*-isomers. On the other hand, as ν_S corresponding to ΔE_S 2($-\beta$), the value of monoalkylbenzene 46882 cm^{-1} (213.3 mμ) corresponding to the center of gravity of singlets of benzene is taken, quite similarly to the case of *o*-monoalkylbiphenyls.

Results of Calculations and Discussion

The results of the calculations are shown in Table III. The calculated value of the angle of twist in *o*-methylbiphenyl is in considerably good agreement with the value 62° deduced from the scale model in which the length of the 1–1′ bond is 1.51 Å, the lengths of C_6H_5–H bond and of the C_6H_5–CH_3 bond are 1.08 and 1.54 Å, respectively, the radii of hydrogen atom and of methyl group are 0.9 and 2.0 Å, respectively, and an ortho hydrogen atom just touches the ortho methyl group.

It is noteworthy that the values of the angle of twist in *o*-ethyl-, *o*-*n*-propyl-, *o*-isopropyl-, and *o*-*n*-butylbiphenyl are equal to each other, and that they are merely slightly larger than that in the methyl analogue. This fact may be considered to indicate that all but the methylene group attached directly to the phenyl ring can adopt conformations such that they cause little or no additional interference, as suggested already by Braude and Forbes[6].

The calculated value of the interplanar angle in *o, o'*-dimethylbiphenyl is eventually closely similar to the value estimated in the earlier paper[7], 70.5°. Therefore, the discussion in the earlier paper may apply also to the present result. Thus, this value 70° of the interplanar angle in *o, o'*-dimethylbiphenyl coincides almost exactly with the corresponding value, 70.6°, found for 2, 2′-dimethylbenzidine dihydrochloride by the X-ray crystal analysis[20], and it is inferred that the preferred configuration of the former is similar to the configuration of the latter which has been found to have the two ortho methyl groups in the *cis*-disposition. This inference of the *cis*-configuration of *o, o'*-dimethylbiphenyl seems to be supported also by the fact that the interplanar angle in gaseous 2, 2′-dichlorobiphenyl found by the electron diffraction method[21] and that in crystalline 2, 2′-dichlorobenzidine found by the X-ray crystal analysis[22] are 74° and 72°, respectively, and that both these compounds have been found to have *cis*-configurations.

If the molecule of *o, o'*-dimethylbiphenyl assumed the *trans*-configuration in which the ortho hydrogen atoms just contact with the ortho methyl groups, the configuration of the biphenyl skeleton would be similar to that in *o*-methylbiphenyl, and consequently *o, o*-′dimethylbiphenyl would show a closely similar spectrum to that of *o*-methylbiphenyl. In fact it is not so. Thus, as already mentioned, the hypsochromic shift of the conjugation band is observed to be markedly larger in the spectrum of *o, o'*-dimethylbiphenyl than in that of *o*-methylbiphenyl.

This fact has been interpreted by Braude and Forbes[6] as follows: "The hypsochromic shift from 2500 to 2350 Å due to one *o*-methyl substituent actually corresponds to an increase in transition energy of 7 kcal./mol., which is the amount by which the energy level of the electronic excited

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[20] (a) F. Fowwether and A. Hargreaves, *Acta Cryst.*, **3**, 81 (1950); *Chem. Abstr.*, **44**, 7118 (1950). (b) A. Hargreaves and W. H. Taylor, *J. Sci. Instruments*, **18**, 138 (1941); *Chem. Abstr.*, **35**, 7261 (1941).

[21] O. Bastiansen, *Acta Chem. Scand.*, **4**, 926 (1950).

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

state has been raised relative to that of the ground state and it is obviously reasonable that the effect of two such substituents should be about twice as great". It seems that they have attributed the hypsochromic shift, viz. an increase in transition energy, to an increase in the difference between the steric repulsion energy in the electronic excited state and that in the ground state.

However, as mentioned already in the preceding part1) of this series, since the transition is considered to be an electron jump without change in nuclear configuration according to the Franck-Condon principle, the steric repulsion energy in the electronic excited state and that in the ground state must be at least approximately of the same magnitude. Therefore, whereas the steric repulsion energy is a contributing factor to the stability of the molecule and hence to determination of the most probable spatial configuration of the molecule, the electronic transition energy must not depend directly on the steric repulsion energy in the ground state, but on the spatial configuration itself. And further, of course, there should be no direct relation between the electronic transition energy and the height of the energy barrier to rotation about the co-annular bond which depends mainly on the difference between the steric repulsion energy in the coplanar configuration and that in the most probable configuration.

From such considerations, the difference between the spectrum of *o*-methylbiphenyl and that of *o*, *o*′-dimethylbiphenyl should be ascribed to the difference of the most probable spatial configurations of the biphenyl skeleton in these compounds. It is obvious that the interpretation by Braude and his coworker is quite unreasonable.

o, *o*′-Diethyl- and *o*, *o*′-diisopropylbiphenyl are inferred to have configurations similar to that of *o*, *o*′-dimethylbiphenyl, although the estimation of the interplanar angle in these compounds is inevitably somewhat uncertain since the conjugation bands of these compounds are vestigial, the positions of the maxima of which can not accurately be determined.

o, *o*′-Di-*tert*-butylbiphenyl exhibits no trace of a discrete conjugation band. This fact may be considered to indicate that the interplanar angle in this compound is so large owing to the bulkiness of the substituents that the $\pi-\pi$ interaction across the co-annular bond is almost completely eliminated.

Relation of Spatial Configurations with Other Properties

The difference of the spatial configurations of the compounds must undoubtedly affect also certain physical and chemical properties of the compounds besides the electronic absorption spectra. Accordingly, the spatial configurations of the biphenyls inferred above on the basis of the absorption spectra may be correlated with various other properties of the compounds. A few examples are given below.

Theilacker and Ozegowsky23) found that 2, 2′-dimethyl-4, 4′-biphenylene-bis-diphenylmethyl has properties closely similar to those of the 2, 2′, 6,6′-tetrachloro analogue which is known to be a true biradical24). In addition, Müller and Hertel25) concluded from the result of measurement of the magnetic susceptibility that this 2, 2′-dimethyl compound is paramagnetic and hence a true biradical in contrast to its parent compound, Chichibabin's hydrocarbon, which had been found to be completely diamagnetic and not a biradical26). Although the latter compound was found afterwards by application of the paramagnetic resonance absorption method to contain about 4% of the biradical form in solution in benzene27), it may be safe to state that in the equilibrium between the diphenoquinone form and the biradical form the latter form is more favorable in the 2, 2′-dimethyl compound than in the parent compound, and that this fact is to be related to the reduced $\pi-\pi$ interaction across the co-annular bond in the former compound as compared with the latter compound.

According to Sherwood and Calvin28), in *p*-amino-*p*′-nitrobiphenyl the *p*′-nitro group exerts a marked effect upon the basicity of the *p*-amino group and this effect is diminished by ortho substitution by two methyl groups. This effect of ortho methyl groups has been ascribed to the blocking of nitro-amino resonance by the forced non-coplanarity of the configuration of the biphenyl skeleton.

Castro, Andrews and Keefer29) recently measured the equilibrium constants and the heats of formation of 1 : 1 complexes of a series of methylbiphenyls with 1, 3, 5-trinitrobenzene. According to their results, whereas the complexes increase in stability as the number of *p*-methyl substituents on the biphenyl nucleus is increased, the complex stability decreases in the order

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23) W. Theilacker and W. Ozegowski, *Ber.*, **73**, 33 (1940).

24) E. Müller, ibid., **72**, 2063 (1939).

25) E. Müller and E. Hertel, *Ann.*, **555**, 157 (1944).

26) E. Müller and I. Müller-Rodloff, ibid., **517**, 134 (1935).

27) C. A. Hutchison, Jr., A. Kowalsky, R. C. Pastor and G. W. Wheland, *J. Chem. Phys.*, **20**, 1485 (1952).

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

29) C. E. Castro, L. J. Andrews and R. M. Keefer, ibid., **80**, 2322 (1958).

biphenyl > *o*-methylbiphenyl > *o, o'*-dimethylbiphenyl > bimesityl, as the number of *o*-methyl substituents is increased. This fact is indicative of the dependence of the complex stability on the factors which prevent coplanarity of the two benzene rings in the biphenyl derivatives, and supports the present conclusion that the degree of deviation from planarity of the configuration of biphenyl skeleton increases as the number of *o*-methyl substituents is increased.

Furthermore, Brownstein[30] measured the nuclear magnetic resonance absorption spectra of some 2-halo- and 4-halobiphenyls and attributed shifts in proton resonance absorption toward a higher field observed for some of the protons in 2-halobiphenyls to steric effects of the halogen upon the ortho protons of the unsubstituted benzene ring. In addition, he explained the melting points of these compounds by the twisting of the benzene rings as the size of the 2-substituent is increased. Thus, whereas a heightening of melting point is observed with increasing molecular weight for the 4-halobiphenyl as would be expected, the melting point of the 2-halobiphenyl is lowered as the molecular weight increases. This was believed to be caused by the decreasing symmetry of the molecule as the benzene rings are twisted further out of plane by the steric effect of the *o*-substituent.

Although the melting point is a very complex property, it may be sure that the spatial configuration of the molecule is an important factor to govern the melting point. A somewhat similar phenomenon to the one mentioned above is observed in the series of methylbiphenyls. Thus, whereas the melting points of biphenyl and of *p*-methylbiphenyl are 69 and 49~50°C (47~48°C), respectively, *o*-methylbiphenyl is liquid at room temperature. In addition, whereas the melting point of *p, p'*-dimethylbiphenyl is 125°C (121°C), that of the *o, o'*-isomer is 18°C. (Data of the melting points are according to Dictionary edited by Heilbron[31]). The fact that the melting point of the *o*-isomer is invariably markedly lower than that of the corresponding *p*-isomer may be at least partly due to the non-planarity of the configuration of the *o*-isomer.

Summary

The method described in the preceding part of this series has been applied with allowance for the electronic bathochromic effect of the substituents to *o*-alkyl- and *o, o'*-dialkylbiphenyls, and the relation between the ultraviolet absorption spectra and the most probable spatial configurations of these compounds has been clarified, resulting in the conclusion that the interplanar angle in *o*-methylbiphenyl as well as its analogues is about 60° and that *o, o'*-dimethylbiphenyl as well as its analogues has the *cis*-configuration in which the interplanar angle is about 70°.

On the basis of the result, the interpretation by Braude and Forbes of the spectra of *o*-methyl- and *o, o'*-dimethylbiphenyl has been criticized.

In addition, the inferred spatial configurations of these biphenyl derivatives have been correlated with some physical and chemical properties of these and some related compounds.

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Department of Chemistry
College of General Education
The University of Tokyo
Meguro-ku, Tokyo

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[30] S. Brownstein, ibid., **80**, 2057 (1958).

[31] I. Heilbron, "Dictionary of Organic Compounds", Oxford University Presss, Inc., New York (1953).