ESR Studies of the Negative Ions of Biphenyl Derivatives. II. Electron Spin Resonance Hyperfine Spectra of 3-Methyl Biphenyl, m, m′-Bitolyl, 2-Methyl Biphenyl, and o, o′-Bitolyl Mononegative Ions

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In a previous paper,[1] the author reported the results of an ESR study of 4-methyl biphenyl and *p, p′*-bitolyl mononegative ions; this study has also provided us with some information on methyl proton splitting which will be referred to later in this paper.

In this article, work on the ESR spectra of 3-methyl biphenyl, *m, m′*-bitolyl, 2-methyl biphenyl, and *o, o′*-bitolyl mononegative ions will be presented in order to clarify further the effect of methyl substitution at various positions on the biphenyl ring in terms of hyperconjugation and the steric effect.

Experimental

The radical anions were produced with potassium metal in dimethoxyethane (DME) and also in tetrahydrofuran (THF). The experimental procedures were described in the preceding paper.

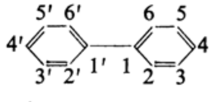
Results

The resolution of the observed hyperfine lines in the ESR spectra for each specimen was found to be better in DME than in THF, except for 3-methyl biphenyl; thus, the spectra observed in DME will be discussed.

With reference to the theoretically-calculated spin density given in Table II, the hyperfine structures of the observed spectra were interpreted adequately by assuming that the magnitude of the methyl splittings and of the ring-proton splittings were almost equal to those at the same positions on biphenyl, in which the splitting ratios at the para-, ortho-, and meta-positions were approximately 8 : 4 : 1.

The proton hyperfine splittings at the meta- and the ortho-positions were derived from an analysis of the terminal and the next-inner groups of the spectrum, while those at the para-positions were derived through the trial and error method by observing the intense splittings around the center of the spectrum.

The general structure of a biphenyl ring is:



In the following sections, ΔH_n and ΔH_n (CH_3) represent the hyperfine coupling constants* of, respectively, the ring protons and of the methyl protons attached to the ring carbon C_n, where *n* denotes a position on the biphenyl ring.

3-Methyl Biphenyl.—The observed spectrum measured in DME at room temperature is shown in Fig. 1(a). Although he made careful observations in range from room temperature to −60°C, the author could not observe any good resolved patterns of ESR hyperfine lines; thus, it was difficult to determine the coupling constants precisely. The integral intensity of each hyperfine line, however, seems to be in good agreement with the theoretical intensity, as is shown in Fig. 1 (b).

The overall width, the number of the groups in which hyperfine lines flocked, and the location of strong intensity lines in the spectrum were all similar to the conditions in biphenyl. Thus, one may assume that the para (ΔH_4 and $\Delta H_{4'}$)-, or the ortho (ΔH_2, $\Delta H_{2'}$, ΔH_6 and $\Delta H_{6'}$)- ring proton splittings are about 5.4 gauss and 2.7 gauss respectively, not far from those of biphenyl. The ring-proton splitting ($\Delta H_{3'}$, $\Delta H_{5'}$ and ΔH_5) and the methyl proton splittings ($\Delta H_3(CH_3)$) at the meta-positions were all about 0.43 gauss.

The methyl splitting was identified from the integration of the septet lines in the terminal groups.

The proton hyperfine splittings thus determined are:

$$\Delta H_4 \simeq \Delta H_{4'} = 5.4 \text{ gauss}$$

$$\Delta H_2 \simeq \Delta H_{2'} \simeq \Delta H_6 \simeq \Delta H_{6'} = 2.7 \text{ gauss}$$

$$\Delta H_3(CH_3) = \Delta H_{3'} = \Delta H_5 = \Delta H_{5'} = 0.43 \text{ gauss}$$

***m, m′*-Bitolyl.**—The observed spectrum measured at −15°C is shown in Fig. 2(a). The overall width and the grouping of every hyperfine line in the spectrum can be easily

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* On leave from the Department of Chemistry, Faculty of Literature and Science, Yamaguchi University, as a research fellow at Kyoto University (1963-1964); leave sponsored by the Japan Society for the promotion of science.

[1] K. Ishizu, This Bulletin, **36**, 938 (1963).

* The hyperfine coupling constant is a synonym of the splitting coefficient which was used in the previous report.

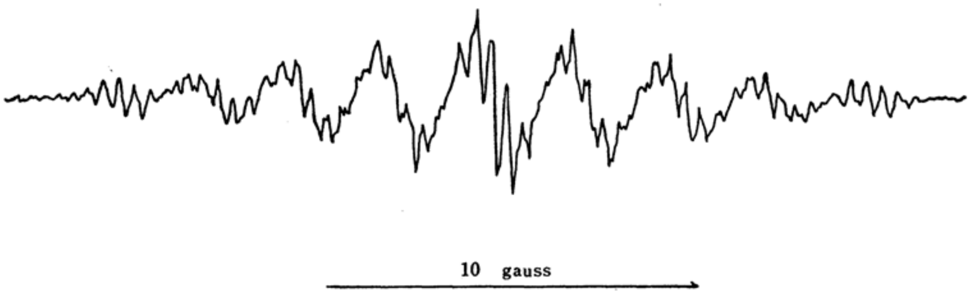

Fig. 1 (a)

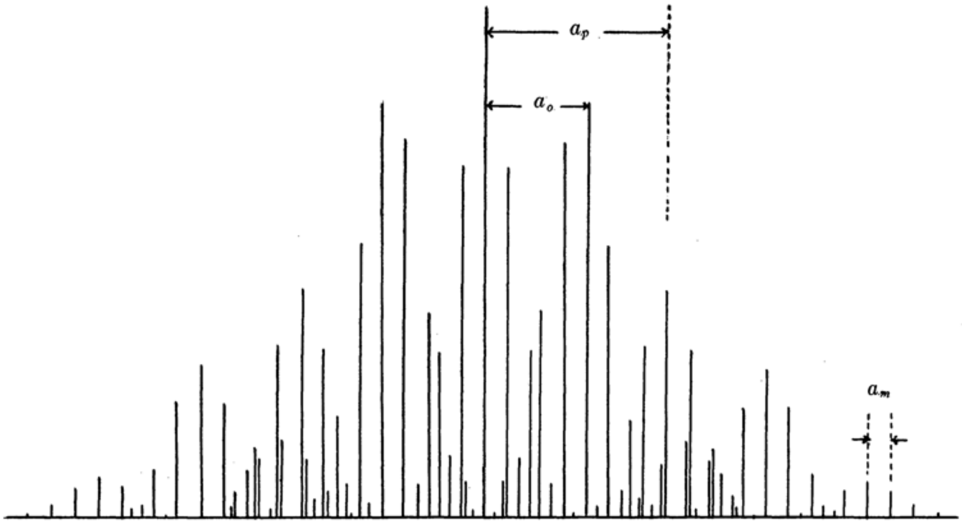

Fig. 1 (b)

Fig. 1. 3-Methyl biphenyl.

(a) : ESR spectrum

(b) : Intensity diagram constructed based upon theoretically calculated spin densities assuming that the splitting parameter of the methyl proton was equal to that of the ring proton. Each of a_p, a_o and a_m is the theoretical proton splitting at the para-, the ortho-, and the meta-position.

compared with those of biphenyl. The observed spectrum consists of three triplets originating from a pair of para (5.15 gauss)-, and two pairs of ortho (2.82, 2.33 gauss)-, ring protons. Each line then splits further into a triplet septet caused by a pair of the metaring protons and the six methyl protons.

With reference to Hückel's MO calculation, in which $\rho_6 > \rho_2$*, the ΔH's of each proton thus determined are as follows:

$\Delta H_4 = 5.15$, $\Delta H_6 = 2.82$, $\Delta H_2 = 2.33$, $\Delta H_3(\mathrm{CH_3}) = 0.49$, $\Delta H_5 = 0.27$ gauss.

The relative intensities of the hyperfine lines estimated on the basis of these ΔH's are shown in Fig. 2(b).

2-Methyl Biphenyl.—The spectrum measured at room temperature is shown in Fig. 3(a). As is illustrated in Fig. 3(b), the terminal group of the spectrum consists of six lines, whose relative intensity ratios are 1:1:2:2:1:1, and the line spacing is alternatively 0.42 and 0.23 gauss. One would expect the hyperfine structures of these six lines to appear as a triplet due to a pair of equivalent ring-proton splittings (0.65 gauss), followed by a doublet due to a pair of equivalent ring-proton splittings (0.42 gauss) at the meta-positions. Thus, it may reasonably be expected that any coupling constant of the remaining meta-proton will be too small to split the hyperfine lines. One may assume that an equivalent pair exists for the meta-ring protons in the non-substituted phenyl group, taking the theoretical prediction of spin density into account. Thus, the ring proton splittings at each meta-position are determined to be:

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* ρ_n: a theoretically-calculated spin density on the ring carbon atom, C_n, of the biphenyl ring.

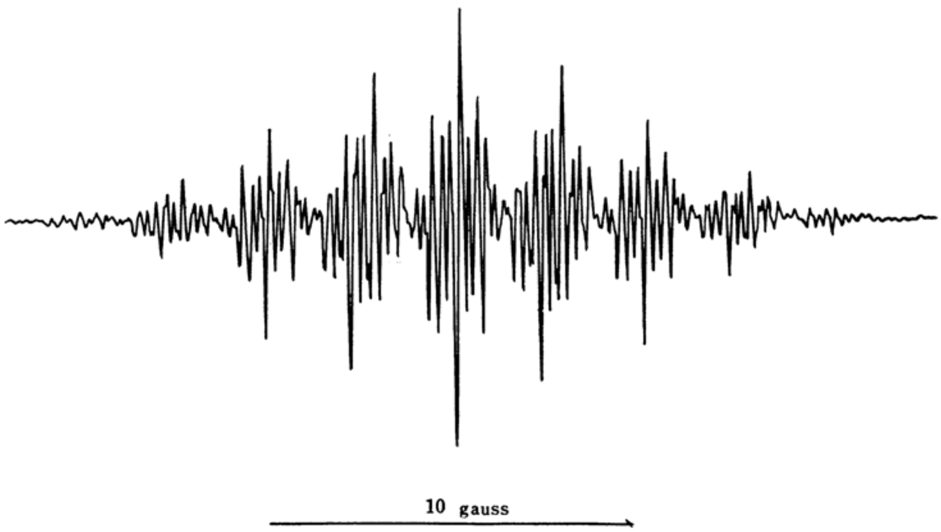

Fig. 2 (a)

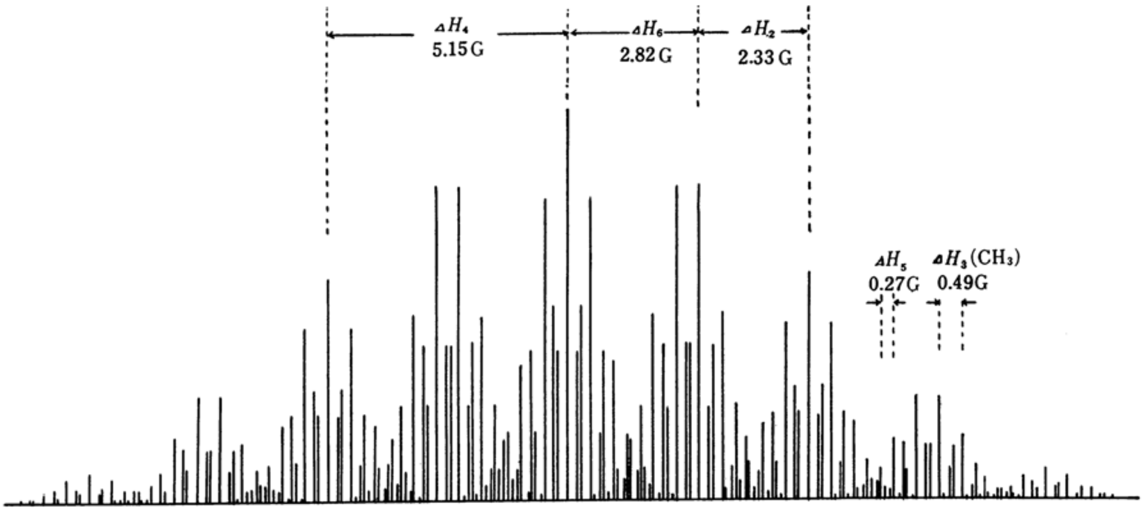

Fig. 2 (b)

Fig. 2. *m, m'*-Bitolyl.

(a) : ESR spectrum
(b) : Calculated spectrum based on experimentally determined proton coupling constants

$\varDelta H_{3'}=\varDelta H_{5'}=0.65$, $\varDelta H_5=0.42$, and

$\varDelta H_3<0.03$* gauss.

The analysis of the wing groups in the spectum shows that the ring and the methyl protons at the ortho-positions will give two kinds of splittings, a triplet (2.88 gauss) and a quintet (2.41 gauss), respectively.

Taking the theoretical spin density at the ortho-positions into account, a triplet is assigned to the ortho-ring proton splittings in the non-substituted phenyl group, and a quintet, to an ortho-ring proton and the three methyl proton splittings in the substituted phenyl group; that is, $\varDelta H_{2'}=\varDelta H_{6'}=2.88$ and $\varDelta H_2(\mathrm{CH_3})=\varDelta H_6=2.41$ gauss. Finally, the para-($\varDelta H_4$, $\varDelta H_{4'}$) proton splitting was found to be 5.25 gauss by the trial and error method. The relative intensities of the hyperfine lines are shown in Fig. 3 (c).

The $\varDelta H_{5'}$ thus determined are:

$\varDelta H_4=\varDelta H_{4'}=5.25$, $\varDelta H_{2'}=\varDelta H_{6'}=2.88$,

$\varDelta H_2(\mathrm{CH_3})=\varDelta H_6=2.41$,

$\varDelta H_{3'}=\varDelta H_{5'}=0.65$, $\varDelta H_5=0.42$, and

$\varDelta H_3<0.03$ gauss.

***o, o'*-Bitolyl.**—The spectrum measured at $-15°$C is shown in Fig. 4(a). The relative intensity ratios of the seven hyperfine lines in

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* The ultimate resolvable width of the spectrometer.

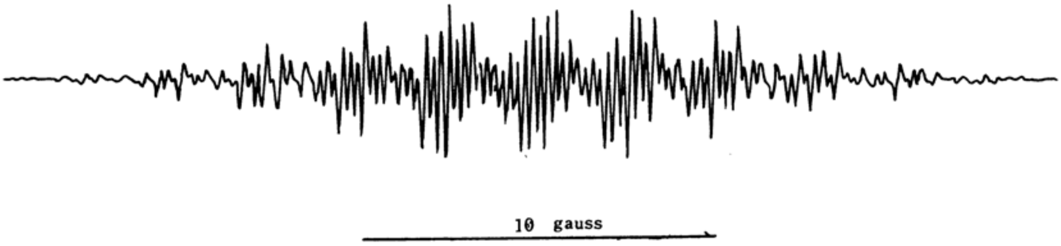

Fig. 3 (a)

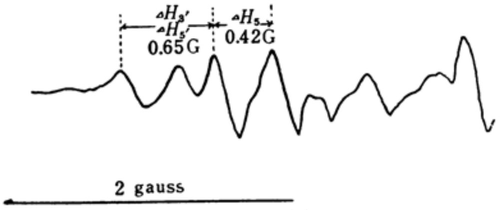

Fig.3 (b)

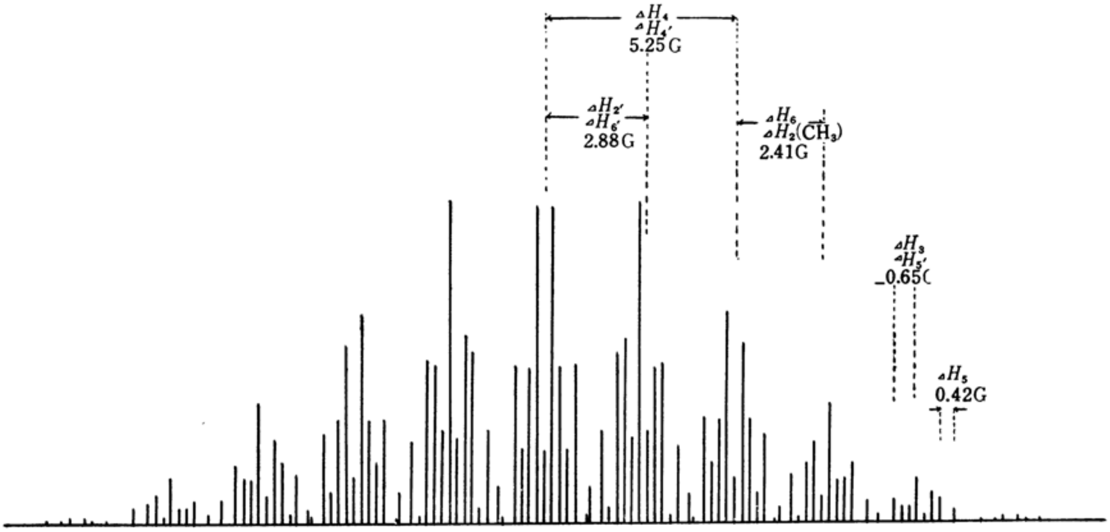

Fig. 3 (c)

Fig. 3. 2-Methyl biphenyl.
(a) : ESR spectrum (b) : An end group of spectrum (c) : Calculated spectrum based on experimentally determined proton coupling constants

all three groups at the wing of the spectrum illustrated in Fig. 4(b), are equal to 1 : 2 : 3 : 4 : 3 : 2 : 1. The ring proton and the methyl proton splittings at the ortho-positions are all equal; that is, $\Delta H_2(\mathrm{CH_3})=\Delta H_6$. Furthermore, the proton splitting ratio at the meta-position is equal to 2 : 1. The ΔH's thus determined are as follows:

$$\Delta H_4=5.12,\ \Delta H_2(\mathrm{CH_3})=\Delta H_6=2.20,$$

$$\Delta H_5=0.56,\ \text{and}\ \Delta H_3=0.28\ \text{gauss.}$$

The spectrum which has been constructed on the basis of the observed coupling constants is shown in Fig. 4(c). Table I gives the overall width, the g-values, and the observed coupling constants of both ring protons and methyl protons in mononegative ions of biphenyl and its derivatives.

Discussion

The Ring Proton Splitting.—The theoretical spin density on both ring carbons and methyl protons were derived by means of Hückel's MO calculation, assuming that each aromatic ring would be on a plane and estimating the resonance integral between neighboring ring carbon atoms ($\beta_{\mathrm{C-C}}$) and the Coulomb integral

Fig. 4. *o*, *o*′-Bitolyl.

(a) : ESR spectrum

(b) : Three groups in a wing of spectrum

(c) : Calculated spectrum based on experimentally detertermined proton coupling constants

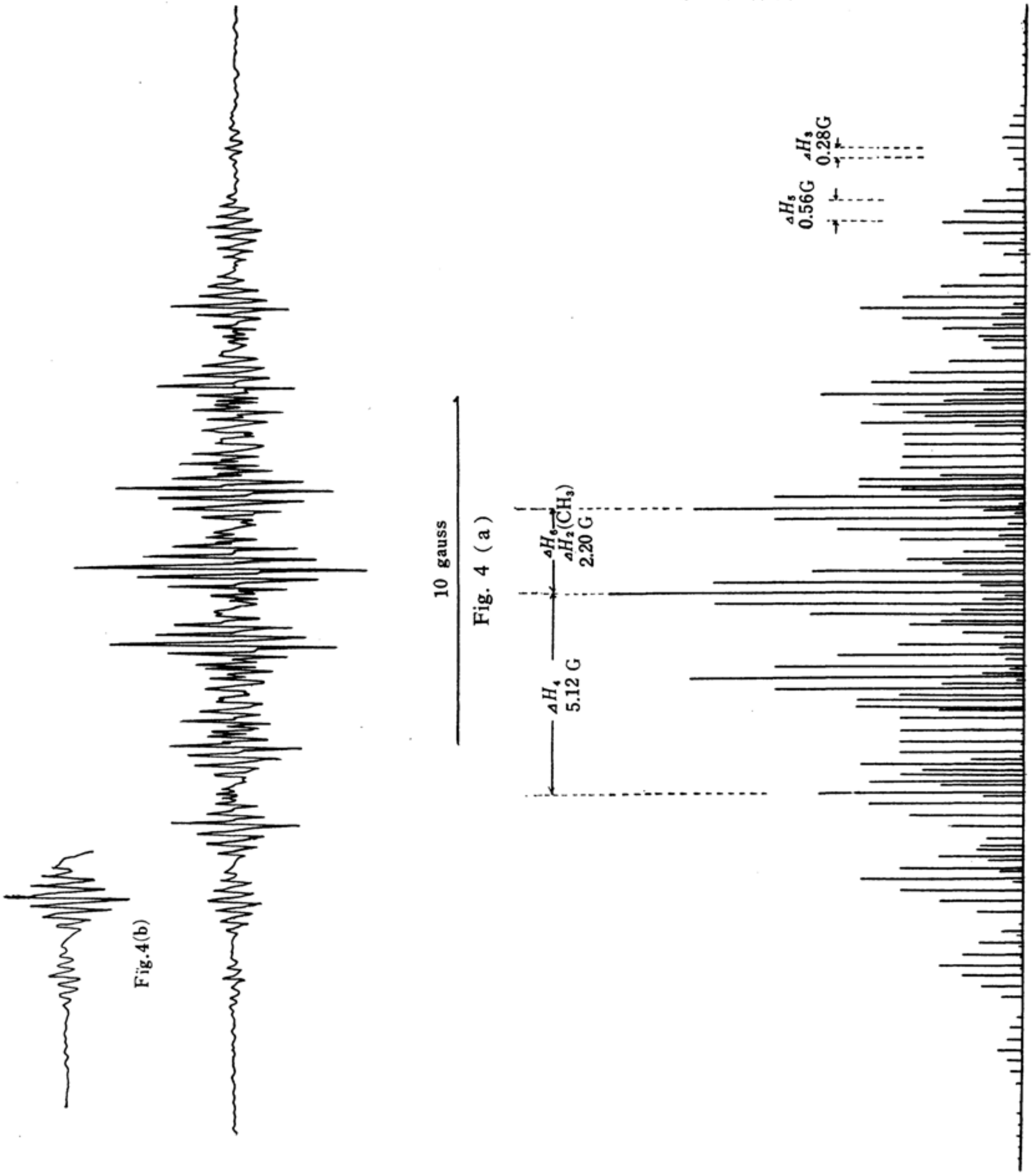

Fig.4(b)

Fig. 4 (a)

Fig. 4 (c)

TABLE I. OVERALL WIDTHS, g-VALUES AND OBSERVED PROTON COUPLING CONSTANTS OF BIPHENYL AND METHYL DERIVATIVE MONONEGATIVE IONS

	g	Overall	ΔH_s									
			2	2′	3	3′	4	4′	5	5′	6	6′
Biphenyl	2.0025	23.5	2.66	2.66	0.41	0.41	5.31	5.31	0.41	0.41	2.66	2.66
4-Methyl	2.0024	33.6	2.85	2.51	0.64	0.32	†5.43	5.43	0.64	0.32	2.85	2.51
p,p'-Bitolyl	2.0025	46.7	2.66	2.66	0.51	0.51	†5.63	†5.63	0.51	0.51	2.66	2.66
3-Methyl-	2.0025	23.7	2.7	2.7	†0.43	0.43	5.4	5.4	0.43	0.43	2.7	2.7
m, m'-Bitolyl	2.0024	23.8	2.33	2.33	†0.49	†0.49	5.15	5.15	0.27	0.27	2.82	2.82
2-Methyl-	2.0027	27.5	†2.41	2.88	<0.03	0.65	5.25	5.25	0.42	0.65	2.41	2.88
o,o'-Bitolyl	2.0025	29.5	†2.20	†2.20	0.28	0.28	5.12	5.12	0.56	0.56	2.20	2.20

†: Methyl proton splitting, Overall ΔH_s: (gauss)

TABLE II. THEORETICAL SPIN DENSITY OF BIPHENYL AND METHYL DERIVATIVE MONONEGATIVE IONS

	ρ												
	1	2	3	4	5	6	1′	2′	3′	4′	5′	6′	CH_3
Biphenyl	0.123	0.090	0.020	0.158	0.020	0.090	0.123	0.090	0.020	0.158	0.020	0.090	—
4-Methyl-	0.123	0.088	0.020	0.157	0.020	0.088	0.120	0.088	0.019	0.155	0.019	0.088	0.0125
p,p'-Bitolyl	0.120	0.087	0.020	0.154	0.020	0.087	0.120	0.087	0.020	0.154	0.020	0.087	0.0125
3-Methyl-	0.122	0.088	0.020	0.159	0.019	0.090	0.123	0.089	0.020	0.158	0.020	0.089	0.0016
m, m'-Bitolyl	0.123	0.088	0.020	0.158	0.019	0.090	0.123	0.088	0.020	0.158	0.019	0.090	0.0016
2-Methyl-	0.123	0.091	0.018	0.157	0.021	0.087	0.122	0.089	0.019	0.157	0.019	0.089	0.0074
o,o'-Bitolyl	0.122	0.090	0.018	0.155	0.020	0·086	0.122	0.090	0.018	0.155	0.020	0.086	0.0074

of a ring carbon atoms (α_C) to be the same as those of benzene (β, α).

Coulson-Crawford's[2] parameters were employed here for the calculation of the methyl fraction ($-C_1-C_2\equiv H_3$); that is, $\beta_{C_1-C}=0.7\ \beta$, $\alpha_{C_2}=\alpha-0.1\ \beta$, $\beta_{C\equiv H_3}=2.5\ \beta$, and $\alpha_{H_3}=\alpha-0.5\ \beta$. The overlap integrals were disregarded for the above cases. For the ring proton splitting, Jarret's[3] calculation agreed well with the observed values, deviating by only about 15%, indicating that the ring-proton splitting parameter is 28 gauss.

However, with regard to the observed proton splitting given in Table I, some distinct spin distribution can be recognized in the case of both ortho-derivatives compared with those of the other meta- or para-derivatives. In the case of 2-methyl biphenyl, there is a certain difference in spin distribution at the ortho- and the meta-positions between a substituted and a non-substituted phenyl group; this difference may be due to a steric effect caused by the methyl group. In the case of o,o'-bitolyl, the magnitude of the proton splitting at the ortho-positions was much reduced, whereas that at the para-position was not.

Comparing the ring-proton splitting ratios $\Delta H_4/\Delta H_6$ of o,o'-bitolyl negative ions with those at the para- and the ortho-positions of other derivatives (e.g., $\Delta H_4/\Delta H_6$ or $\Delta H_4/\Delta H_2$), the largest value was obtained in the case of o,o'-bitolyl (2.35), although those of the others are all within the 1.80～2.17 range; moreover, the theoretical values are all equal to 1.76, including that of o,o'-bitolyl.

Recently McLachlan[4] has suggested that a reduction of the ring-proton splitting will take place selectively at the ortho- and at the meta-positions, so that $\Delta H_4/\Delta H_6$ will increase when both phenyl rings are assumed to be twisted in the biphenyl negative ion. Thus, a large $\Delta H_4/\Delta H_6$ value in the o,o'-bitolyl negative ion will probably indicate the presence of steric hindrance, as will be described in the following section.

The Methyl Proton Spitting.—In an ESR investigation of methylated, aromatic free radicals, hyperconjugation has been studied from two distinct theoretical points of view. One is the molecular orbital theory, in which the π-π coupling between the methyl group and the odd-ring orbital is considered to play an important role. Several workers' investigations have applied the method to the study of methyl substituted semiquinones[5] and methyl anthracene[6], using Coulson and Crawford's parameters. The other is the valence bond theory; McLachlan[7] calculated the hyperfine

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[2] C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, **1953**, 2052.

[3] H. S. Jarret, *J. Chem. Phys.*, **25**, 1066 (1956).

[4] A. D. McLachlan, *Mol. Phys.*, **3**, 244, (1960).

[5] R. Bersohn, *J. Chem. Phys.*, **24**, 1066 (1956).

[6] J. R. Bolton, A. Carrington and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

[7] A. D. McLachlan, ibid., **1**, 233 (1958).

splitting produced by protons of a methyl group in a π-electron radical such as Würster's blue, invoking the spin exchange polarization between the odd electron and the methyl group.

Taking these theoretical studies of hyperconjugation into consideration, the methyl proton splitting in each methylated biphenyl may be calculated in the following way.

The spin density (a_M) on the methyl protons is calculated on the basis of Hückel's MO method, utilizing Coulson-Crawford's parameters; then the theoretical methyl proton splittings (a_M) are calculated by making use of the following relation 1. The results are shown in Table III (A).

$$a_M = \rho_H \times 502 \text{ gauss} \qquad (1)$$

where the splitting of a bare proton was estimated to be 502 gauss.

Furthermore, by referring to McLachlan's suggestion, the theoretical methyl splittings (a_M) were calculated on the basis of Hückel's spin density (ρ_C) on the corresponding ring carbon atoms of the biphenyl negative ion, using the following relation 2;

$$a_M = Q_M \rho_C \qquad (2)$$

where Q_M is the methyl proton splitting parameter (which had been found to be 25∼28 gauss after McLachlan)

Here, Q_M is estimated to be 28 gauss, since the magnitudes of the observed methyl splittings are all close to those of the ring proton at the relevant positions on the biphenyl ring. The results are shown in Table III (B).

TABLE III. THE ODD π ELECTRON ENERGY LEVELS AND THE EXPERIMENTAL AND THEORETICAL METHYL SPLITTINGS OF METHYLATED BIPHENYL MONONEGATIVE IONS

	Energy ($\times\beta$)	Methyl splitting (gauss)		
		(A)	(B)	(C)
Biphenyl	−0.704	—	—	—
4-Methyl-	−0.702	6.27	4.42	5.42
p, p-Bitolyl	−0.699	6.27	4.42	5.63
3-Methyl-	−0.704	0.80	0.56	0.43
m, m'-Bitolyl	−0.704	0.80	0.56	0.49
2-Methyl-	−0.703	3.71	2.52	2.41
o, o'-Bitolyl	−0.702	3.71	2.52	2.20

(A) Theoretical methyl splitting predicted by the Hückel's MO method by using the Coulson-Crawford parameters.
(B) Theoretical methyl splitting calculated from the relation $a_M = Q_M \rho_C$.
(C) Experimentally determined methyl splitting.

The molecular orbital calculations (A) agree well with the observed (C) and the calculated values in the case of the para-derivatives, while McLachlan's predictions (B) give satisfactory results in the case of the meta-derivatives.

As for the energy level of the odd π orbital shown in Table III, which was calculated in the course of the molecular orbital treatment (A), it is recongnized that the most effective perturbation of the energy level occurs in the case of the para-substitution, whereas there is no change in energy level in the case of the meta-derivatives compared with that of a biphenyl negative ion.

In the process of the interaction between the unpaired electron and the methyl group in these negative ions, when the π-π interaction is dominant, it may be assumed that the delocalization of the unpaired electron will perturb the energy level of the odd π orbital; thus, the magnitude of the methyl splitting will vary according to the perturbed energy level of the odd π orbital. Therefore, the theoretical methyl splitting calculated by the molecular orbital method A would be close to the observed values in this case.

However, when spin polarization is an important process, the perturbation of the energy level is assumed to be small. Thus, it may reasonably be expected that the hyperfine interaction of the methyl proton will be solely proportional to the spin density on the relevant ring carbon atoms of the unsubstituted negative ion; hence, McLachlan's prediction B would be more reliable than A.

From these arguments for the theoretical calculation, one may assume that the π-π interaction between the methyl group and a ring π orbital is likely to be the main process of hyperconjugation in the case of the para-derivatives. On the other hand, spin polarization would be dominant in the case of the meta-derivatives.

In the case of the ortho-derivative, one may suppose that the steric effect may change the methyl splitting as well as the ortho-ring proton splitting. In the case of 2-methyl biphenyl, the theoretical value obtained by the relation 2 is in good agreement with those observed. However, in the case of *o, o'*-bitolyl, the magnitude of the observed methyl splitting is appreciably less than that of the 2-methyl biphenyl negative ion or the theoretical value. It will be established in the following section that the reduction of the methyl splitting originates in steric hindrance in the case of the *o, o'*-bitolyl negative ion.

The Effect of Steric Hindrance.—In order to confirm the steric effect on both the ring proton and the methyl proton splitting, the spin density was calculated with the modification that the resonance integral of C_1–C_1 bond was estimated to be $\beta \cos \theta$, where θ is a twisting angle between both phenyl rings. The dependence of the spin density of the ring carbon atoms and that of the methyl splitting on the twisting angle θ are shown in Figs. 5 and 6 respectively.

In Fig. 6(a), the methyl splitting is presented by the relation 1 on the basis of the spin densities on the methyl protons which were calculated for twisted models of the *o,o'*-bitolyl negative ion. In Fig. 6(b), the methyl splitting is calculated by utilizing the relation 2 described in the last section on the basis of the theoretical spin density of a twisted biphenyl negative ion.

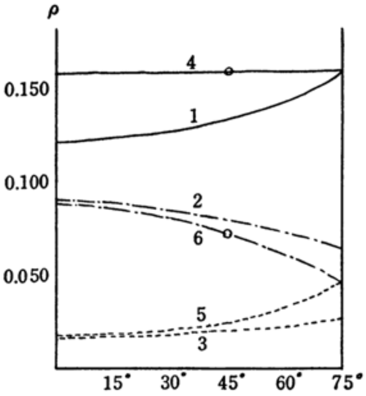

Fig. 5. Dependence of theoretical spin density of ring carbon atoms on twisting angle θ between the phenyl rings in *o,o'*-bitolyl negative ion, where the numbers represent the positions on the biphenyl ring.

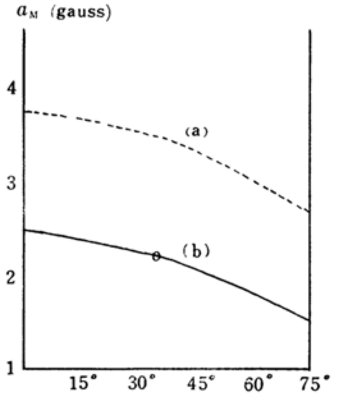

Fig. 6. Dependence of theoretical methyl splitting on twisting angles θ between the phenyl rings in *o,o'*-bitolyl negative ion.

(a) is plotted with the theoretical methyl splitting predicted by the Hückel's MO method using the Coulson-Crawford's parameter, applied for the twisted model of *o,o'*-bitolyl negative ion.

(b) is plotted with the theoretical methyl splitting obtained from the relation $a_M = Q_M \rho_C$, where the spin density on the ring carbon atom (ρ_C) are calculated for twisted biphenyl negative ion, and the methyl splitting parameter Q_M is estimated to be 28 gauss.

As is illustrated in Fig. 5, the spin density on the ring carbon atoms at the para (ρ_4)-position was enhanced gradually with an increment of θ, while conversely, those of the ortho (ρ_2, ρ_6)-positions were reduced.

This is a possible reason why the observed ring-proton splitting ratio, $\Delta H_4/\Delta H_6$, becomes larger in the *o,o'*-bitolyl negative ion than in other derivatives.

One will see that the theoretical spin density ratio, ρ_4/ρ_6, approaches the observed proton splitting ratio around $\theta = 45°$. Furthermore, it will be found that the magnitude of theoretical methyl splitting decreases with the increment of θ, as is shown in Fig. 6; hence, the theoretical value becomes equal to the observed values around $\theta = 30°$ in Fig. 6(b). In Fig. 6(a), the theoretical value is considerably larger than the observed values because of overestimated parameters in the methyl fraction.

When the results of both the ring proton splitting and the methyl proton splitting discussed in twisted models of the *o,o'*-bitolyl negative ion were put together, Hückel's calculation led to the conclusion that the two phenyl rings are twisted about 30°～45° from each other.

It has been well known on the basis of the investigation of the electronic spectra,[8] that the phenyl rings are twisted out about 70° in the neutral molecule of *o,o'*-bitolyl. When these twisting angles in the negative ion are compared with those in the neutral molecule, one may conclude that there is a greater tendency toward coplanarity between the two phenyl rings in the negative ion than in the neutral molecule of *o,o'*-bitolyl.

Recent ESR studies of such other ortho-derivatives as *o*-terphenyl,[9] *o, o'*-dinitro-bipheyl[10] have also suggested that this conclusion is justified.

Summary

The electron spin resonance of 3-methyl-biphenyl, 2-methyl-biphenyl, *m,m*-bitolyl, and *o,o'*-bitolyl has been observed. The overall

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[8] H. Suzuki, This Bulletin, **32**, 135 (1959).

[9] H. Nishiguchi, Y. Nakai, K. Nakamura, Y. Deguchi and H. Takaki, *Rev. Phys., Chem. Japan.*, **32**, 57 (1962).

[10] K. Kawamura, Y. Nakai, Y. Deguchi and H. Takaki, Private communication.

width and ring-proton coupling constants of the mononegative ions of each methylated biphenyl have been interpreted by utilizing the calculated spin density derived by Hückel's MO treatment. It has been found that the splitting parameters of the ring proton and the methyl proton were both about 28 gauss.

Hyperconjugation has been effected through the π-π interaction in the case of the para-derivatives, while spin polarization is important in the case of the meta-derivatives. In the case of the ortho-derivatives, the magnitude of the methyl splitting decreased with steric hindrance, which either brought about a fair amount of unbalanced spin density on biphenyl carbon atoms, or markedly reduced the magnitude of the ortho-proton splitting.

From Hückel's calculation, one may conclude that both of the phenyl rings are twisted about 30°～45° in the *o, o'*bitolyl negative ion, in which the twisting angle is much smaller than that in the neutral molecule.

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