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ESR Studies of the Negative Ions of Biphenyl Derivatives. III. Restricted Rotation of Alkyl Group in Some *ortho* or *para* Higher Alkylated Biphenyl Anion Radicals*[1]

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The electron spin resonance has been observed for the anion radicals of 4,4′-diethyl biphenyl, 4,4′-diisopropyl biphenyl, 4,4′-dicyclohexyl biphenyl, 2,2′-diethyl biphenyl, and 2,2′-diisopropyl biphenyl. Both of the β- and γ-proton coupling constants of alkyl groups have been precisely determined, and the positive temperature dependence has been verified for the β-proton coupling constant of 4,4′-dialkyl biphenyls. The ratio (R) of β-proton coupling constant of the other alkyls to the methyl proton coupling constant has been derived, and the evidence of the restricted rotation has been widely established for each derivative based on the angular dependence of the β-proton coupling constant, which can be expressed as follows:

$$a_i^{\beta} = \rho_{\pi} < Q >, \quad Q = B_0 + B\cos^2\theta$$

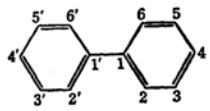
The minimum R value obtained for 2,2′-diethyl biphenyl enabled us to assume that a rotation of the alkyl group would be tightly locked at the *ortho* position. The R value of 2,2′-diisopropyl biphenyl revealed that the isopropyl β-proton would lie on the biphenyl aromatic plane. The anomalous R values associated with the *ortho*-alkylated biphenyls can be well understood as resulting from the facts that anion radicals have a more dominant character than do neutral molecules to reduce a twisting angle between the two phenyls, and that the free rotation of the alkyl group is strongly restrained by the steric hindrance between the alkyl group and the closely-oriented *ortho*-ring proton.

The theory of hyperconjugation has been widely accepted for numerous radicals based on the ESR observation of the methyl-proton splitting.

In many cases the observed methyl splitting has been successfully explained in terms of McLachlan's splitting parameter[1] on the assumption that a methyl group is freely rotating. In the case of the other alkyl derivatives, however, it has been established that the quantities of the β-*[2] proton splitting for alkyl groups differ from molecule to molecule because of the restricted rotation of the alkyl group.

In this study, ESR observations are made of anion radicals of 4,4′-diethyl biphenyl, 4,4′-diisopropyl biphenyl, 4,4′-dicyclohexyl biphenyl, 2,2′-diethyl biphenyl, and 2,2′-diisopropyl biphenyl.

The coupling constants of both the β- and the γ-*[2] proton in each alkyl group are determined, and the temperature dependence of the β-proton coupling constant is studied, in order to establish the relation between the preferred conformation of the alkyl groups and their proton splitting in these radicals. Our investigation of *ortho* derivatives is continuing, and we are likely to demonstrate that the rotation of the alkyl group can be strongly hindered at the *ortho* position. The general structure of a biphenyl ring is:



Experimental

The *ortho*- or *para*-alkylated biphenyls were made by an Ullman reaction on either *ortho* or *para* iodo alkyl

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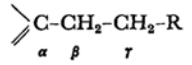
*1 A part of this work was presented at 17 th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964 and at the 18th Annual Meeting, Osaka, April, 1965.

*2 The hydrogen atoms bonded to the sp^3 hybridized carbon atom at either the β- or γ-position are described as β-protons or γ-protons, as is shown in the illustration. The coupling constants are denoted as a_i^{β} and a_i^{γ}.



1) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

benzene, according to the following process. The iodo compound (0.04 mol) was heated with 0.22 mol of activated copper powder in a bath kept at *ca.* 230—280°C for 15 hr. The organic product was extracted with *n*-hexane. After the removal of the solvent, the residue was fractionated under reduced pressure or recrystallized from ethyl alcohol. The materials thus obtained were all purified by silica gel chromatography, using *n*-hexane as the solvent. The physical constants[2,3] of the materials are listed below:

4,4′-diethyl biphenyl, mp 82.5°C; 4,4′-diisopropyl biphenyl, 64.8°C; 4,4′-dicyclohexyl biphenyl, mp 199°C; 2,2′-diethyl biphenyl, bp 110.5—111.2°C/7 mmHg, n_D^{21} =15649; 2,2′-diisopropyl biphenyl, mp 68°C.

The anion radicals were prepared in a solution of dimethoxyethane by reduction with potassium metal held in an acetone - dry ice bath.

The ESR spectrometer employed here and its operating conditions have been described in a previous paper.[4]

Results and Discussion

4,4′-Diethyl Biphenyl. In Fig. 1(a), we show the ESR spectrum of the 4,4′-diethyl biphenyl anion measured at 0°C. The observed hyperfine structures were adequately analyzed, and the hyperfine coupling constants of the ring protons, a_i^H, and the alkyl proton, a_4^β, were determined in the manner described before,[4] that is:

$a_4^\beta = 3.99$, $a_2^H = 2.68$ and $a_3^H = 0.51$ gauss.

The analyzed spectrum given in Fig. 1(b) is in good accordance with the observed spectrum.

With a depression in the temperature, the spectrum changed the hyperfine structures; Fig. 1(c) was recorded at −50°C. Both the a_i^H and a_4^β values were confirmed by the reconstruction of

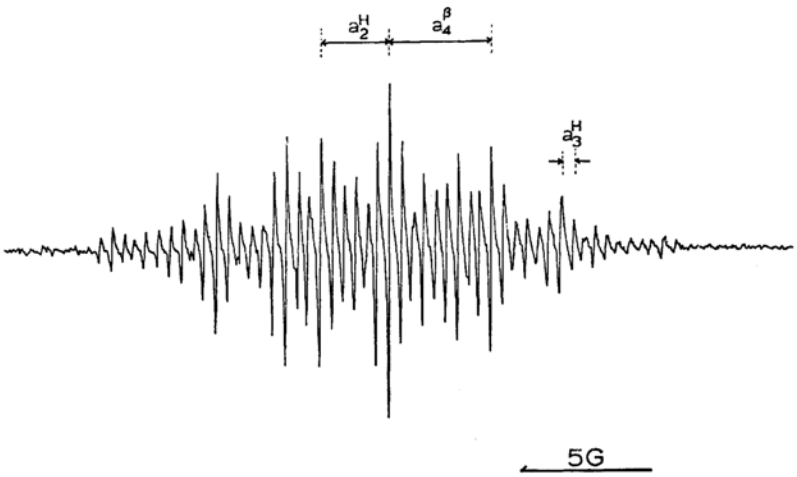


Fig. 1(a)

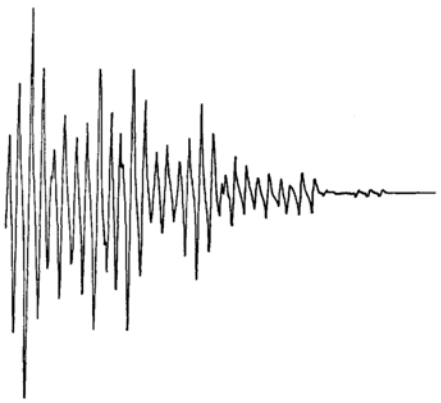


Fig. 1(b)

2) M. E. Pauline, D. M. Hall and E. E. Turner, *J. Chem. Soc.*, **1956**, 2286.

3) Bun-Hoi and P. Cagruiant, *Compt. rend.*, **216**, 381 (1943).

4) K. Ishizu, This Bulletin, **36**, 938 (1963).

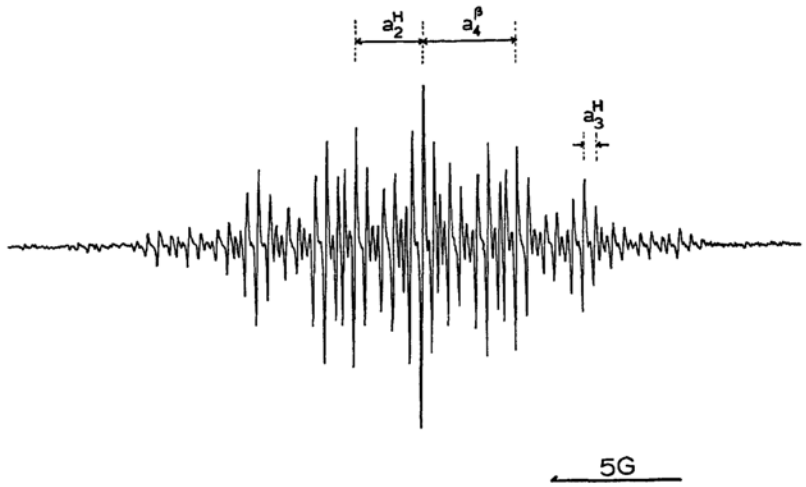


Fig. 1(c)

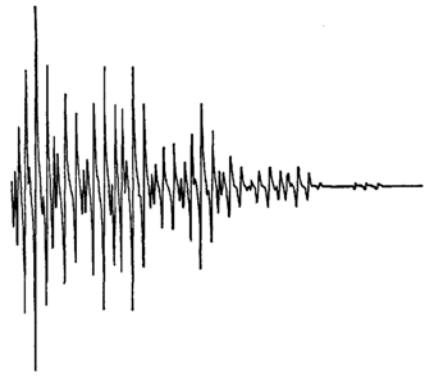


Fig. 1(d)

Fig. 1. 4,4'-Diethyl biphenyl.

(a) ESR spectrum recorded at 0°C. (b) A part of simulated spectrum of (a).
(c) ESR spectrum recorded at −50°C. (d) A part of simulated spectrum of (c).
A line shape is respectively assumed to be as a Lorentzian with the line width of 0.175G (b) and 0.100G (d).

the spectrum, as is shown in Fig. 1(d).

$a_4^\beta = 3.76$, $a_2^H = 2.65$ and $a_3^H = 0.42$ gauss.

In the present experiments, the γ-proton splitting of the ethyl group could never be detected.

On the basis of a comparison of the hyperfine coupling constants obtained in the two cases, one may say that the modified hyperfine structures are caused by a diminution of the value for a_4^β with a lowering of the temperature, whereas either a_2^H or a_3^H remains constant or has only a minor change.

4,4'-Diisopropyl Biphenyl. The spectrum measured at −30°C is given in Fig. 2(a), in which one may see that the smallest splitting (0.09 gauss) resulted from the isopropyl γ-proton. The spectrum consists of seven groups, whose relative intensity ratios are 1:6:15:20:15:6:1; the separation between the neighboring groups is about 2.6 gauss. This means that the a_4^β of isopropyl groups has the closing quantity of a_2^H, the *ortho* proton coupling constant.

The coupling constants deduced by the trial-and-error calculation of the line intensity are given as follows:

$a_4^\beta = 2.85$, $a_4^\gamma = 0.09$, $a_2^H = 2.66$
and $a_3^H = 0.45$ gauss.

When the observation temperature was lowered to −50°C, a reduction of the value for a_4^β was again noted and the hyperfine structures of the spectrum varied as is shown in Fig. 2(b). There is probably a smaller variation in the value for a_4^γ at the same

time, but we had failed to detect any important change in the value for a_4^{γ} anywhere. The hyperfine coupling constants determined at -50°C are:

$$a_4^{\beta} = 2.66,\ a_4^{\gamma} = 0.09,\ a_2^{H} = 2.66$$
$$\text{and } a_3^{H} = 0.47 \text{ gauss.}$$

4,4′-Dicyclohexyl Biphenyl. In Fig. 3, we give the observed spectrum of the 4,4′-dicyclohexyl biphenyl anion recorded at room temperature. Except for a_4^{γ}, the other hyperfine coupling constants, a_4^{β}, a_2^{H}, and a_3^{H}, were very similar to those for 4,4′-diisopropyl biphenyl; that is,

$$a_4^{\beta} = 2.92,\ a_4^{\gamma} = 0.24\ a_2^{H} = 2.60$$
$$\text{and } a_3^{H} = 0.47 \text{ gauss.}$$

The value of a_4^{γ} is interesting, for it is much larger than that of 4,4′-diisopropyl biphenyl. The large value of a_4^{γ} for 4,4′-dicyclohexyl biphenyl can probably be attributed to the fact that the methylene groups are tightly locked in the cyclohexyl ring, although it freely rotates in the case of isopropyl groups.

2,2′-Diethyl Biphenyl. The ESR measurement was carried out at -70°C, as is shown in Fig. 4. The ethyl proton splitting, a_2^{β}, was easily estimated from the quintet splitting of 1.02 gauss. The other four sets of triplet splitting (4.97, 2.19, 0.59 and 0.18 gauss) assumed here were found to be very close to those for *o,o′*-bitolyl already studied;[5] the values for a_4^{H}, a_6^{H}, a_5^{H}, and a_3^{H} were determined to be as follows:

$$a_4^{H} = 4.97,\ a_2^{\beta} = 1.02,\ a_6^{H} = 2.19,$$
$$a_5^{H} = 0.59 \text{ and } a_3^{H} = 0.18 \text{ gauss.}$$

2,2′-Diisopropyl Biphenyl. In Fig. 5, we show the spectrum of the 2,2′-diisopropyl biphenyl anion radical observed at -70°C. In this case, one may specify two sets of triplet splitting (5.41 and 2.17 gauss) which are close to those of a_4^{H} and a_6^{H} for *o,o′*-bitolyl on the one hand. On the other hand, in the terminal group of the spectrum, one may see eleven lines equally spaced at 0.28 gauss, and the splitting has the relative intensity ratio of 1 : 2 : 5 : 8 : 10 : 12 : 10 : 8 : 5 : 2 : 1. This suggests that either a_2^{β} or a_5^{H} is equal to 0.58 gauss and that a_3^{H} is nearly half the value of a_5^{H}.

The hyperfine coupling constants thus estimated are:

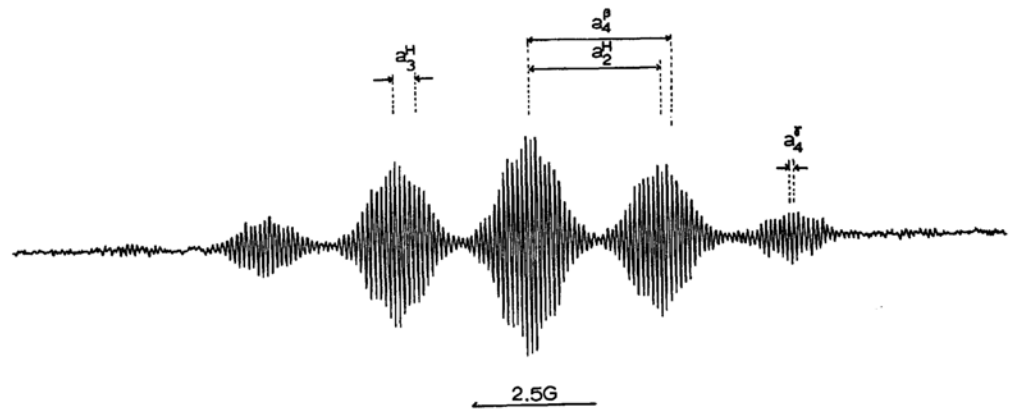


Fig. 2(a)

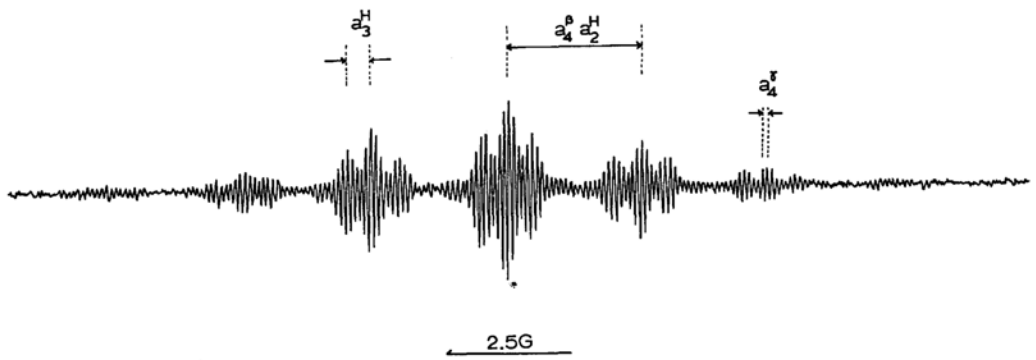


Fig. 2(b)

Fig. 2. 4,4′-Diisopropyl biphenyl.
(a) ESR spectrum recorded at -30°C. (b) ESR spectrum recorded at -50°C.

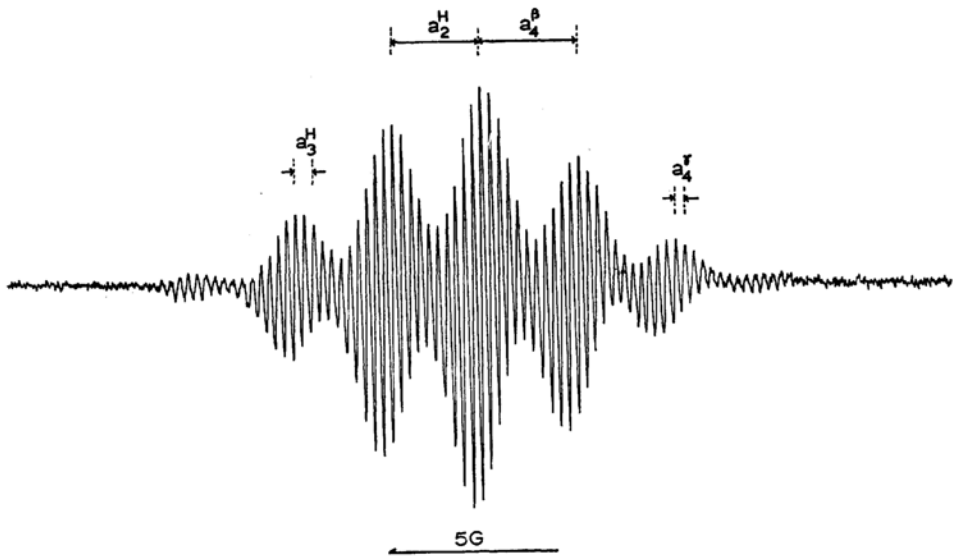


Fig. 3. 4,4'-Dicyclohexyl biphenyl.

$a_4^H = 5.14$, $a_6^H = 2.17$, $a_5^H = a_2^\beta = 0.85$ and $a_3^H = 0.28$ gauss.

The observed proton splittings for alkylated biphenyl anion radicals are summarized in Table 1.

Ring-proton Splitting. A small perturbation is usually caused in the unpaired π distribution by an alkyl substitution into an aromatic ring. Indeed, as is shown in Table 1, this is also true for all the alkyl derivatives studied in the present work. In the case of *ortho* derivatives, however, it should be particularly noticed that the same magnitude of the ring-proton splitting can be observed regardless of the alkyl substitution; this is because the magnitude of the ring-proton splitting for *ortho* derivatives is a measure of not only an inductive effect due to the alkyl group, but also of the degree of steric hindrance between the two phenyl groups. The relation between the HMO spin density on the biphenyl π orbital and the steric hindrance between the two phenyls has already been established, and the ring-proton splitting ratios, a_4^H/a_6^H, have been taken as a parameter for estimating the degree of steric hindrance in the twisted biphenyls.[5]

Table 1. Proton coupling constants of alkyl biphenyl anion radicals (gauss)

4,4'-Dialkyl biphenyl

	a_2^H	a_3^H	a_4^β	a_4^γ	$\frac{a_4^\beta}{a_4^{CH_3}}$
p,p'-Bitolyl[a]	2.66	0.51	5.63	—	—
4,4'-Diethyl	2.68	0.51	3.99	—	0.71
4,4'-Diisopropyl	2.66	0.45	2.85	0.09	0.51
4,4'-Dicyclohexyl	2.60	0.47	2.92	0.24	0.52

2,2'-Dialkyl biphenyl

	a_2^β	a_3^H	a_4^H	a_5^H	a_6^H	$\frac{a_2^\beta}{a_2^{CH_3}}$
o,o'-Bitolyl[b]	2.20	0.28	5.12	0.56	2.20	—
2,2'-Diethyl	1.02	0.18	4.97	0.59	2.19	0.46
2,2'-Diisopropyl	0.58	0.28	5.14	0.58	2.17	0.26

Observation temperatures: a) room temperature, b) −15°C

Compared with the a_4^H/a_6^H ratio for *o,o'*-bitolyl (2.32) and those for 2,2'-diethyl biphenyl (2.27) and 2,2'-diisopropyl biphenyl (2.37), one may speculate that the biphenyl ring in the present anion radicals has a conformation which more or less resembles that for *o,o'*-bitolyl, in which two phenyls are twisted by 30—45°. From this point of view, our present results may be accepted as additional evidence to support the previous proposal that the anion radicals have a more greater tendency than do the neutral molecules to hold the biphenyl ring in a coplanar conformation.[6] Furthermore, the present results establish a base for a direct discussion of alkyl proton splitting with relation to the restricted rotation of an alkyl group.

Alkyl-proton Splitting. It has been pointed out that the β-proton coupling constant can be expressed by the following equation:[7]

$$a_i^\beta = <Q>\rho_\pi \quad (1)$$

$$Q = B_0 + B\cos^2\theta \quad (2)$$

where θ is the angle between the carbon-hydrogen

5) K. Ishizu, This Bulletin, **37**, 1093 (1964).

6) K. Ishizu, H. Hasegawa, H. Chikaki, H. Nishiguchi and Y. Deguchi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 1522 (1965).

7) C. Heller and H. M. McConnel, *J. Chem. Phys.*, **32**, 1535 (1960).

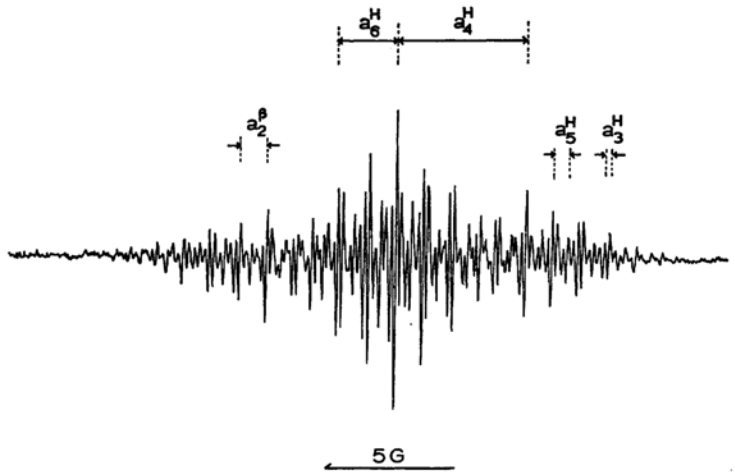


Fig. 4. 2,2′-Diethyl biphenyl.

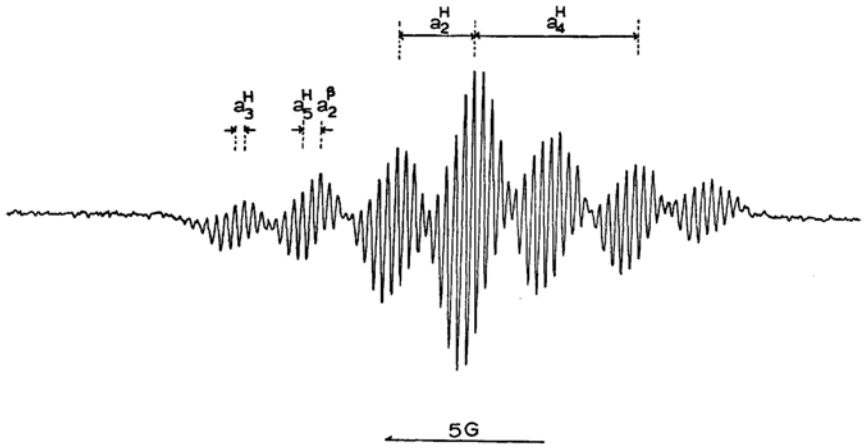


Fig. 5. 2,2′-Diisopropyl biphenyl.

bond and axis of the ring carbon $2p_z$ orbital; $<Q>$, the average quantity in Eq. (2), and ρ_π, the π electron spin density on the atom to which the alkyl group is bonded. The splitting parameter, B_0, defining a contribution from spin polarization is regarded as small in comparison with B, the parameter for hyperconjugation.[8] The methyl group in a radical has been thought to be freely rotating; thus, $<Q>$ becomes $B/2 \approx 25$ gauss, since $<\cos^2\theta> = 1/2$.

If the other alkyl groups were freely rotating, their β-proton splitting would have the same quantity for the methyl proton splitting. A large discrepancy has, however, been observed between the β-proton splitting of a methyl and those of the other alkyl groups; this has been discussed in terms of a preferred conformation of alkyl groups resulting from restricted rotation.[9]

For ease of comparison, the ratio, R, of the β-proton coupling constant to the methyl-proton coupling constant has been tabulated in Table 1.

The observed R value for 4,4′-diethyl biphenyl has been found to be close to those for such *para*-substituted benzene derivatives as 4-ethyl nitrobenzene ($R=0.74$) and 4-ethyl phenoxyl ($R=0.85$).[10]

According to this model, the theoretical R value for the ethyl group should be equal to either 0.5 or 1.50 if it is rigidly locked in the conformation illustrated in Fig. 6(a) and (b). The present R value (0.71) for 4,4′-diethyl biphenyl suggests

8) J. P. Colpa and E. de Boer, *Mol. Phys.*, **10**, 233 (1966).

9) D. H. Geske, "Progress in Physical Organic Chemistry," Vol. 4, Interscience Publishers, New York, N. Y. (1967), p. 182.

10) T. J. Stone and W. A. Waters, *J. Chem. Soc.*, **213** (1964).

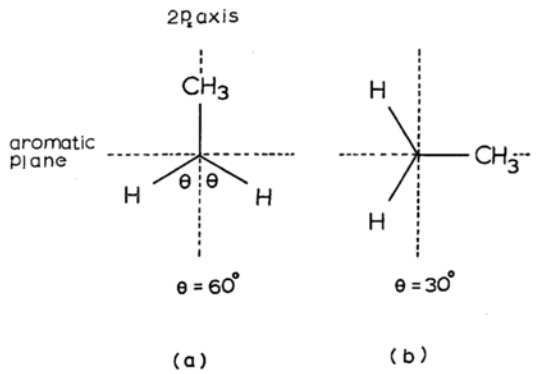


Fig. 6. Equilibrium confomation of a rotating ethyl group.

that alkyl groups more likely take the position of Fig. 6(a) rather than that of Fig. 6(b), but retain some residual rotation about their equilibrium positions.

From this assumption, the positive temperature dependence of a_4^β can be well understood as resulting from the thermal acceleration of a rotation. A similar temperature dependence has been reported for the hexaethyl benzene cation radical.[11] The β-proton coupling constant for either 4,4′-diisopropyl or 4,4′-dicyclohexyl biphenyl indicates that the β-proton would be oriented at $\theta=60°$, as calculated by Eqs. (1) and (2). These observed R values are nearly equal to those for the 4-isopropyl nitrobenzene anion ($R=0.56$)[9] and 4-isopropyl phenoxyl ($R=0.50$).[10]

In the case of 2,2′-diethyl biphenyl, the observed R value is much like those of ethyl cyclooctatetraene ($R=0.49$),[12] the 9-ethyl anthracene ($R=0.58$)[13] anion radical, and the hexaethyl benzene cation radical[11] ($R=0.46$), in which the rotation of the ethyl group has been considered to be strictly restrained, forcing it to take the preferential conformation illustrated in Fig. 6(a). The large diminution in the observed R value for 2,2′-diisopropyl biphenyl in comparison with the value for 4,4′-diisopropyl biphenyl indicates that the isopropyl β-proton is closer to the aromatic plane of biphenyl.

A molecular model is set up for 2,2′-diisopropyl biphenyl; it shows that the isopropyl free rotation is greatly restricted, when the two phenyls are twisted by about 45° taking account of the results for hindered methyl biphenyls.[5,6]

One may see that the isopropyl β-proton comes into contact with the 2′-*ortho* proton and nearly falls on the aromatic plane, as is illustrated in Fig. 7.

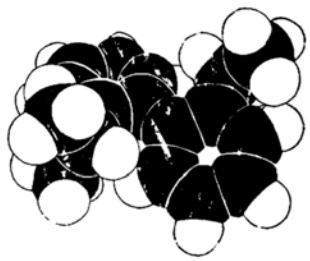


Fig. 7. A Stuart model of 2,2′-diisopropyl biphenyl anion radical.

The anomalous decrease in R values obtained for the present *ortho* derivatives can thus be attributed to the fact that the free rotation of the alkyl group is greatly restricted by the steric hindrance at the *ortho* position, where the alkyl groups are assumed to behave as torsional oscillators rather than rotators. The present results for the *ortho* alkyl proton-splitting also provide new experimental evidence to justify the previous proposal concerning hindered methyl biphenyls.

The authors wish to thank Professor Hideo Takaki for his encouragement through the course of this work. They are also indebted to Mrs. Ikuyo Higuchi for her assistance in the preparation of the samples.

11) M. K. Carter and G. Vincow, *J. Chem. Phys.*, **47**, 302 (1967).
12) A. Carrington and P. F. Todd, *Mol. Phys.*, **8**, 299 (1964).
13) D. Bachmann, *Z. Phys. Chem.*, **43**, 198 (1964).