ESR and ENDOR Studies of Hindered Internal Rotation of Higher Alkyl Groups in 4,4′-Dialkylbiphenyl Anion Radicals

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ESR and ENDOR spectra were obtained for the anion radicals of 4,4′-diisopropylbiphenyl, 4,4′-dicyclohexylbiphenyl and 4,4′-dicyclopentylbiphenyl. Both the β- and γ-proton coupling constants of the alkyl groups were precisely determined. The temperature dependence of the β-proton splittings of the alkyl groups were investigated. According to the Heller-McConnell relationship for hyperconjugation, $a_4^\beta=(B_0+B_2\cos^2\theta)\rho_\pi^2$, the positive temperature dependence of the alkyl β-proton splitting was adequately interpreted utilizing a revised model with restricted rotation. The rotational potential barrier and the energy difference of the two equilibrium states obtained were 1.2 and 0.5, 1.2 and 0.6, and 1.2 and 0.6 kcal/mol for the 4,4′-diisopropyl-, 4,4′-dicyclohexyl-, and 4,4′-dicyclopentylbiphenyl anions, respectively. The energy difference of the non-bonding interatomic interaction was calculated in terms of the Lennard-Jones 6—12 potential. Excellent agreement is found between the experimentally-determined value of the potential barrier and that calculated theoretically. ENDOR observations carried out for 4,4′-dicyclohexyl- and 4,4′-dicyclopentylbiphenyl anion radicals in solution demonstrated that γ-protons revealed two different hyperfine coupling constants. These hyperfine coupling constants were assigned to the stereochemically different γ-protons. The ratio of these γ-protons splittings suggest that hyperconjugation plays an important role in producing a spin density of the γ-protons as has been proposed for explanations of the β-proton splittings.

Restricted rotation of the alkyl groups has been extensively studied by ESR for a number of aromatic radicals.

Rotational potentials of the alkyl groups have been proposed from the analysis of the magnitudes of the β-proton coupling constants, and their temperature dependence has often been discussed based on the McConnell-Heller relationship with the aid of Boltzmann statistics.

In this work, ESR and ENDOR techniques were applied to the study of the anion radicals of 4,4′-diisopropylbiphenyl, 4,4′-dicyclopentylbiphenyl, and 4,4′-dicyclohexylbiphenyl.

Analysis of the ESR spectra, which contains complicated hyperfine structure due to the extra γ-proton splitting, was greatly simplified by ENDOR measurement, and the β-proton coupling constants of the alkyl groups and their temperature dependence were accurately determined. The temperature dependence of the β-proton splitting was theoretically investigated based on the revised model of restricted rotation. A new potential function, which has a double minimum, has been proposed,[1] and the energy barriers were calculated in terms of the rotational wave functions expanded in a Fourier series.

The potential barrier height and corresponding energy difference between the two equilibrium states were estimated by comparing the observed temperature dependence with that calculated theoretically.

On the other hand, the energy difference of the non-bonding interaction between the isopropyl group and the neighboring aromatic protons was calculated on the basis of a Lennard-Jones 6—12 potential. The maximum repulsion energy between the isopropyl and the ring protons thus calculated justified the value of the potential barrier determined experimentally.

In addition to the studies of the temperature dependence of the β-proton splittings, the dependence of γ-proton splitting was also investigated using ENDOR. A large difference between the hyperfine splitting of the two γ-protons, which have stereochemically distinct conformations, was clearly detected for the cycloalkyls. The magnitude of the γ-proton splitting is reasonably understandable under the assumption that a direct hyperconjugation is also the dominant mechanism producing the spin density of the γ-protons.

Experimental

The 4,4′-dialkylated biphenyls were prepared from the coupling of *para*-alkyl phenyl magnesium bromide in the presence of anhydrous cobaltous chloride, according to the following process.[2]

0.068 mol of freshly distilled *para*-alkyl bromobenzene was dissolved in about 30 ml of dry tetrahydrofuran (THF) and was added to magnesium chips (0.074 mol) mixed in a like amount of dry THF. To ensure the absence of any unreacted bromo-compound, the Grignard solution was refluxed for 3 hr. After reaction, the solution was dropped into a mixture of 0.05 mol of anhydrous cobaltous chloride and 0.05 mol of ethylbromide in about 30 ml of THF, and the mixture was refluxed for 4 hr. The organic product was extracted with ether. After the removal of the solvent, the residue was recrystallized from ethyl alcohol.

The materials thus obtained were all purified by silica-gel chromatography, using *n*-hexane as the solvent.

The physical constants of the white crystalline solids are listed below.

		λ_{max} nm(ε)
4,4′-diisopropylbiphenyl	mp 64.8 °C	
	UV(Hexane)	256.5 (29400)
4,4′-dicyclohexylbiphenyl	mp 204 °C	
	UV(Hexane)	258 (21300)
4,4′-dicyclopentylbiphenyl	mp 144—146 °C	
	UV(Hexane)	259.5 (22400)

The anion radicals were prepared in a solution of dimethoxyethane (DME) by reduction with potassium and sodium metal. The ESR spectra were measured in the temperature range from +20 °C to −90 °C using a Japan Electron Optics (JEOL) JES-ME-3X type spectrometer equipped with 100 kHz magnetic field modulation.

The ENDOR spectra were measured in the temperature

range from −90 °C to −50 °C using a JEOL ES-EDXI type spectrometer operating with 80 Hz magnetic field modulation.

About 150 W of continuous radio waves, frequency modulated at 6.5 kHz, were present in the cavity for NMR excitation.[3]

The magnetic field was calibrated using a perylene cation radical prepared in concentrated sulfuric acid.

Results

The ENDOR spectra of the 4,4′-diisopropylbiphenyl anion, the reference compound of the cycloalkyl derivatives, are shown in Fig. 1.

By comparison with the ENDOR signal of the biphenyl anion,[17] the signal at 14.50, 17.15 and 17.64 MHz can be assigned to the splitting due to the *meta*-, the alkyl β-, and the *ortho*-protons respectively. In addition, the splittings due to the γ-protons are recorded in the vicinity of the free proton frequency.

With elevation of the temperature, it is observed that the signals of alkyl β-protons designated by the dotted line in the figure show a higher frequency shift, that is, the positive temperature dependence of the alkyl β-protons is thus fairly well demonstrated as is in previous ESR observations.[4] The temperature dependence of the β-proton splitting of the isopropyl has been theoretically treated in terms of the restricted rotation of the alkyl group. The calculation of the β-proton splitting as a function of temperature has already been carried out with the proposed adequate potential function in a previous paper.[1]

The ENDOR spectra of the 4,4′-dicyclopentylbiphenyl anion, shown in Fig. 2, can easily be analyzed with reference to the hyperfine splittings of the 4,4′-diisopropylbiphenyl anion. Of particular interest is the fact that γ-protons of the cyclopentyl give rise to two different hyperfine splittings, although the isopropyl γ-proton produces only one hyperfine splitting. Observation of the two different γ-splittings for the cycloalkyls may be attributed to the fact that methylene groups are tightly locked in the cycloalkyl groups, while the methyl group in isopropyl undergoes free rotation.

Computer calculation of the ESR line intensities based on the hyperfine coupling constants determined by the present ENDOR measurements are in excellent agreement with the observed line intensities as shown in Fig. 3.

The ENDOR spectra of the cyclohexylbiphenyl anions (Fig. 4) are very similar to those of the cyclopentyl anions, where the equatorial and the axial γ-proton splittings are also highly resolved.

In Fig. 5, the slopes of the plots are compared for the cycloalkyls and isopropyls. A slight increase of the slope noted for cycloalkyls suggests that some modifications of the rotational function occur. A detailed analysis of the rotational potential function will be discussed in the following section.

The proton coupling constants of each derivative thus determined are summarized in Table 1.

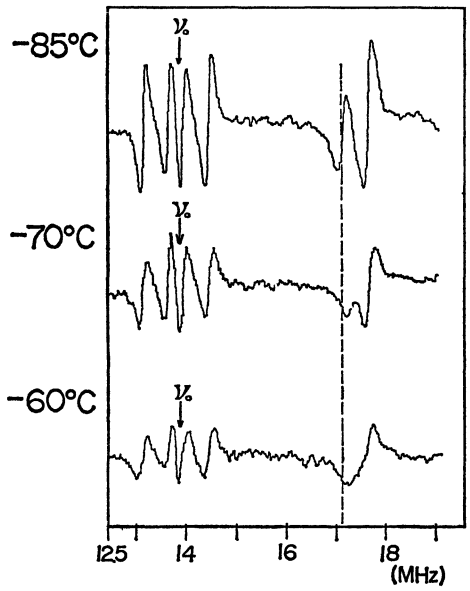

Fig. 1. ENDOR spectra of the system 4,4′-diisopropylbiphenyl-DME-K.

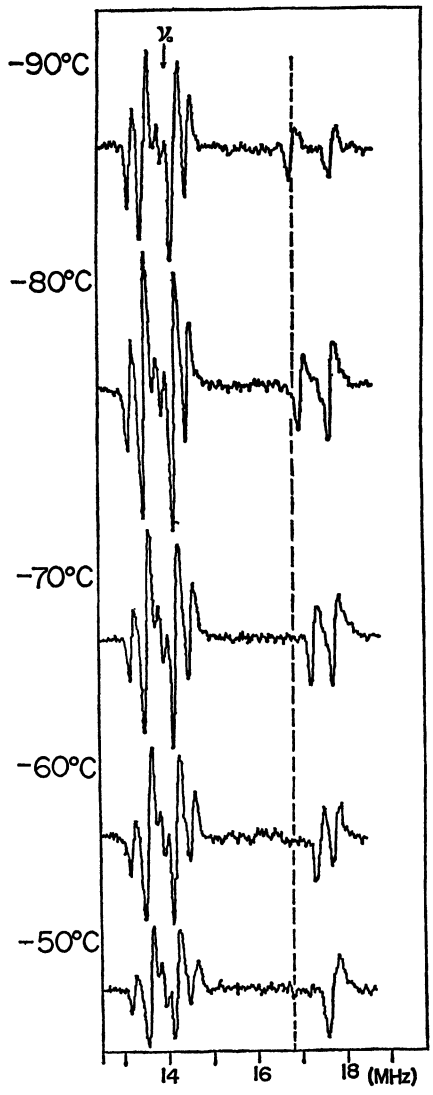

Fig. 2. ENDOR spectra of the system 4,4′-dicyclopenthylbiphenyl-DME-K.

Table 1. Proton coupling constants of the 4,4'-dialkylbiphenyl anion radicals (G)

	a_2^H	a_3^H	a_4^β	$a_4^{\gamma 1}$	$a_4^{\gamma 2}$	$a_4^\beta/a_4^{CH_3}$
p,p'-Bitolyl[4]	2.66	0.51	5.63	—	—	—
4,4'-Diisopropyl	2.70	0.46	2.35	0.10	—	0.417
4,4'-Dicyclohexyl	2.70	0.44	2.21	0.24	0.80	0.393
4,4'-Dicyclopentyl	2.72	0.45	2.20	0.24	0.90	0.391

The observed temperature is −85 °C.

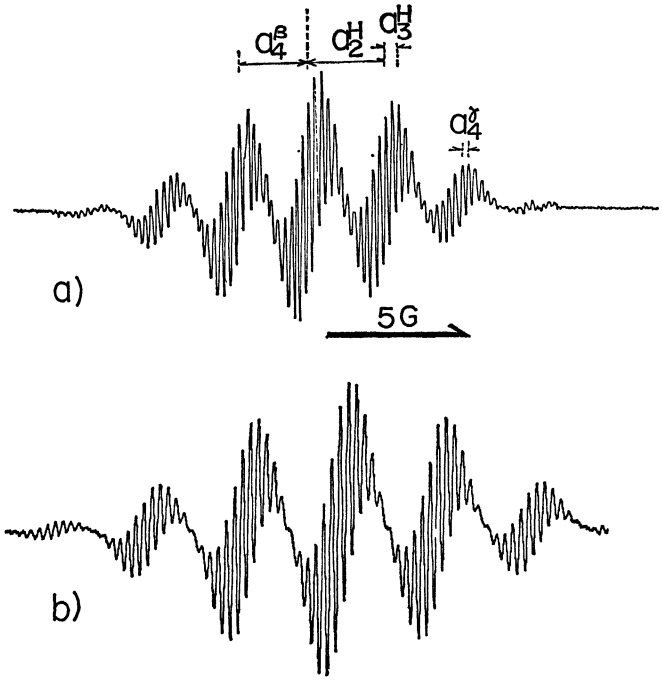

Fig. 3(a). ESR spectrum of the system 4,4'-dicyclopenthylbiphenyl-DME-K at −60 °C. (b). A part of simulated spectrum of (a).

Discussion

Alkyl β-Proton. The magnitude of the β-proton splitting can often be calculated using the following equations:

$$a_4^\beta = \langle Q(\theta)\rangle \rho_4^\pi \tag{1}$$

and

$$Q(\theta) = B_0 + B_2 \cos^2\theta \tag{2}$$

where B_0 and B_2 are empirical parameters, ρ_4^π is the spin density at the *para*-position and θ is the angle between the axis of the $2p_z$ orbital and the aliphatic C–H bond of the alkyl group, both projected on the plane perpendicular to the bond between the methylene carbon of the alkyl and the aromatic carbon.

$\langle Q(\theta)\rangle$ is the quantum mechanical average of $\cos^2\theta$ over the appropriate rotational wave functions $\psi_i(\theta)$. The β-proton splitting as a function of temperature was calculated based on Eqs. (1) and (2), with the aid of Boltzmann statistics.[6]

$$a_4^\beta = B\rho_4^\pi \langle \cos^2\theta\rangle, \qquad \theta = \alpha + \theta_0 \tag{3}$$

$$\langle \cos^2\theta\rangle = \frac{\sum_{i=0}^{\infty} \langle \psi_i(\alpha)\,|\cos^2(\alpha+\theta_0)|\,\psi_i(\alpha)\rangle e^{-E_i/kT}}{\sum_{i=0}^{\infty} e^{-E_i/kT}} \tag{4}$$

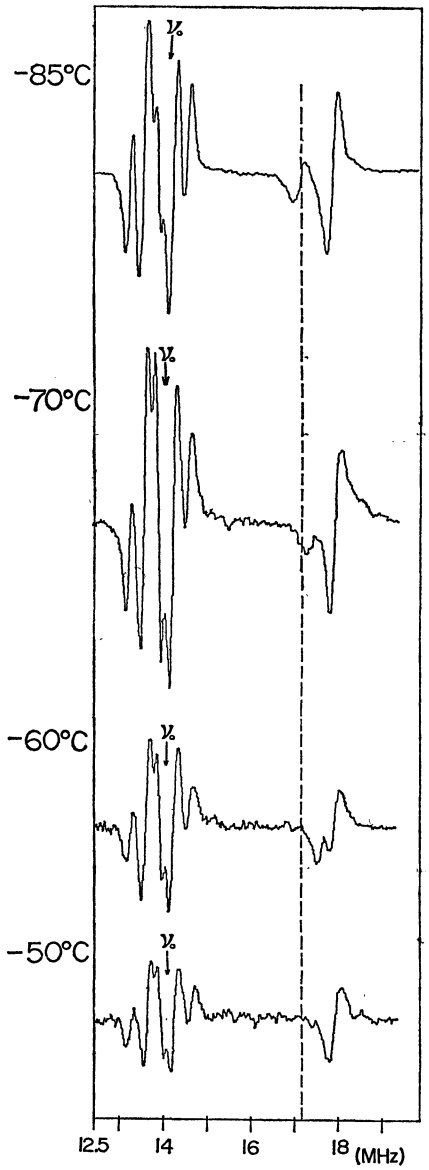

Fig. 4. ENDOR spectra of the system 4,4'-dicyclohexylbiphenyl-DME-K.

The contribution of B_0 was neglected in Eq. (2) and the value of $B\rho_4^\pi$ was estimated from the methyl proton splitting of the 4,4'-dimethylbiphenyl anion radical assuming free rotation of the methyl group, with $B\rho_4^\pi$ being 2×5.6 G.[4,8]

In Eq. (4), the wave function $\psi_i(\alpha)$ and the eigenvalue E_i are obtained by solving the following equation:

$$-\left(\frac{\hbar^2}{2I}\right)\left(\frac{d^2\psi_i}{d\alpha^2}\right) + [V(\alpha) - E_i]\psi_i = 0 \tag{5}$$

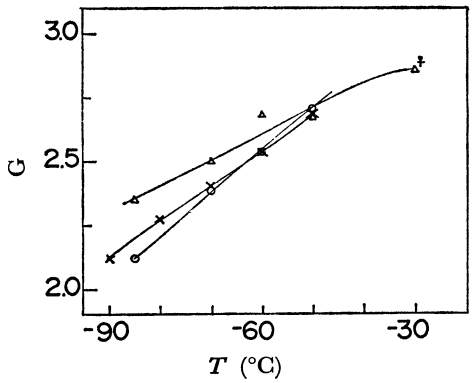

Fig. 5. Temperature dependence of the hyperfine coupling constants for the alkyl β-protons measured by ENDOR.
△; 4,4′-diisopropylbiphenyl, ○; 4,4′-dicyclohexylbiphenyl, ×; 4,4′-dicyclopentylbiphenyl,
♀; ESR data.[4]

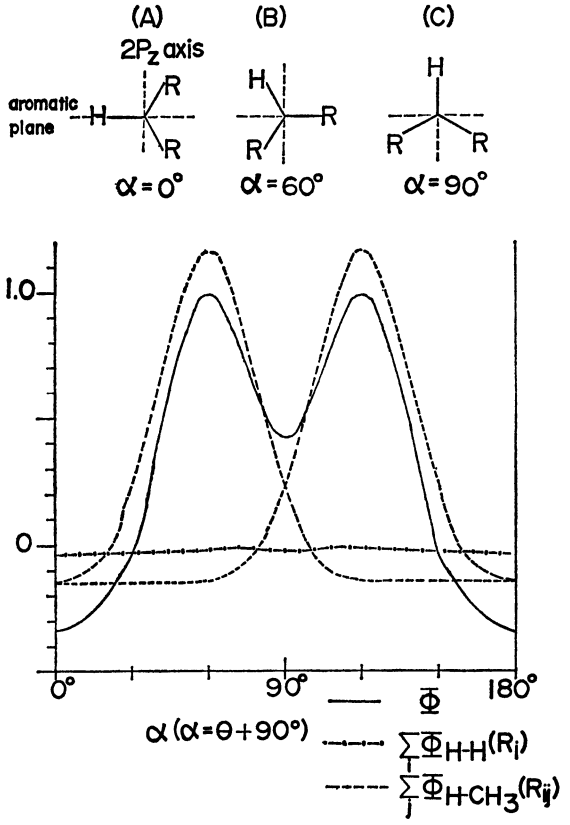

Fig. 6. Conformations of the 4,4′-diisopropylbiphenyl anion and non-bonded interaction energies between the rotating isopropyl and ring *meta* protons as a function of α.

where the moment of inertia I of the molecular fragment ϕ–R can be calculated to be 0.70×10^{-38} g·cm^2 for 4,4′-diisopropylbiphenyl, 1.90×10^{-38} g·cm^2 for 4,4′-dicyclohexylbiphenyl and 1.60×10^{-38} g·cm^2 for 4,4′-dicyclopentylbiphenyl assuming that a prefered rotation of the residual group occurs about the longer axis of the 4,4′-dialkylbiphenyl molecules.

Before solving Eq. (5) numerically, we must know the valid rotational potentials $V(\alpha)$ of the alkyl groups. For 4,4′-diisopropylbiphenyl, restricted rotation of the isopropyl group has already been discussed and the appropriate potential function obtained is illustrated in Fig. 6, as reported in a previous publication.[1] Since the principal steric repulsions occur between the γ-methyl and *meta* C–H groups of the biphenyl ring for 4,4′-diisopropylbiphenyl, and between the γ-methylene and *meta* C–H groups for the 4,4′-dicycloalkylbiphenyls, the rotational potential structures should be essentially the same in both cases. From the above considerations, the rotational potential barrier $V(\alpha)$ of each isopropyl, cyclohexyl and cyclopentyl group was approximated by:

$$V(\alpha) = V_0 \sum_{i=0}^{3} a_i \cos 2i\alpha \tag{6}$$

$$a_0 = \frac{1}{18}\left(\frac{9V_m}{V_0}+4\right),\quad a_1 = \frac{4}{9},\quad a_2 = \frac{2}{9},$$

$$a_3 = \frac{1}{18}\left(8-\frac{9V_m}{V_0}\right)$$

where V_0 and V_m are the potential energy differences between the lowest potential at state [A] and the highest potential at state [B] and that between the lowest potential at state [A] and the medium value at state [C], respectively, as is illustrated in Fig. 6. At the most stable conformation [A], the β-hydrogen of these alkyl groups is in the plane of the aromatic ring and the dihedral angle of the β-proton, θ_0 in Eq. (3), is equal to $\pi/2$. The Hamiltonian matrix $\langle i|\mathscr{H}|j\rangle$ was diagonalized by expanding the wave function in a Fourier series.

$$\psi_i(\alpha) = \sum_{j=0}^{\infty} (C_{ij}\sin j\alpha + D_{ij}\cos j\alpha) \tag{7}$$

We have calculated the temperature dependence of $\langle\cos^2\theta\rangle$ as a function of V_0 and V_m for three 4,4′-dialkylbiphenyls. For example, $\langle\cos^2\theta\rangle$ calculated for 4,4′-diisopropylbiphenyl in the temperature range

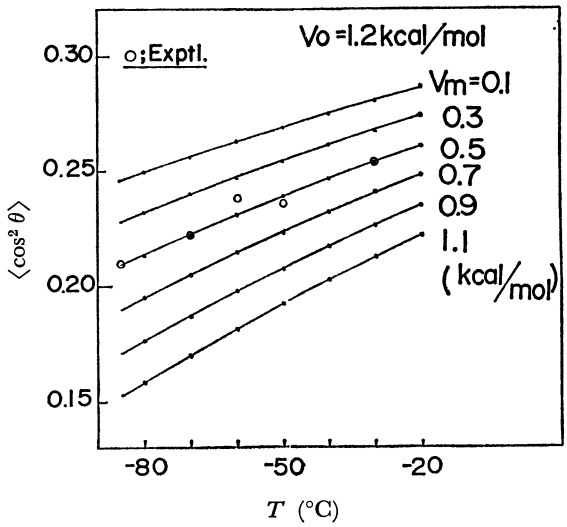

Fig. 7. Theoretical temperature dependence of $\langle\cos^2\theta\rangle$ for rotating isopropyl.
Numerical calculations were carried out taking the energy difference between the two minima, V_m, as the variable parameter, where the maximum barrier of the potential, V_0, was fixed to be 1.2 kcal/mol everywhere.

from −80 °C to −20 °C for various values of V_0 and V_m are shown in Fig. 7.

The best agreement between the calculated and experimental temperature dependences of $\langle\cos^2\theta\rangle$ is obtained with $V_0=1.2$, $V_m=0.5$, $V_0=1.2$, $V_m=0.6$ and $V_0=1.2$, $V_m=0.6$ kcal/mol for 4,4′-diisopropyl, 4,4′-dicyclohexyl and 4,4′-dicyclopentyl biphenyl.

Calculation of the Repulsive Potential Energies between the Isopropyl and the Aromatic Protons. In a previous publication,[8] calculation of the energy of the non-bonding interaction has been reported for the rotating ethyl group in the 4,4′-diethylbiphenyl, and it was found a simple calculation of the non-bonding interaction was in excellent agreement with the value determined experimentally. The interactions between the counter-cation and the radical anions had been disregarded everywhere, because it was known from conductivity measurements,[9] NMR shift observation[10] and studies of the temperature dependence of the ENDOR intersities of several alkylated biphenyl anions[11] that the radical anions may exist as solvent separated ion-pairs and may act freely under the present experimental circumstances.

In the present studies, similar calculations of the non-bonded interaction between rotating alkyl and aromatic protons are applied to the 4,4′-diisopropyl derivative using the following approximations.

[1] The methyl groups in the isopropyl are treated as a rare gas atom of Kr, since the methyl group is thought to be rapidly rotating in comparison with the motion of the isopropyl group, and not only is it non-polar in nature, but also its spherical size as given by the van der Waals radius are almost the same as those of the Kr atom.

[2] Two kinds of interatomic interactions were considered in the present calculations. The first is the interaction between the ring-*meta* protons and the alkyl β-proton, $\Phi_{H_m\text{-}H_\beta}$. The second is the interaction between the ring-*meta* protons and the methyl groups, $\Phi_{H_m\text{-}CH_3}$. All other interactions are neglected.

The total interatomic potential was calculated from a summation of the energy of interacting pairs, and each interatomic interaction was estimated using the Lennard-Jones 6—12 potential function, thus

$$\Phi_{H_m-H_\beta}(R_i) = A_{H-H}/R_i^{12} - B_{H-H}/R_i^6 \quad (8)$$

and

$$\Phi_{H_m-CH_3}(R_{ij}) = A_{H-Kr}/R_{ij}^{12} - B_{H-Kr}/R_{ij}^6 \quad (9)$$

where R_i is the interatomic distance between the ring-*meta* proton and the alkyl β-proton and R_{ij} is that between the ring-*meta* proton and the methyl group. As shown in Fig. 8, R_i and R_{ij} were calculated as functions of the rotation angle of the alkyl (α) by taking the bond angle of the tetrahedral carbons to be 109°29′ and that of the ring carbons to be 120°. The bond distances between the carbon and hydrogen atoms were estimated to be 1.09 Å everywhere, and carbon-carbon distance to be 1.52 Å for the aliphatic group, 1.45 Å for the alkyl carbon-ring carbon separation, and 1.40 Å for the aromatic ring.[12] The numerical values of parameters A_{H-H}, B_{H-H}, A_{H-Kr}, and B_{H-Kr} in the Lennard-Jones 6—12 potential have already been established by Yasuda[13] and Oobatake.[14]

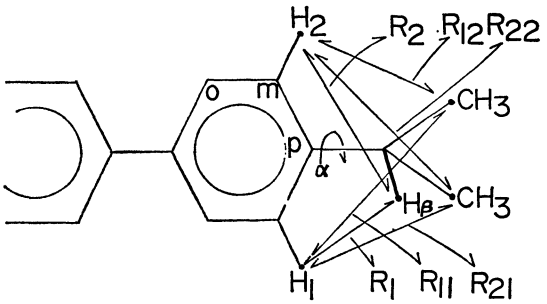

Fig. 8. Scheme of the distance R_{ij} and R_i between ring *meta* protons and methyl groups in the isopropyl and between ring *meta* protons and isopropyl β-proton.

We have already used these values to calculate of the potential barrier height of the rotating ethyl group in 4,4′-diethylbiphenyl[8] and the calculated value was in excellent agreement with the value obtained from the measurement of the temperature dependence of the β-proton splittings, using the following parameters:[13]

$$A_{H-H} = 4.7\times10^2 \text{ kcal}\cdot\text{Å}^{12}/\text{mol}, \qquad B_{H-H} = 9.2 \text{ kcal}\cdot\text{Å}^6/\text{mol}$$

$$A_{H-Kr} = 3.3\times10^4 \text{ kcal}\cdot\text{Å}^{12}/\text{mol}, \qquad B_{H-Kr} = 1.2\times10^2 \text{ kcal}\cdot\text{Å}^6/\text{mol}.$$

The interatomic potential energy Φ is given by

$$\Phi = \sum_{i=1}^{2}\Phi_{H_m-H_\beta}(R_i) + \sum_{i,j=1}^{2}\Phi_{H_m-CH_3}(R_{ij}) \quad (10)$$

In Fig. 6, we give the plot of the interatomic potential energy as a function of the rotating angle (α) of the alkyl group.

The maximum repulsion energy thus calculated was 1.4 kcal/mol when a methyl group is fixed on the aromatic ring [state (B)], while the configuration [A], in which the β-proton is in the plane of the aromatic ring, is found to be the most stable. The potential height (V_m) calculated for the configuration [C], in which the β-hydrogen is parallel with the axis of the $2p_z$ ring carbon, was 0.7 kcal/mol.

The potential function of the isopropyl thus calculated, assuming the non-bonded interatomic interaction, shows not only a double minimum but also is in satisfactory agreement with the value obtained from the measurement of the temperature dependence of the β-proton splittings.

In conclusion, the rotation of the isopropyl, cyclohexyl and cyclopentyl groups may be more or less restricted in the potential as given in Fig. 6, which have the maximum repulsion energy of ~1.2 kcal/mol, this value being slightly above the thermal activation energy at 300 K.

From these considerations, it can be said, at room temperature the isopropyl, cyclohexyl and cyclopentyl groups in para alkylated biphenyl retain fairly large degrees of freedom of rotation affected by the thermal activation, in contrast to the tight restriction of rotation of the alkyls as seen in the space-filling molecular-models.

Alkyl γ-Proton Splitting. The difference in the magnitude of the γ-proton hyperfine coupling of the cycloalkyls may be attributed to the stereochemically different γ-protons, and this offers a useful test to determine whether direct hyperconjugation is the dominant mechanism producing the spin density at these protons, as already reported by Adams *et al.*[7] In cyclohexyls, the axial and equatorial γ-protons remain stereochemically equivalent in pairs against restricted rotation of the cyclohexyl group in the rotational potential, where we assign the larger coupling (240 mG at −85 °C) to the equatorial protons, and the smaller one to the axial protons.

In Fig. 9, it is seen that the equatorial γ-proton splitting of the cyclohexyl decreases with elevation of the temperature, but the other axial γ-proton splittings exhibit only minor increases or remain constant. The similar temperature dependence of the cyclohexyl of the phenoxyl radical has already been reported,[7] and the importance of hyperconjugation of the γ-methylene group has been noted.

Hyperconjugation with a $2p_z$-orbital gives a spin density contribution at the γ-proton of the form

$$a_4^{\gamma} = (A_\gamma + B_\gamma \cos^2\theta)\rho_4^{\pi}. \qquad (11)$$

For a γ-proton, θ is the usual dihedral angle and A_γ and B_γ are empirical constants defined in the same ways as is done for β-protons. The major exchange interaction may be expected between a γ-proton and an unpaired electron in a $2p_z$-orbital on the adjacent ring carbon atoms. The interactions attributed to the other ring carbons were all neglected because the spin density of the ring *meta* carbon is about 1/10 of that of the ring *para* carbon,[15] and the distance between the γ-proton and ring *ortho* carbon is too great.

In the 4,4′-dicyclohexylbiphenyl anion, the axial and equatorial protons move on the same circle during rotations of alkyls about the C_p–C_α bond, and we can write

$$a_4^{\gamma e} = A_{\gamma e} + B_\gamma \cos^2(\theta + \theta_e^0) \qquad (12)$$

and

$$a_4^{\gamma a} = A_{\gamma a} + B_\gamma \cos^2(\theta + \theta_a^0) \qquad (13)$$

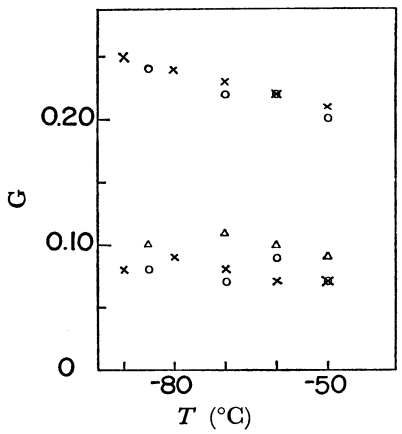

Fig. 9. Temperature dependence of the hyperfine coupling constants for the alkyl γ-protons measured by ENDOR.
△; 4,4′-Diisopropylbiphenyl, ○; 4,4′-dicyclohexylbiphenyl,, ×; 4,4′-dicyclopenthylbiphenyl.

where θ_e^0 and θ_a^0 are the equilibrium dihedral angles of the equatorial and axial protons, respectively. θ_e^0 and θ_a^0 were calculated to be 5°35′ and 54°25′ by taking the aliphatic C–H bond length to be 1.10 Å and the alicyclic C–C bond length to be 1.52 Å.[12]

A qualitative explanation of the $a_4^{\gamma e}/a_4^{\gamma a}$ ratio can be made assuming that the alkyl β-proton exchanges rapidly between state [A] and state [C] as shown in Fig. 6, and the contribution of the other state [B] is negligible. The ratio (n_A/n_C) of the populations at state [A] to that at state [C] is estimated using

$$n_A/n_C = \exp(V_m/kT) \qquad n_A + n_c = 1 \qquad (14)$$

where V_m is the energy difference between state [A] and state [C], 0.6 kcal/mol. At −85 °C, the values of n_A and n_C are estimated to be 0.87 and 0.17, respectively, and therefore the ratio $a_4^{\gamma e}/a_4^{\gamma a}$ can be calculated assuming the $|A_{\gamma e}|$ and $|A_{\gamma a}| \ll B_\gamma$, that is, that

$$\frac{a_4^{\gamma e}}{a_4^{\gamma a}} = \frac{n_A\langle\cos^2 5°35'\rangle + n_C\langle\cos^2 95°35'\rangle}{n_A\langle\cos^2 54°25'\rangle + n_C\langle\cos^2 144°25'\rangle} = 2.1. \qquad (15)$$

The calculated value of $a_4^{\gamma e}/a_4^{\gamma a}$ is nearly the same as the experimental value of 3.0.

In the case of the 4,4′-dicyclopentylbiphenyl anion, the equilibrium dihedral angles θ_0^{e1} for the pseudo-axial γ-protons and those for the equatorial γ-protons θ_0^{e2} have almost the same value, 21°, but two γ-protons in the methylene group do not move on the same circle during rotation about the C_4–C_α bond. This means that each γ-proton is separated from the ring C_4 carbon by the distinct distance of 1.51 abd 2.97 Å, respectively. Since B_γ in Eq. (11) should be represented by the exchange integral between the C_γ–H_γ bond and the $2p_z$-orbital on C_4 as discussed by McLachlan,[16] it will be a function of the distance between the $2p_z$-orbital on C_4 and the γ-proton, which is on the plane perpendicular to the nodal plane of the $2p_z$-atomic orbital. We can, therefore, assign the larger coupling to the proton taking a position closer to the ring C_4 carbon atom at a distance of 1.51 Å and that for the smaller one at a distance of 2.97 Å.

In view of the above discussion, it is seen that different hyperfine couplings observed for cyclohexyl γ-protons are attributed to the difference in the averaged value of $\cos^2\theta$. On the other hand, in cyclopentyl γ-protons, the different B_γ values produce nonequivalent γ-proton splittings.

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The numerical calculations were carried out on the FACOM 230-75 at the Data Processing Center, Kyoto University.

References

1) F. Nemoto, F. Shimoda, and K. Ishizu, *Chem. Lett.*, **1974**, 639.
2) M. S. Kharasch and E. K. Frelds, *J. Amer. Chem. Soc.*, **63**, 2316 (1941).
3) T. Yamamoto, K. Sato, and T. Miyamae, *Japan. J. Appl. Phys.*, **11**, 1508 (1972).
4) K. Ishizu, K. Mukai, H. Hasegawa, K. Kubo, H.

Nishiguchi, and Y. Deguchi, This Bulletin, **42**, 2808 (1969).
5) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).
6) E. W. Stone and A. H. Maki, *ibid.*, **37**, 1326 (1962).
7) R. F. Adams and N. M. Atherton, *Mol. Phys.*, **17**, 673 (1967).
8) F. Nemoto and K. Ishizu, *J. Phys. Chem.*, in press.
9) P. Chang, R. V. Slates, and M. Szwarc, *ibid.*, **70**, 3180 (1966).
10) G. W. Canters and E. de Boer, *Mol. Phys.*, **26**, 1185 (1973).
11) To be published.
12) L. Pauling, "The Nature of the Chemical Bond," 3rd Edition, Cornell University Press, Ithaca, N.Y. (1960), p. 260.
13) H. Yasuda, *Prog. Theor. Phys.*, **45**, 1361 (1971).
14) M. Oobatake and T. Ooi, *ibid.*, **48**, 2132 (1972).
15) K. Ishizu, M. Ohuchi, F. Nemoto, and M. Suga, This Bulletin, **46**, 2932 (1973).
16) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).
17) R. Biehl, K. P. Dinse, and K. Mobis. *Chem. Phys. Lett.*, **10**, 605 (1971).