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ENDOR STUDY OF HINDERED INTERNAL ROTATION OF THE ALKYL GROUP IN THE 4,4'-DIISOPROPYL BIPHENYL ANION RADICAL

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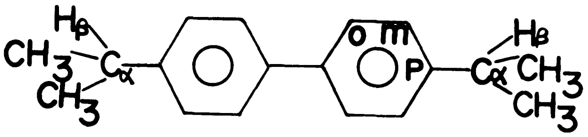
Utilizing ENDOR observations for the 4,4'-diisopropylbiphenyl anion, the β-proton coupling constants were determined and their temperature dependence was investigated. The positive temperature dependence of the β-proton coupling constant was interpreted utilizing a revised model of restricted rotation for isopropyl groups (see Fig.3-b). The energy difference, E_o between the two equilibrium states of this restricted rotational system was estimated to be 0.4 Kcal/mol .

Restricted rotation of the alkyl groups has been extensively studied by ESR for a number of aromatic radicals. The magnitudes of the β-proton coupling constants , a_β^R were often compared with those of the freely rotating methyl, $a_\beta^{CH_3}$. The equilibrium dihedral angles θ between the $2p_\pi$-orbital of the aromatic carbon and the sp^3-hybrid orbital of the alkyl carbon were calculated by taking the ratio $a_\beta^R / a_\beta^{CH_3}$, based on the McConnell-Heller equation.$^{1)}$

In the case of the higher alkyl groups such as isopropyl or cyclohexyl, a complicate overlapping of the hyperfine structures has given rise to a complex ESR spectrum due to the γ-proton splitting. In particular, analysis of the spectrum was not facilitated by line broadening at the low temperature region.

In this communication, the ENDOR observations were applied to the studies of the 4,4'-diisopropylbiphenyl anion.



The previous results determined by ESR[2)] were reconfirmed, and, in addition, the temperature dependence of the β-proton coupling constant was precisely investigated. With the proposal of a revised model for restricted rotation, the observed temperature dependence was analyzed utilizing Boltzmann statistics, and the energy barrier of restricted rotation was estimated.

The anion radical was prepared by reduction with potassium metal in dimethoxyethane(DME). The ENDOR spectra were recorded by a JEOL type ES-EDX 1 spectrometer, operating with 80 Hz magnetic field modulation. About 150 watts of the continuous radio wave frequency-modulated by 6.5 Khz are running inside of the cavity for NMR excitation.[3)] The ENDOR spectra were measured in the temperature range from -60 °C to -85 °C.

The ENDOR spectra of the 4,4'-diisopropylbiphenyl anion measured at several temperatures revealed excellent resolution of the splittings and the positive temperature dependence of the β-proton coupling constant was clearly recognized as shown in Fig. 1.

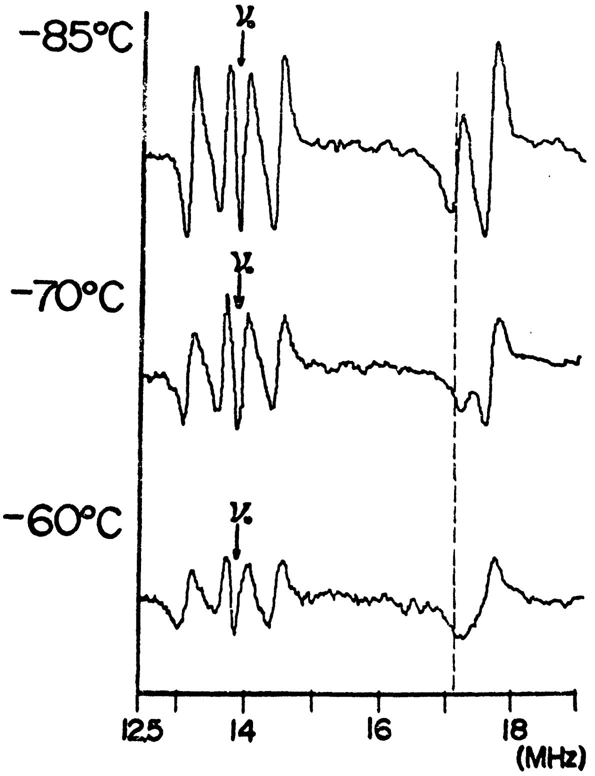


Fig. 1. ENDOR spectra of 4,4'-diisopropylbiphenyl anion.

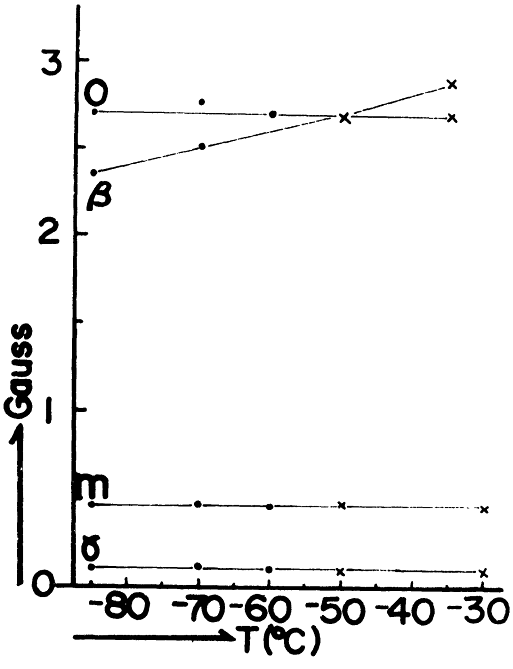


Fig. 2. Plots of the hyperfine coupling constants against temperature. O represents ortho-proton coupling constant; m, meta-proton; β, isopropyl β-proton; γ, isopropyl γ-proton. X, ESR data [2)] ; ●, ENDOR data

The hyperfine coupling constants measured at -85 °C are 2.70, 0.46, 2.35, and 0.10 gauss, which can be assigned to the ortho-, meta-, isopropyl β-, and the isopropyl γ-protons with reference to these values as previously reported by ESR measurements respectively.$^{2)}$ As shown in Fig. 2, the magnitude of the isopropyl β-proton coupling constant increases with the elevation of temperature, but the coupling constants for the ring protons remain constant or show only a minor change.

The β-proton coupling constant a_{β}^{R} of the alkyl groups of this restricted rotation was utilized in the McConnell-Heller expression as follows:

$$a_{\beta}^{R} = Q(\theta)\rho_k = B\rho_k\langle\cos^2\theta\rangle \qquad (1)^{\#}$$

Here, B is the constant, θ represents the dihedral angle and ρ_k is the π-spin density on the atom to which the alkyl group bonded. The value of $B\rho_k/2$ has been obtained from the coupling constant of the methyl $a_{\beta}^{CH_3}$ assuming a free rotation. The experimental value of $\langle\cos^2\theta\rangle$ can be calculated from the ratio $R = a_{\beta}^{R} / a_{\beta}^{CH_3}$. For the 4,4'-diethylbiphenyl anion, the R value was calculated to be 0.70 at -60 °C.$^{2)}$ The average values of $\cos^2\theta$ at various temperatures have been calculated by Boltzmann statistics assuming that the alkyl group is rotating under the restriction of a potential barrier. The value of this potential barrier height, V, has been obtained by the slope of the plot of the observed temperature dependence, these were calculated taking the potential barrier V as the variable parameter.

According to the preliminary studies of the 4,4'-diethylbiphenyl anion,$^{4)}$ the ethyl group can be considered to rotate about the C_p-C_α axis in a simple twofold potential and the potential barrier of the restriction is supposed to be in the order of 1 Kcal/mol. The calculation of the Lennard-Jones repulsion energy between the non-bonded ethyl and the neighboring aromatic protons supported this result and, at the same time, the importance of the interaction between the non-bonded γ-methyl and the ring protons was demonstrated.

In the case of 4,4'-diisopropylbiphenyl anion, the potential function should be modified, because one may consider three kinds of different equilibrium conformations for the isopropyl group as shown in Fig. 3-a. The rotating isopropyl group will have the lowest potential at state (A), the medium value at state (C), and will be in the highest potential at state (B). Thus the appropriate potential function of the isopropyl will show a double minimum as is illustrated in Fig. 3-b.

The simpler equation of $Q(\theta)$ has been used and for a detailed discussion of this reason, see reference 5).

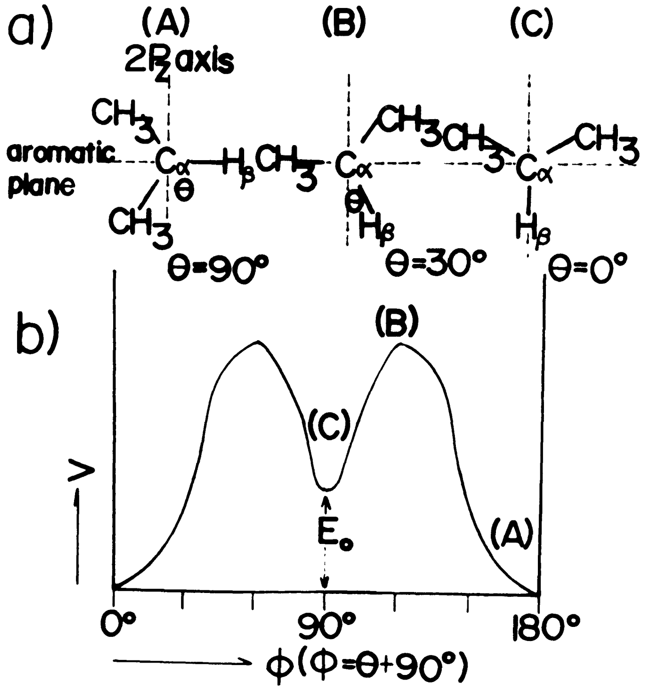


Fig. 3.

a) Various conformations of a rotating isopropyl group.

b) Rotational potential as a function of φ .

V is in arbitary units.

If the isopropyl group prefers to take state (A), the a_β^R / $a_\beta^{CH_3}$ ratio should be smaller than 0.1. On the other hand if state (C) is more likely, the ratio (R=2.0) would be much larger than those of methyl and ethyl group observed in the 4,4'-dimethyl or 4,4'-diethyl biphenyl anion as explained by the theoretical calculation by E. W. Stone et al.$^{5)}$ The experimental value of a_β^R / $a_\beta^{CH_3}$ (0.5) suggests that the observed a_β^R is the averaged value due to the rapid exchange between state (A) and state (C), where the contribution of state (B) will be probably small, since the principal steric repulsion can be expected between the isopropyl methyl and the aromatic ring protons.

According to this model, the potential energy difference, E_0 between states (A) and (C), is calculated from the observed values of a_β^R at various temperatures as follows:

$$a_\beta^R = B\rho k(n_A \cos^2 90^\circ + n_C \cos^2 0^\circ) \qquad (2)$$

$$n_A / n_C = \exp \frac{E_0}{kT} \quad , \quad n_A + n_C = 1 \qquad (3)$$

where the $B\rho k$ is estimated from the methyl proton coupling constant in the 4,4'-dimethylbiphenyl anion, and n_A / n_C denotes the population ratio at states (A) and (C). The population at state (B) was neglected everywhere. E_0 is determined from the

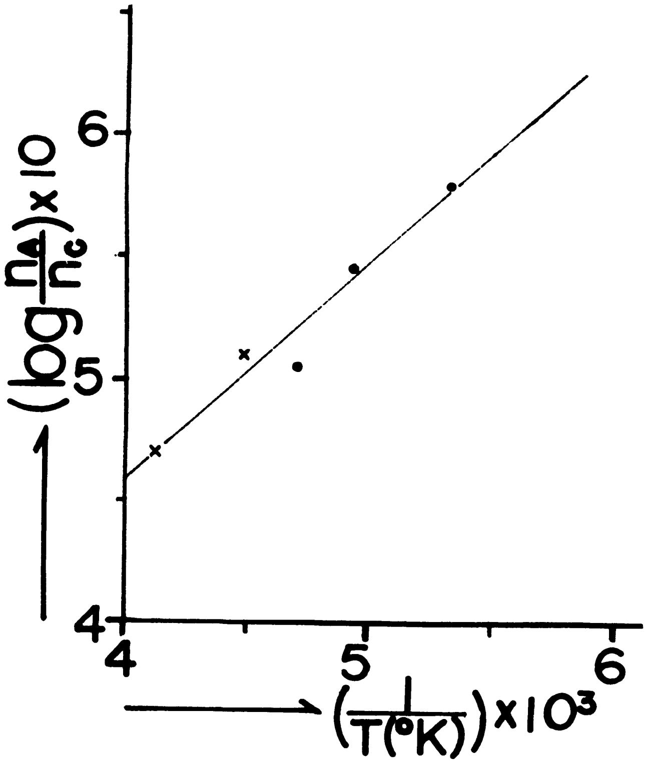


Fig. 4.

Plots of the logarithm of the population ratio as a function of reciprocal temperature.

The line drawn through the points represents the linear least-squares analysis of the data.

X, ESR data2) ; ●, ENDOR data

slope of the linear plot between log n_A/n_C and 1/T as seen in Fig. 4. E_0 thus estimated is about 0.4 Kcal/mol. The average value of $\cos^2\theta$ at -30°C is 0.253 and the average value of dihedral angle θ is calculated to be 60°.2)

In order to improve the present qualitative treatment of the restricted rotation for the isopropyl, more detailed calculations of the potential functions are now under way.

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