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ENDOR Studies on the Hindered Alkylbiphenyl Anion Radicals

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Synopsis. ENDOR observations were carried out for the anion radicals of 2,2′-bitolyl, 2,2′-diethylbiphenyl, and 2,2′-diisopropylbiphenyl. The spin densities obtained from the ring protons at the *ortho*-positions showed a depression in the order of the spherical bulkiness of the substituents, and the degrees of the steric hindrance of the biphenyl ring were estimated based on McLachlan's MO calculation. ENDOR experiments demonstrated that methyl groups undergo free rotation, but it is greatly hindered in each higher alkyl derivative.

Recently, ENDOR tequniques have often been applied to conformational studies of the aromatic free radicals. In particular, the multiple hyperfine components of the complex molecule have been successfully resolved, and the structures of the radicals have been discussed in detail on the basis of the accurate analysis of the spin densities.[1-3] In our previous ESR studies of the 2,2′-dialkylbiphenyl anion radicals, we have proposed that the coplanarity of the biphenyl ring would be enhanced by the delocalization of the unpaired electron and that the free rotation of the higher alkyl groups would be greatly hindered by the steric hindrance caused by the anomalous coplanarity of the biphenyl rings.[4]

In the present communication, we wish to report the ENDOR studies of the anion radicals of several hindered alkylbiphenyls, such as *o,o′*-bitolyl, 2,2′-diethylbiphenyl, and 2,2′-diisopropylbiphenyl. The validity of the ring-proton splittings assumed by ESR measurements was reconfirmed. In addition, the present ENDOR observations offered new experimental evidence to support the fact that the rotation of the ethyl and isopropyl groups at the *ortho*-position is nearly locked, while the methyl group of *o,o′*-bitolyl undergoes free rotation.

Experimental

The alkylbiphenyls used in this experiment were synthesized in the manner described in a previous paper.[5] The anion radicals were prepared by reduction with potassium metal in dimethoxyethane (DME) at the temperature of dry ice and aceton. The ENDOR spectra were recorded by a JEOL-type ES-EDX-1 spectrometer under operating conditions similar to those described elsewhere.[6] The ESR intensity began to saturate at a microwave output of about 2 mw on the dial scale of a JES-ME-3 ESR spectrometer, and the ENDOR spectra were successfully recorded in the temperature range from −65 to −85 °C.

Results and Discussion

Figure 1 shows the ENDOR spectra of the biphenyl (a), *o,o′*-bitolyl (b), 2,2′-diethylbiphenyl (c), and 2,2′-diisopropylbiphenyl (d) anion radicals. The ENDOR spectrum of the *o,o′*-bitolyl anion radical can be easily analyzed in terms of absorptions due to the *meta*-ring (14.21, 14.55 MHz), the *ortho*-ring and methyl (17.04 MHz) and the *para*-ring protons (21.26 MHz), in comparison with the ring-proton absorption of the biphenyl anion radical (*meta*: 14.37, *ortho*: 17.58 and *para*: 21.34 MHz). In the previous ESR studies of the 2,2′-diethylbiphenyl anion radical, we assumed that the methylene protons of the ethyl group reveal an equivalent splitting.[7] The ENDOR spectrum of the 2,2′-diethylbiphenyl anion radical (Fig. 1-(c)) was, however, clearly resolved into two kinds of different absorptions due to non-equivalent β-ethyl protons at 15.48 and 17.16 MHz.

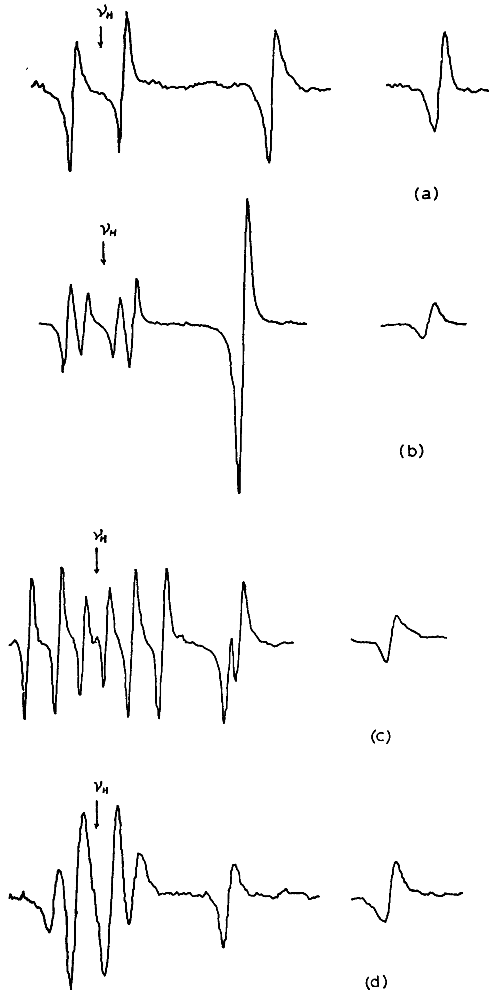

Fig. 1. The higher frequency half of the ENDOR spectra recorded at −85 °C.
(a) biphenyl, (b) *o,o′*-bitolyl, (c) 2,2′-diethylbiphenyl (d) 2,2′-diisopropylbiphenyl, ν_H: free proton frequency

Table 1. Coupling constants of the hindered dialkylbiphenyls (G)

Position	2	3	4	5	6
Biphenyl	2.66	0.38	5.34	0.38	2.66
o,o'-Bitolyl	2.27	0.26	5.21	0.51	2.27
2,2'-Diethyl	2.29 1.07	0.19	5.20	0.59	2.11
2,2'-Diisopropyl	0.28	0.28	5.16	0.57	1.96

It is important to note here that each of the absorption frequencies of the ring protons (*meta*: 14.18, 15.40, *ortho*: 16.90 and *para*: 21.15 MHz) is nearly comparable with that of the *o,o'*-bitolyl anion radical. A similar conformational dependence of the spin-density distribution can be seen in 2,2'-diisopropylbiphenyl, but the splitting of the isopropyl-β-proton is greatly reduced and its absorption overlaps with one of the *meta* proton absorptions (14.25 MHz) in the vicinity of the free-proton frequency. The proton-coupling constants of the 2,2'-dialkylbiphenyls are summarized in Table 1. It is interesting that the experimental spin densities decrease with the order of the spherical bulkiness of the substituents.

This probably means that the higher alkyl groups bring a larger steric hindrance into the biphenyl ring than that in the methyl derivative. A quantitative estimation of the twisting angle (θ) of the phenyl rings for the higher alkyl derivatives needs elaborate MO calculations, and the hyperconjugative effect of the higher alkyl groups should be rigorously taken into account.

In a qualitative approach, however, the θ-values for higher alkyl derivatives can be estimated using the results calculated for the methyl derivative, since a perturbation of the ring-spin density due to the hyperconjugation of the higher alkyls is usually small. As is shown in Fig. 2, the θ-values of the ethyl and the isopropyl derivatives would be in the range from 40 ° to 50 °.

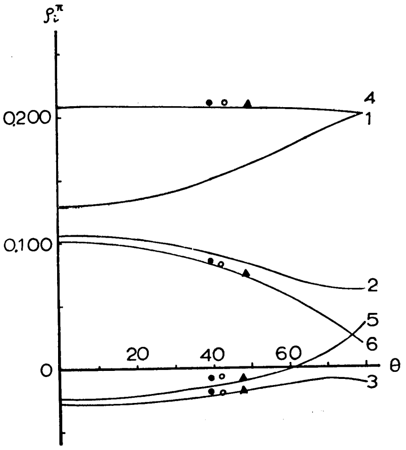

Fig. 2. Dependence of theoretical spin density of ring carbon atoms on twisting angle θ between the phenyl ring in 2,2'-bitolyl anion radical. Experimental values are shown in the figure using the following notation. ●···: *o,o'*-bitolyl, ○···: 2,2'-diethylbiphenyl, ▲···: 2, 2'-diisopropylbiphenyl
Twisting angles θ of the higher alkyl derivatives were tentatively estimated based on the figure calculated for bitolyl anion radical. The Coulson and Crawford's parameters of the hyperconjugation were used in the calculation of the methyl group.[10]

In the previous paper, we proposed that the rotation of the higher alkyl groups at the *ortho*-positions may be seriously hindered and that the alkyl groups behave as torsional oscillators rather than as free rotators.[7] According to the present ENDOR experiments, this is indeed true; the *ortho*-methyl proton splitting in *o,o'*-bitolyl was found to be equivalent, while the methylene protons of the ethyl group exhibited non-equivalent splittings. Futhermore, the methine proton of the isopropyl group revealed an exceptionally small value.

The dihedral angles of the ethyl methylene-protons at the equilibrium conformation were calculated to be $\varphi_1=54$ ° and $\varphi_2=66$ ° respectively, using the McConnell-Heller equation[8] with $B_0\approx O$; that is, $A^H=[B_0+B_2\langle\cos^2\varphi\rangle]\rho_i^\pi\approx B_2\langle\cos^2\varphi\rangle\rho_i^\pi$ (1), where $B_2=50$ G.

The ρ_2^π (0.0908) of *o,o'*-bitolyl, estimated from Equation (1), is in excellent agreement with the theoretical value, 0.0913 ($\theta=40$ °), predicted by the MO calculation based on the free rotation of the methyl group, that is, $\langle\cos^2\varphi\rangle=1/2$.

In the case of the ethyl derivative, however, the $\rho_2^\pi\cdot$(exp) value, 0.129, obtained from Equation (1) using $\varphi_1=54$ ° and $\varphi_2=66$ ° is considerably larger than the theoretical value (0.0913). Recently, the importance of the B_0 term contributing to the β-proton splitting of the higher alkyls has been demonstrated by an ENDOR study of the *p,p',p''*-triisopropyl trityl radical.[9] The discrepancy in the experimental values between the methyl and the ethyl derivatives is probably attributable to the neglect of the B_0-term.

If $B_0/B_2=+0.06$ is tentatively assumed, the following values of ρ_2^π, which seem to be more reliable, are obtained: $\rho_2^\pi(\text{methyl})=0.081$ and $\rho_2^\pi(\text{ethyl})=0.094$.

The large diminution in the isopropyl methine-proton splitting also indicates a tight lock of the rotation of the alkyl group. The dihedral angles of the methine proton with the twisting angle of $\theta=50$ ° ($\rho_2^\pi=0.0822$) are calculated to be 89 °, assuming the B_0/B_2 ratio to be $+0.06$. This means that the isopropyl methine-proton is fixed in a position close to one of the aromatic planes of the twisted biphenyl.

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