CHEMISTRY LETTERS, pp. 267-268, 1972. Published by the Chemical Society of Japan

EXCEPTIONAL HINDERED INTERNAL ROTATION OF THE ALKYL GROUP IN THE 4,4'-DI-N-PROPYL BIPHENYL ANION

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The ESR spectra of the 4,4'-di-n-propyl biphenyl anion have been observed in either DME or DMF with reduction by potassium. The experimental evidence suggests that an anomalous restricted rotation of the alkyl group takes place in the 4,4'-di-n-propyl biphenyl anion, where the alkyl-β-protons exhibit the nonequivalent splittings in a solution.

Based on the ESR observation, the evidence of an internal restricted rotation of the alkyl groups has now been widely established and the temperature dependence of the alkyl-β-proton splitting has been well understood in terms of the $\cos^2\theta$ rule as is discussed by Stone and Maki[1]. In these studies, the hyperfine coupling constants of each alkyl-β-proton have an equal value and show a slight amount of temperature dependence[2-6].

We report here the experimental evidence of the fact that an anomalous restricted rotation of the alkyl group takes place in the 4,4'-di-n-propyl biphenyl anion, where the alkyl-β-protons exhibit the nonequivalent splittings.

A purity of the material was qualified by UV and NMR. The physical constants of the compound are listed below[8].

MP, 60-61°C ; UV(Hexane)λ_{max}mμ(ε) , 257(20700) ; (Found : C,89.61 ; H,9.42%)

The radical anion was produced with potassium metal in dimethyl cellosolve(DME) and N,N-dimethyl formanide(DMF). The experimental procedures were described in the proceeding paper[7].

In Fig.1a, we show the ESR spectrum of the 4,4'-di-n-propyl biphenyl anion measured at -50°C. The hyperfine coupling constants of the ring-ortho and ring-meta protons were easily determined in the manner as described before[6].

The smallest splitting (160mG) can not be ascribed to alkali metal splitting but to γ-proton splitting of the alkyl groups. The hyperfine structures are identical with that shown in Fig.1a, even though the ion-pair formation is suppressed using DMF as the solvent. In order to fully understand the observed spectrum, we assume that a normal quintet splitting of the four β-protons of the alkyl groups falls apart into two sets of triplet splittings. The computor simulated spectrum given in Fig.1b is in excellent accordance with the observed spectrum using the following hyperfine coupling constants;

$$a_4^{\beta_1}=3.62\ ,\quad a_4^{\beta_2}=3.15\ ,\quad a_4^{\gamma}=0.16\ ,\quad a_2^{H}=2.68 \text{ and } a_3^{H}=0.48 \text{ Gauss}$$

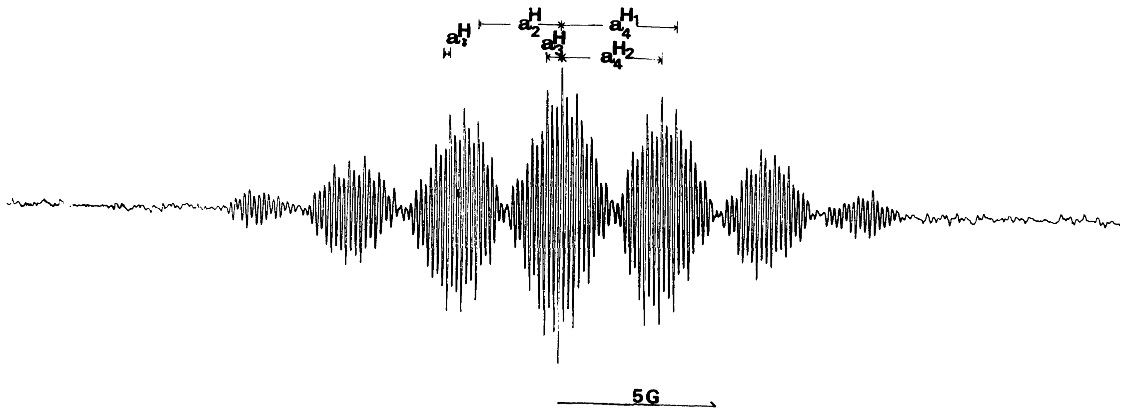

Fig.1a Observed ESR spectrum of the 4,4'-di-n-propyl biphenyl anion, produced with potassium in DME, at -50°C.

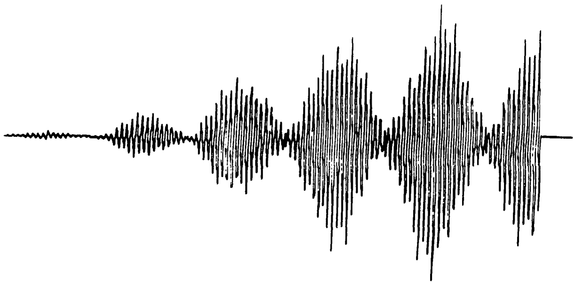

Fig.1b A part of computor simulated spectrum.

When temperature is raised to +20°C, the spectrum begins to show the line width variation which may be attributed to the time dependent alternation of the equilibrium positions of the rotating alkyl-β-protons. A lower limit of the lifetime is thus estimated to be the order of 10^{-7} sec for the alkyl-β-protons which occupy in the two sites of the rotational potential minima. Our investigation of n-butyl, n-amyl and n-hexyl derivatives is continuing and the hyperfine structures are consistently explainable with assumption of the two distinct values for the alkyl-β-proton coupling constants. The γ-proton splitting is observed only for the case of n-propyl and it has never been recognized for another n-alkylated biphenyl. In the case of the other aromatic systems only the ethly-γ-proton splitting has been usually detected.[2-6]

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(Received January 5, 1972)