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ESR ^{13}C Hyperfine Structures of the Meta-substituted *t*-Butyl Biphenyl Anion Radical*[1]

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The ESR observation of the ^{13}C hyperfine structure has never been established for biphenyl anion radicals, because the weaker ^{13}C hyperfine structures were incidentally smeared out by superimposed ring proton hyperfine splittings, particularly those due to the meta-protons.

In the present studies, all of the meta positions were substituted by *t*-butyl groups and we attempted to reduce the superposition of the proton hyperfine structures; that is, the 3,3′,5,5′-tetra-*t*-butyl biphenyl was synthesized and the ESR ^{13}C hyperfine splittings were tentatively studies for the anion radical of this alkylated biphenyl.

Experimental

The synthesis of the 3,3′,5,5′-tetra-*t*-butyl biphenyl has not been described in the literature, however, the material was obtained from the Grignard reagent of the 3,5-di-*t*-butyl bromobenzene[1] prepared in an anhydrous tetrahydrofuran (THF) by following the process of Kharasch and Fields.[2] A pure material recrystallized from ethyl alcohol melted at 172.8—173.3°C. Found: C, 88.62; H, 11.17%. Calcd: C, 88.82; H, 11.18%. IR absorption in KBr. γ (=CH); 837 cm^{-1}, δ' (ring); 720 cm^{-1}. UV absorption in *n*-hexane. $\lambda_{\max}$; 253 mμ ; ε ; 17300 M^{-1} cm^{-1}.

The anion radicals were prepared in a solution of THF by reduction with lithium. The ESR spectra were recorded at room temperature.

Results and Discussion

The proton hyperfine structures shown in Fig. 1, consist of only nine lines, and a_2^H and a_4^H were determined to be $a_2^H=-2.59$ and $a_4^H=-5.14$ gauss respectively, which are closed to those for the biphenyl anion radical. Both $\rho_2^\pi=0.100$ and $\rho_4^\pi=0.218$ were calculated using Colpa-Bolton's equation: for an anion radical, $a_i^H=Q^H_{CH}(0)\rho_i^\pi-K^H_{CH}[\rho_i^\pi]^2$, $Q^H_{CH}(0)=-27$, and $K^H_{CH}=-12$ gauss.[3] As is designated by the figures (1)—(4) in the lower part of Fig. 2, ^{13}C hyperfine splittings are observed as the doublet lines of (1) 0.90, (2) 1.98, (3) 4.34, and (4) 8.20 gauss, and the intensity ratios are (1) : (2) : (3): (4)=1 : 2 : 2 : 1. These intensity ratios distinguished either a_1^C or a_4^C from a_2^C and a_3^C. The a_4^C is assumed to be (4) 8.20 gauss, since the contribution of the spin-polarization is negligible as a result of the small value of ρ_3^π, thus, its magnitude depends substantially on the large spin density of ρ_4^π.

Following the method of Karplus-Fraenkel,[4] the a_i^C values have been calculated by the following equation:

$$a_i^C = (S^C+\sum_{i=1}^{3} Q^C_{C_iX_k})\rho_i^\pi+\sum_{i=1}^{3} Q^C_{X_kC_i}\rho_k^\pi$$

where $S^C=-12.7$ is the contribution from the 1s electron of C_i, $Q^C_{C_iX_k}$($Q^C_{C_iH}=19.5$, $Q^C_{C_iC_k}=14.4$), the $\sigma-\pi$ interaction parameter produced by ρ_i^π on the C_i atom, and where $Q^C_{C_kC_i}=-13.9$ represents a polarization from the neighboring atom, C_k. By substituting the values of a_4^C and ρ_4^π into the equation, $\rho_3^\pi=-0.016$ was primarily determined. In the same manner, $\rho_1^\pi=0.113$ can be derived from $\rho_2^\pi=0.100$ and $a_1^C=-0.90$. Here, the negative value is assigned for for a_1^C, for the normalization of the spin density,

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*[1] This work was presented at 8th ESR Symposium of the Chemical Society of Japan, Hiroshima, November 15th, 1969.

[1] P. D. Bartlett, M. Roha and R. M. Stiles, *J. Amer. Chem. Soc.*, **76**, 2349 (1954).

[2] M. S. Kharasch and E. K. Fields, *ibid.*, **63**, 2316 (1941).

[3] J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

[4] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

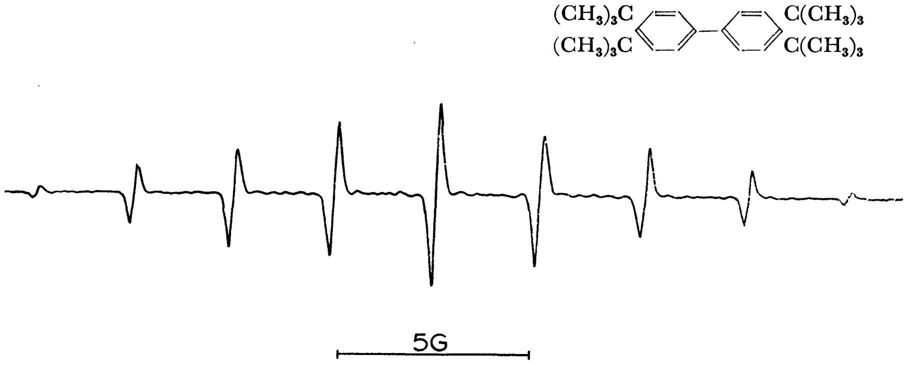

Fig. 1. Proton hyperfine structures of 3,3′,5,5′-tetra-*t*-butyl biphenyl anion radical.

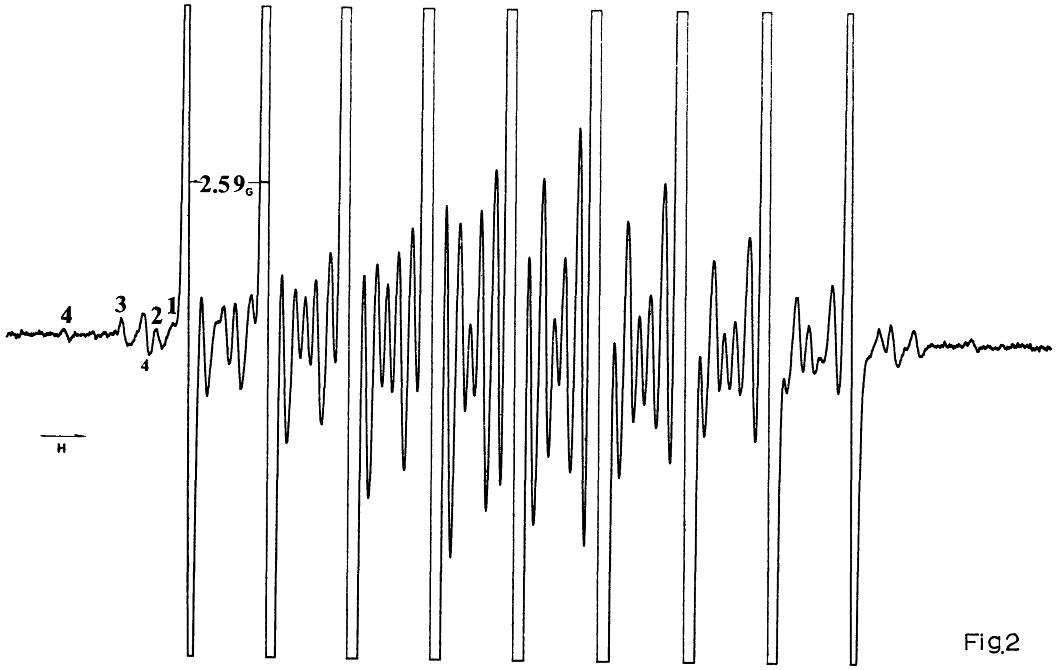

Fig.2

Fig. 2. ^{13}C hyperfine structures of 3,3′,5,5′-tetra-*t*-butyl biphenyl anion radical.

TABLE 1. EXPERIMENTAL AND THEORETICAL VALUES OF THE ^{13}C COUPLING CONSTANT AND THE SPIN DENSITY

Position		1	2	3	4
a_i^C (gauss)	(Exp)	−0.90	1.98	−4.34	8.20
	(Calcd)[a]	−0.95	2.53	−4.83	7.02
ρ_i^π	(Exp)	0.113	0.100	−0.016	0.218
	(Calcd)	0.134	0.114	−0.020	0.182

a) Theoretical values of a_i^C were calculated based on the McLachlan's spin density.

$\sum\rho_i^\pi=1$, cannot be held if the positive value is assumed. Finally, we proved that the observed values of both a_2^C and a_3^C are consistently explainable with the present ρ_i^π value and that a_3^C also has a negative value; that is, a_2^C: Obsd 1.98, Calcd 2.21 gauss, a_3^C: Obs. −4.34, Calcd.[*2] −4.98 gauss.

[*2] $a_3^C=(S^C+2Q_{C-C(CH_3)_3}^C)\rho_3^\pi+Q_{C_iC_3}^C(\rho_2^\pi+\rho_3^\pi)$
The spin density on the *t*-butyl group was neglected and $Q_{C-C(CH_3)_3}^C \doteqdot Q_{C-CH_3}^C=16.3$ gauss[5] was assumed.

5) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).

McLachlan's MO calculation was carried out taking the Coulomb integral of the meta-position to be $\alpha_3=\alpha-0.15\beta$; the results are summarized in Table 1. A good agreement can be obtained between the observed ^{13}C hyperfine coupling constant and their theoretical values. The ^{13}C coupling constants for the biphenyl anion radical would also be similar to those established by the present work, since it has been shown that an alkyl substitution always causes only a minor perturbation in the spin density.6)

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6) K. Ishizu, K. Mukai, H. Hasegawa, K. Kubo, H. Nishiguchi and Y. Deguchi, This Bulletin, **42**, 2808 (1969).