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A HINDERED ROTATION OF THE SUBSTITUENTS IN SOME PHENOXYL RADICAL AS STUDIED BY ENDOR

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The ENDOR spectrum of bis-(3,5-di-t-butyl phenoxyl)-methyl was observed from -80°C to -20°C. The hyperfine coupling constants of both the ring and the t-butyl protons were precisely measured, and the saturation behavior of these ENDOR absorption was investigated. The temperature dependence of the hyperfine coupling constants was studied and the evidences of a restricted rotation of both phenoxyl and t-butyl groups were demonstrated in this radical.

The technique of the Electron Nuclear Double Resonance (ENDOR) has now been widely applied to the studies of numerous phenoxyl radicals in solutions.[1)2)] In the present communication, we wish to report the experimental evidences that a restricted rotation of both phenoxyl and t-butyl groups takes place in the case of the phenyl derivative (PGLV) of the well known Galvinoxyl radical (GLV). The radical was prepared by oxidation of bis-(3,5-di-t-butyl-4-phenoxyl) phenyl methane (m.p.: 166.2 ∿ 166.8°C) with an excess of lead dioxide in n-Heptane. We show the ENDOR spectrum of GLV radical in Fig. 1(a), and that of PGLV radical in Fig. 1(b). The two sets of outermost ENDOR lines shown in Fig. 1(b) are easily assigned to the meta ring protons of phenoxyl group taking into accounts of their ESR hyperfine coupling constants (a = 1.3 G).[3)] From the present ENDOR studies, however, one will see that the four meta ring protons are no longer equivalent and give at least two kinds of different splitting;

$$a^1_{ring} = 1.363 \text{ G}, \quad a^2_{ring} = 1.282 \text{ G}$$

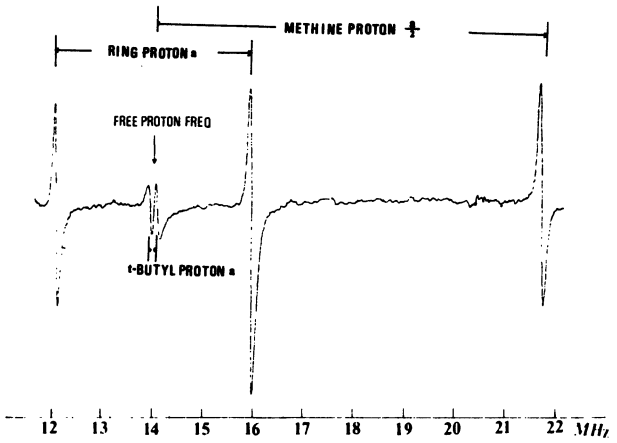

Fig. 1 (a)
The ENDOR spectrum of the Galvinoxy radical: at -80°C.

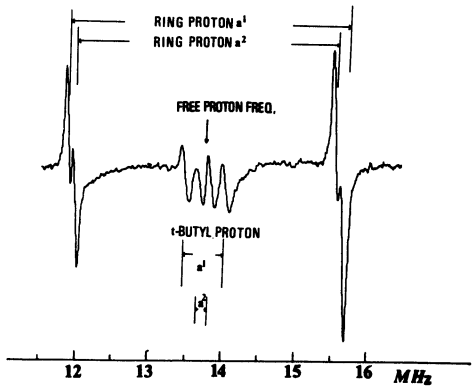

Fig. 1 (b)
The ENDOR spectrum of the phenoxyl derivative (PGLV): at -80°C.

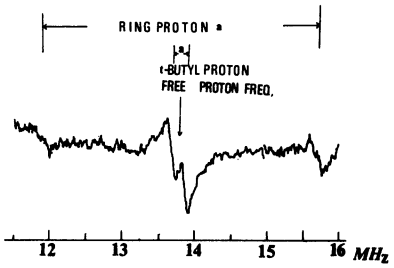

Fig. 1 (c)
The ENDOR spectrum of the phenoxyl derivative (PGLV): at -20°C.

As is seen in Fig. 1 (b), the ENDOR absorption of the t-butyl protons of the GLV radical arises neighboring to the free proton frequency and appears as the simple doublet line ($a_{t\text{-butyl}}$ = 0.047G). In the case of the present derivative, the t-butyl protons clearly give the two different sets of doublet splitting ($a^{1}_{t\text{-butyl}}$ = 0.204G) ($a^{2}_{t\text{-butyl}}$ = 0.053G). As the observed temperature is elevated, however, the outer set of the t-butyl absorption starts to broad, at the same time, the

resolved lines of the phenoxyl ring protons also collapses into the single absorption as is shown in Fig. 1(c).

In order to put the present results on the more fixed experimental base, the saturation behavior of each absorption lines in Fig. 1(b) was investigated as is shown in Fig. 2. We confirmed that the saturation factors of the ENDOR lines of each ring and t-butyl proton are almost comparable with those for GLV radical everywhere. Based on the present investigations, it will be concluded that a free rotation of both the phenoxyl and the t-butyl groups could be restricted by the substitution of phenyl group into the central methine proton of the GLV radical. This will be probably due to the result that the substituted phenyl group brings the steric hindrance into the phenoxyl group and the phenyl groups are twisted out in the same manner as is proposed for the tri phenyl methyl radical. [4)]

Thus, each group is estimated to rotate at a rate greater than 2×10^5 times per second at -20°C and more slowly at -80°C.

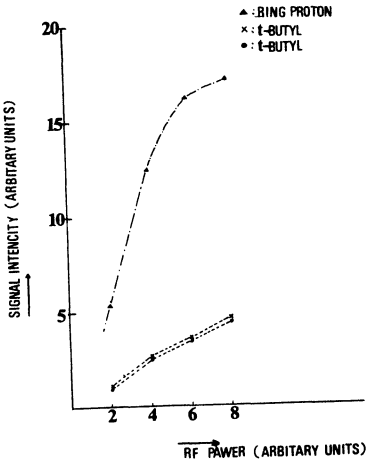

Fig. 2
The saturation behavior of ENDOR spectrum of phenoxyl derivative (PGLV)

Literature

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