

ESR Studies of Stable Free Radicals : 2,2,6,6-Tetramethyl-4-Hydroxypiperidine-1- Oxyl-4-Derivatives (II)

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The ESR absorption spectra of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl-4-derivatives have been observed at room temperature. The substitution at 4-position have not evidently affected to the hyperfine interaction.

Organic stable free radicals such as 2,2,5,5-tetramethylpyrrolidine-1-oxyl (Fig. 1-a) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TADIN) (Fig. 1-b) have already studied by many investigators with use of the ESR or magnetic susceptibility technique.¹⁻³⁾ The ESR absorption spectra of TADIN derivatives have been observed by Rassat *et al.*¹⁾ Kreilick²⁾ has observed not only the normal 3 hyperfine lines arising from ¹⁴N but also 7 to 13 lines from the protons. The observation of these hyperfine structure of protons will result in the evidence of direct interaction of an unpaired electron on the NO group with the protons, because these compounds have no π system except the NO group. However, in the ESR absorption spectra of these series, they have obtained a lower resolved spectrum of 2,2,6,6-tetramethyl-4-ketopiperidine-1-oxyl (TAAO) (Fig. 1-c) compared with those of 4-substituted TADIN derivatives.

We might expect that the 4-substituted groups would affect the hyperfine coupling constants of ¹⁴N and protons. Only two of the 4-substituted derivatives, *i.e.* methyl

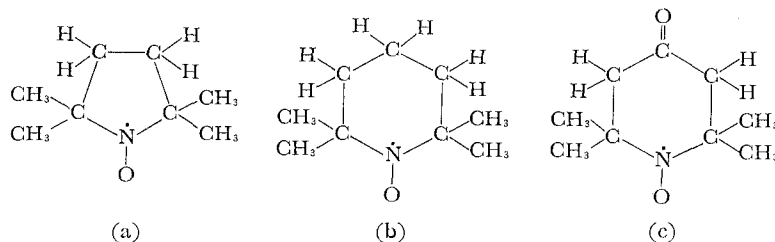


Fig. 1.

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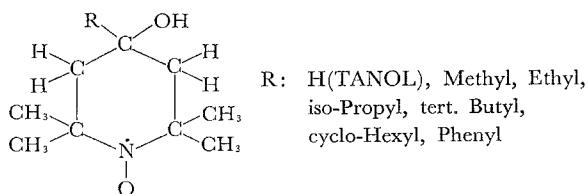


Fig. 2.

and ethyl derivatives of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (TANOL) (Fig. 2) have been studied by Rassat *et al.*¹⁾ and Rozantsev *et al.*⁴⁾

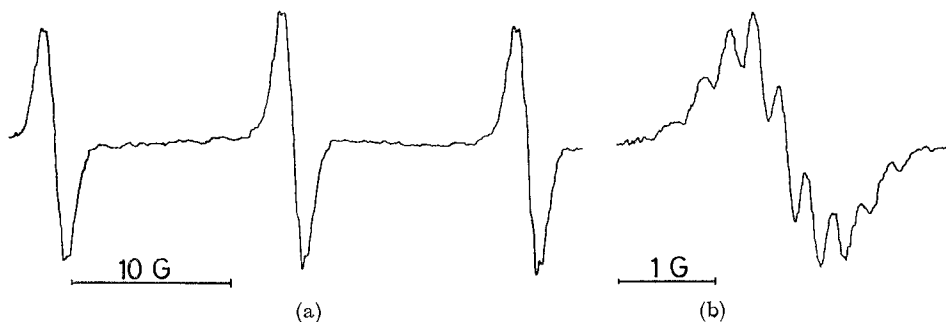
In their ESR absorption spectra the proton hyperfine lines have been observed only in TANOL. In the present paper we report ESR absorption spectra of 4-substituted TANOL derivatives in order to clarify the effect of 4-substituted groups on the hyperfine coupling constants of ^{14}N and protons. Furthermore, as we have observed an anomalous line alternation in the ESR absorption spectra of TAAO and methyl-TANOL, we should like to discuss the mechanism of this phenomena.

Preparation of the samples was previously reported in this bulletin.⁵⁾ In case of the observation of the ESR absorption spectra the solvent was well purified, dehydrated and degassed by the ordinary method.⁶⁾ An aqueous solution of peroxyamine disulfonate was used as a standard for the magnetic field. All the ESR absorption spectra were observed with ME-3X type spectrometer of Japan Electron Optics Laboratory Co., Ltd., equipped with 100 KHz field modulation.

We have observed the similar ESR absorption spectra in all TANOL derivatives and one of them shown in Fig. 3.

The triplet splitting in Fig. 3-a arises from a nitrogen nuclear spin ($I=1$).

Therefore the hyperfine components in Fig. 3-b can be attributed to the hyperfine interaction of protons. Taking into account the molecular framework in Fig. 2, one can easily estimate that the nine lines are due to hyperfine interaction of 12 methyl



- (a) The ESR absorption spectrum of Ethyl-TANOL in THF solution at room temperature under low resolution.
(b) One of the three ^{14}N lines under high resolution.

Fig. 3.

Table I. Hyperfine Coupling Constants of ^{14}N (A_{N}) and Protons* (A_{H}) for TANOL and its Derivatives. (in gauss)

Sample	A_{N}	A_{H}
TANOL	15.5	0.43
Methyl-TANOL	15.1	0.38
Ethyl-TANOL	15.1	0.34
iso-Propyl-TANOL	15.3	0.41
tert. Butyl-TANOL	15.2	0.42
cyclo-Hexyl-TANOL	15.2	0.41
Phenyl-TANOL	15.2	0.41

* methyl protons

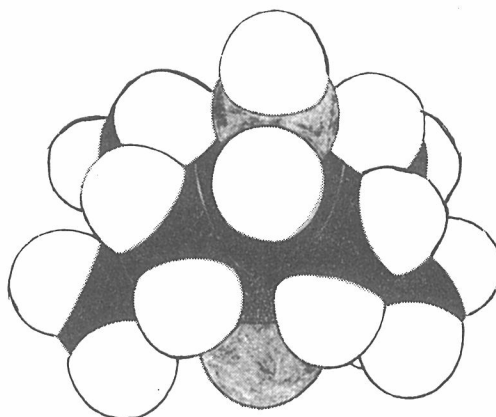


Fig. 4. Stereomodel of TANOL

protons; possible line intensities are 1 : 12 : 16 : 220 : 495 : 792 : 924 : 792 : 495 : 220 : 66 : 12 : 1. The coupling constants obtained in tetrahydrofuran (THF) solution are summarized in Table I.

As seen from Table I, 4-substituted groups of TANOL derivatives have little influence on the ^{14}N and proton's hyperfine coupling constants and play no important role in the spin density distribution. Namely, an unpaired electron is almost localized on the NO group masked by the four methyl groups (Fig. 4), which may cause large stability of these radicals. Thus, we have concluded that the ESR absorption spectra of both hyperfine coupling constants of ^{14}N and of protons were not affected by 4-substituted groups.

On the other hand, we have observed an interesting temperature dependence of ESR absorption spectra on crude TAAO and methyl-TANOL, which are shown in Fig. 5.

The spectrum at low temperature which suggests an existence of two radical species coalesces into simple three lines at room temperature. These line shape variation lead to some chemical exchange phenomena occurred sometimes in solution.

We presume this phenomenon, on the one hand, that there are the exchange of

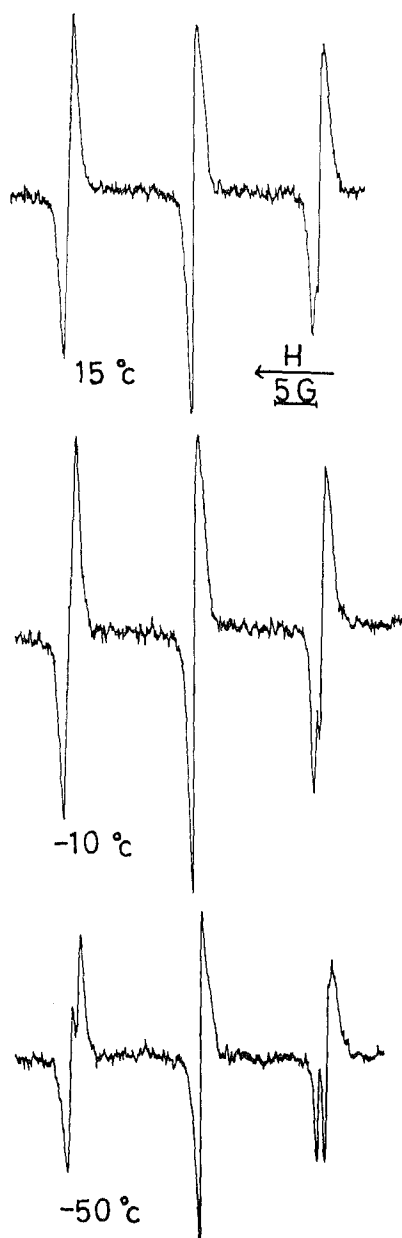


Fig. 5. Typical ESR absorption spectra of methyl-TANOL in THF.

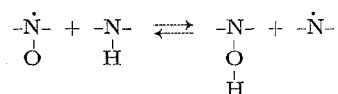


Fig. 6.

molecular frameworks between boat-form and chair-form. On the other hand, equilibrium of two different species such as an aminoxyl radical and an amino radical (Fig. 6) exist.

We are now investigating these mechanism in more detail. These results will be published elsewhere.

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