The ENDOR Spectrum of 1,7,7-Trimethylbicyclo[2.2.1]heptane-2,3-dione Semiquinone in Solution

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Synopsis. The ENDOR spectra of 1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-dione semiquinone (camphorsemiquinone anion) showed a sharp temperature variation in the intensity of each ENDOR line. The relationship between the optimum temperature for the ENDOR enhancement and the relaxation mechanisms was discussed on the basis of the experimental results.

Sharp variations with the temperature in the relative intensities of ENDOR signals have been a problem of much interest in connection with the discussion of the relaxation mechanism[1–4] and finding the optimum conditions for ENDOR experiments[3] in solution. Generally, the nuclear relaxation due to the electron-nuclear dipolar (END) interaction[2] and the flip-flop transition due to the modulation of isotropic hyperfine interaction[4] are known to be effective for ENDOR enhancement in solution. The camphorquinone anion has a rigid structure, as is shown in Fig. 1; therefore, the hyperfine interaction can hardly be expected to be modulated by the internal motions of the molecule.[4] Moreover, an unpaired electron delocalizes in the O–C–C–O moiety, and the END interaction is estimated to be small because β, γ, and δ-protons are distant from the unpaired electron. Thus, it seemed it would be interesting to observe the ENDOR of this anion and discuss the mechanisms of ENDOR.

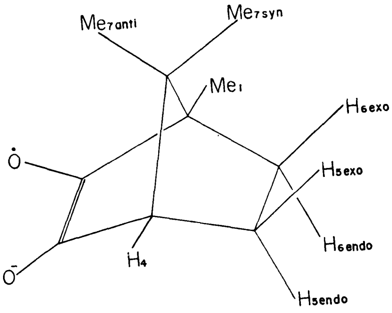

Fig. 1. The molecular structure of camphorquinone.

1,7,7-Trimethylbicyclo[2.2.1]heptane-2,3-dione (camphorquinone) was reduced with sodium (or potassium)-isopropoxide in isopropyl alcohol, which had been dehydrated by refluxing with calcium hydride, and then transferred to a sample tube by vacuum distillation. Samples were diluted until the effect of the Heisenberg spin exchange or intermolecular dipolar interaction on the ESR spectrum became negligible. For ENDOR observation, the magnetic field was fixed at an intense peak of the high-field side, as is indicated in Fig. 2.

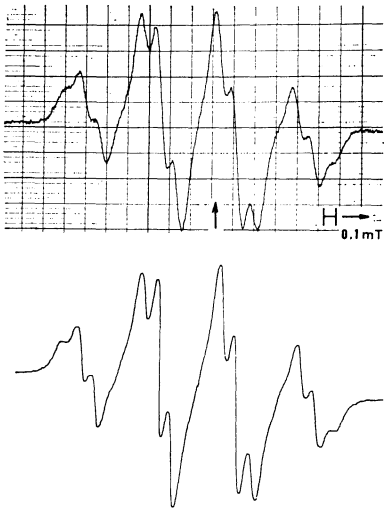

Fig. 2. ESR spectrum of camphorquinone anion in isopropyl alcohol. Upper, experimental spectrum; lower, spectrum simulation using A_{iso}'s given in Table 1.

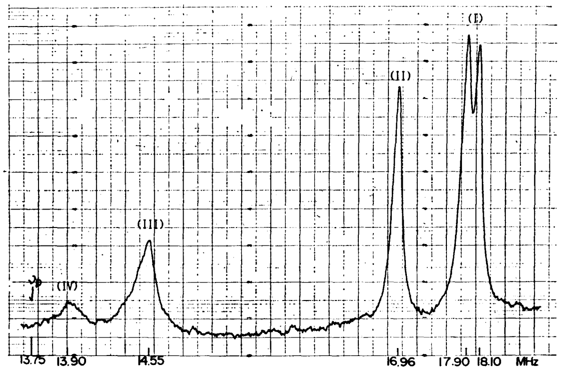

Fig. 3. ENDOR spectrum of camphorquinone anion in isopropyl alcohol at −40 °C.

The ENDOR spectrum at frequencies higher than that of the free proton frequency (ν_p=13.75 MHz) is shown in Fig. 3, where the ENDOR lines are numbered from I through IV from the high-frequency side. The doublet at 18 MHz showed a tendency to enlarge the incision as the microwave power decreased. This doublet may result from two hyperfine interactions of a similar, but slightly different magnitude; it is not caused by the coherence effect because of the absence of any change in the splitting on a decrease in the rf power.

For a series of compounds with a molecular frame similar to camphorquinone, by the varying substituents, the ESR spectra were analysed in detail by Russell.[5] In the ENDOR spectrum of camphorquinone, a slight

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Table 1. The values of A_{iso} and A_{aniso}

Proton	A_{iso}/mT	$A_{aniso}{}^{a)}$/mT
H_{exo}	0.309 0.297	0.03
H_{endo}	0.015	0.14
H_4	0.23	0.22
$Me_{7\,syn}$	0.058	—
$Me_{7\,anti}$	0.015	—

a) The largest value among the anisotropic hyperfine coupling constants.

difference in the hyperfine splittings for two *exo*-protons, which had been assumed by Russell to be equivalent, came to light (see Table 1). This difference may be due to the slight asymmetry of the structure of this ion. The broadening of the ENDOR lines, (III) and (IV), seems to show an overlap of ENDOR lines for the protons with slightly different hyperfine splitting constants from each other, but no further resolution could be obtained.

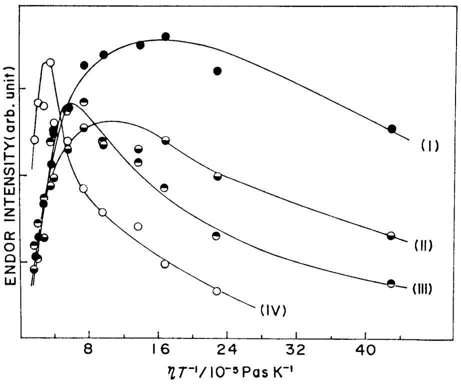

Fig. 4. Dependence of ENDOR intensity on η/T in isopropyl alcohol.
(I) *exo*-protons, (II) proton at 4 position, (III) *syn*-protonin the methyl group at 7 position, (IV) *endo*-protons (also *anti*-proton in the methyl group at 7 position).

For each peak of the ENDOR spectrum, the dependency of the intensity on η/T, where η is the viscosity coefficient of the solvent, was examined, and the optimum temperature where ENDOR enhancement reaches its maximum was obtained (Fig. 4). According to the assignment with the values of A_{iso}, which give adequate ESR simulation, it was presumed that the (I)—(IV) ENDOR lines correspond to H_{exo}, H_4, $Me_{7\,syn}$, and H_{endo} (also $Me_{7\,anti}$) protons respectively.

The END term and isotropic term for each proton are given in Table 1. The isotropic term was determined from the ESR spectrum simulation and then confirmed more minutely by ENDOR. The END term was estimated by the theory of McConnell and Strathdee,[6] using the unpaired electron density calculated by the HMO method.

When the END mechanism dominates for α protons on the aromatic ring, it has been found that the proton with the larger END term shows a maximum ENDOR intensity at a lower value of η/T than the proton with the smaller END term.[3] In the present system, the same relationship was found on H_{exo}'s and H_4 protons, but not on H_{endo} and H_4 protons. As the reason for this discrepancy, it was postulated that the $Me_{7\,anti}$ proton has an A_{iso} value very close to those for $H_{5\,endo}$ and $H_{6\,endo}$; thus, the multiplicity of the electron-spin state increases and the optimum temperatures of the H_{endo}'s shift to higher values.[7]

The anisotropic interaction of the $Me_{7\,anti}$ protons with an unpaired electron may be supposed to be fairly large when these methyl protons move to the vicinity of the π-conjugate system in the semiquinone anion in the course of the internal rotation of the methyl group. Then, the relaxation of the nuclear spins of the methyl protons may be greatly accelerated by the modulation of the anisotropic interaction due to the molecular motion or internal motions of the methyl group. This possibility, however, is not supported at the present stage of experiments, for no clear difference in the relaxation behavior has been found between the $Me_{7\,anti}$ protons and the $Me_{7\,syn}$ protons, which have a much smaller anisotropic interaction. This is probably due to the shorter correlation times of the motions induced by the Brownian motion of the solvent molecules.

In the $H_{5\,exo}$, $H_{6\,exo}$, and H_4 protons, a smaller difference was found between the optimum temperatures for the H_{exo}'s and H_4 than would be expected from the difference between their END terms; this may be due to the shift of the optimum temperature for H_{exo}'s to a higher value because of the higher multiplicity for H_{exo} protons.

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