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PROTON NMR STUDY ON THE LONG RANGE ORDERED ORGANIC FREE RADICAL, TRIPHENYL VERDAZYL

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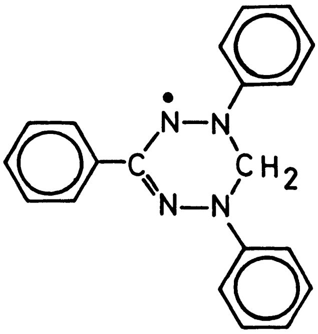
Proton NMR measurement in the magnetically long range ordered state of the polycrystalline organic free radical, triphenyl verdazyl, has been observed. The results give a microscopic evidence of long range order with the Néel temperature, 1.76 K.

There are a number of NMR studies on organic free radicals. In the solid state, however, a few investigations have been reported so far. Recently it has become clear that some of the organic free radicals undergo a magnetic phase transition. Evidence from the heat capacity measurements has been given for BDPA-Bz,1) p-Cl-BDPA,2) TANOL,3) and TANOL-Suberate.4) Thus, the investigation of the magnetic properties of the organic free radicals in the long range ordered state has received considerable attention.

Saito et al. have reported a microscopic evidence of the magnetic long range ordering of TANOL from a proton NMR investigation.5) The proton NMR measurements have also been carried out on BDPA-Bz and p-Cl-BDPA in the paramagnetic and antiferromagnetic state and no signals in the antiferromagnetic ordered state have been detected, although the anomalous behavior in the vicinity of the magnetic transition temperature has been observed.6) Takizawa et al. have performed NMR study of a single crystal of DANO radical, observing several kinds of shifted lines from the free proton resonance position.7) The temperature dependence of these shifts showed the onset of the long range order of DANO. We also observed the temperature-dependent absorptions, although very weak, in the polycrystalline organic free radical, triphenyl verdazyl (TPV) , and this report gives a microscopic evidence of the magnetic phase transition of TPV.

From the magnetic susceptibility and the ESR measurements it has been pointed out that TPV radical may belong to the linear antiferromagnetic Heisenberg magnet with a ferromagnetic interaction between the linear chains and may undergo a magnetic long



triphenyl verdazyl (TPV)

range ordering at 1.7 K because of the interchain interaction.[8] The Néel temperature was supposed from the susceptibility minimum and the linewidth broadening of ESR in the vicinity of 1.7 K. In addition to these results, there are no sufficient indications showing the long range ordering.

The sample preparation method is followed as described in the literature.[9] The proton NMR measurements were carried out using Pound-Watkins type and Robinson type spectrometers at the oscillation frequency of 30.0 MHz. The magnet field was modulated at 80 Hz and the phase sensitive detection was employed following the use of a narrow band amplifier.[6]

In the paramagnetic region the line shape, roughly speaking, consists of two partially resolved components, one shifted upfield and the other around the free proton position. The resonance position of the former absorption line is much temperature-dependent and that of the latter is almost temperature-independent. Figure 1 shows the NMR spectrum at 7.4 K, in which one can recognize shoulders on both of the strong absorption lines mentioned above. These two shoulders are also much temperature dependent. The temperature variations of the paramagnetic shifts of the upfield lines are in good agreement with the magnetic susceptibility result.[8] The most highly resolved spectra were obtained near 7 K, where the susceptibility shows a broad maximum. As the temperature is lowered and approaches to the transition temperature, the two partially resolved components coalesce to one absorption line, in the wing of which a weak shoulder is detected in the upper field side. Then the intensity of the absorption line decreases abruptly to about 30 % of the maximum intensity observed at the temperature just above the transition temperature. These phe-

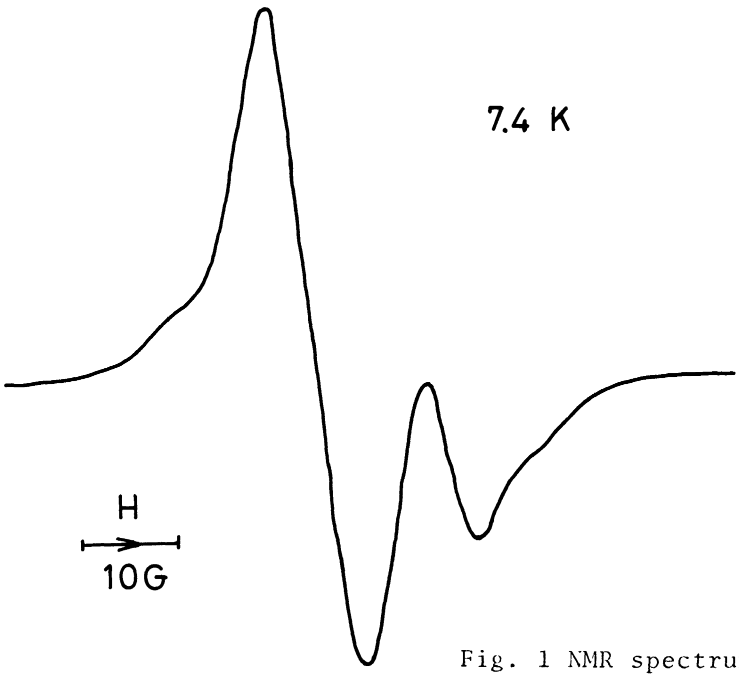


Fig. 1 NMR spectrum of TPV at 7.4 K

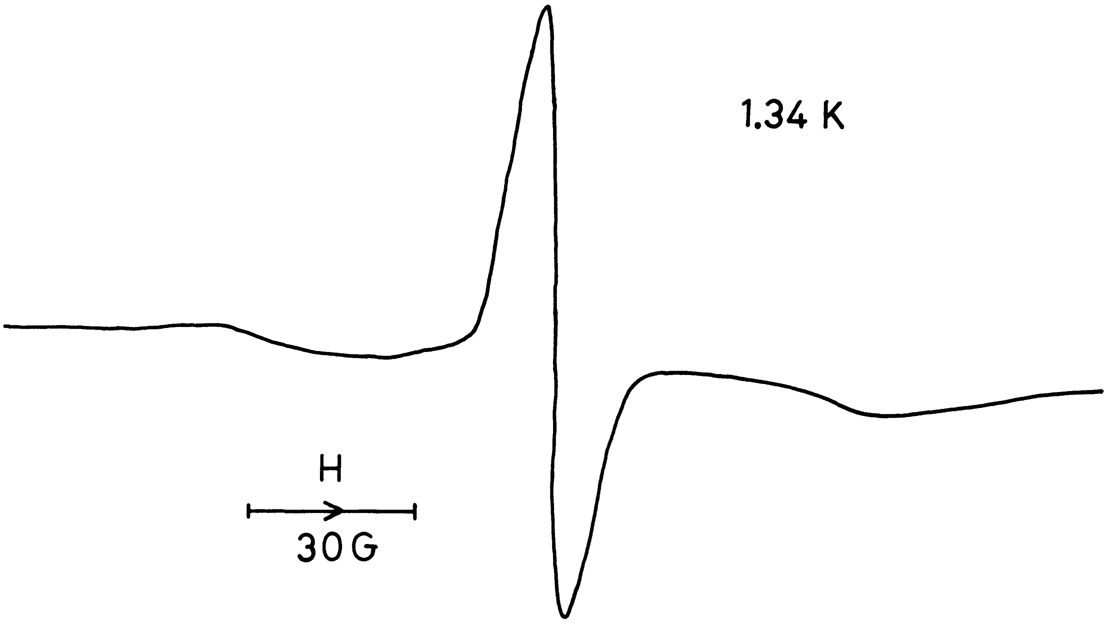


Fig. 2 NMR spectrum of TPV at 1.34 K

nomena are identical with those of BDPA-Bz and p-Cl-BDPA reported in the literature.6)

In the long range ordered state, the proton NMR spectra are as shown in Fig. 2. On both sides of the absorption line , which is observed around the free proton position, the temperature-dependent feeble absorption lines can be observed. These may be attributed to the NMR shift caused by the sublattice magnetization of the long range ordered unpaired electron spins in TPV radical. In the antiferromagnetic state the spin system forms the two sublattices with antiparallel spin directions with each other.10) Thus, the average of the spin S, $\langle S \rangle$, of one sublattice has opposite sign with that of the other and so that this causes both high and low field shifts of the resonance lines. Consequently, the two absorption lines in the high and low sides can be explained to be due to the antiferromagnetically long range ordering of the electron spins in TPV radical.

From the temperature dependence of the sublattice magnetization, which is proportional to the NMR shift in the long range ordered state, the Néel temperature was estimated to be 1.76 K, which is compared with 1.7 K determined from the magnetic susceptibility minimum temperature.8) The Néel temperature determined from this NMR study, 1.76 K, is more reliable since it was found in p-Cl-BDPA that the Néel temperature is slightly larger than the susceptibility minimum temperature.2, 11)

The NMR absorption in polycrystalline samples may be broadened and become very weak because of the dipolar interaction in addition to the anisotropic hyperfine interaction, so that the experiment on a single crystal will be requested. In conclusion, it was shown that, from a microscopic point of view, the organic free radical, TPV, experiences a magnetic phase transition at 1.76 K. The detailed analysis of the absorption line-shape in the paramagnetic and antiferromagnetic regions is now in progress.

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