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The Chlorine Nuclear Quadrupole Resonance in an Organic Free Radical, *p*-Cl-BDPA

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Synopsis. The ^{35}Cl nuclear quadrupole resonance in a stable organic free radical, 1,3-bisdiphenylene-2-*p*-chlorophenyl-allyl, has been measured from 4.2 to 1.6 K. On lowering the temperature, the resonance line became weaker and broader, and it disappeared near the Néel temperature. This behavior has been interpreted in terms of the presence of a hyperfine interaction.

The magnetic property of a stable organic free radical, *p*-Cl-BDPA (1,3-bisdiphenylene-2-*p*-chlorophenyl-allyl), has been investigated by examining the magnetic susceptibility and by ESR, PMR, and heat capacity measurements.[1-3] The *p*-Cl-BDPA radical has the molecular structure shown in Fig. 1. The unpaired electron is delocalized over the whole molecular framework. In the paramagnetic region, *p*-Cl-BDPA exhibits a one-dimensional antiferromagnetism, with a Heisenberg-type isotropic exchange interaction ($J/k=-4.4$ K), and undergoes a magnetic-phase transition to the antiferromagnetic state ($T_N=3.25$ K). In this note, we would like to report on our results on the ^{35}Cl nuclear quadrupole resonance (NQR) in a polycrystalline sample of *p*-Cl-BDPA. One of the objects of this study is to investigate the effects on the NQR of the electron-spin fluctuation near the magnetic-phase transition.

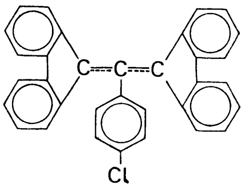

Fig. 1. Molecular structure of *p*-Cl-BDPA

There have been few works so far concerned with the ^{35}Cl NQR measurements of paramagnetic organic substances, except for the charge-transfer complexes which exhibit a weak paramagnetism.[4] At room and liquid nitrogen temperatures, we could not find any ^{35}Cl resonance line in *p*-Cl-BDPA, probably because of the line broadening. In order to improve the signal-to-noise ratio, therefore, we carried out NQR measurements in the liquid-helium-temperature region, as a saturation effect at low temperatures usually encountered in diamagnetic substances could be excluded in our paramagnetic sample.

A sample of about 1.5 g of *p*-Cl-BDPA was prepared according to the procedure of Kuhn and Neugebauer,[5] as introduced in a previous paper.[1] The ^{35}Cl NQR line was searched for in the frequency range of 30—40 MHz at the temperature of liquid helium with a Dean-type super-regenerative detector,[6] equipped with the frequency modulation of 40 Hz. We could find one broad line on an oscilloscope; its signal-to-noise ratio was about three. The resonance frequency was determined to be 35.117±0.005 MHz on the oscilloscope by use of a VHF signal generator (Meguro-Denpa-Sokki MSG-235) and a frequency counter (Takeda Riken TR-5667). The resonance was also studied by means of a recording technique employing a narrow-band amplifier and a phase-sensitive detection. A typical tracing is shown in Fig. 2(a). On lowering the temperature from 4.2 K by pumping of liquid helium, the resonance line became broader and weaker; it was not detected at 3.0 K, not even by the recording procedure, as is shown in Figs. 2(b) and (c). The resonance frequency did not appreciably change in the 4.2—3.5 K temperature range. Unsuccessful attempts were made to find new ^{35}Cl resonance lines at 1.6 K. When the temperature returned to 4.2 K, the resonance line was reproduced at the same frequency.

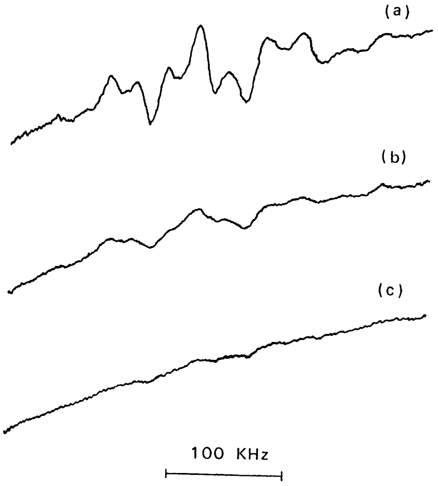

Fig. 2. Tracings of ^{35}Cl nuclear quadrupole resonance in a polycrystalline sample of *p*-Cl-BDPA.
(a) T=4.2 K, (b) T=3.4 K, (c) T=3.2 K
In each case the quenching frequency was about 40 kHz.

We have already investigated the mechanisms of the electron-proton hyperfine interaction in an organic free radical by PMR in single crystals of the DPPH–benzene complex.[7] Taking these results into account, the Hamiltonian for a free radical in which one chlorine nucleus interacts with the electric-field gradient at the chlorine site and one unpaired electron can be described by the following equation:

$$\mathscr{H} = \mathscr{H}_Q + aS\cdot I + S\cdot D\cdot I \qquad (1)$$

where $\mathscr{H}_Q$, a, and D are the quadrupolar Hamiltonian, the isotropic hyperfine coupling constant, and the traceless dipolar tensor respectively. The second term is an isotropic-hyperfine part arising from Fermi contact interaction, and the third term is an anisotropic part due to the electron-nuclear dipolar interaction. These terms depend upon the spin densities on the chlorine atom and the carbon atom adjacent to the chlorine. In our concentrated paramagnetic system, the correlation time is short in comparison with the nuclear precessional frequency because of the strong electron-exchange interaction; therefore, the resonance line is subjected to the so-called exchange narrowing, and then the electron spin, S, of Eq. (1) is replaced by $\langle S\rangle+\delta S$. Here, $\langle S\rangle$ is the time average of S, and δS is the electron-spin fluctuation, which may provide a mechanism for nuclear-spin relaxation at low temperatures through the hyperfine interaction.[8] In the paramagnetic region, $\langle S\rangle$ vanishes when there is no external field. Hence, the pure NQR eigenvalues are unaffected by the presence of the hyperfine interaction. The ^{35}Cl resonance frequency of *p*-Cl-BDPA is near that of chlorobenzene, which has been determined to be 34.6216 MHz at the temperature of liquid nitrogen.[9] This fact indicates that the electric-field gradient at the chlorine site is not intensively affected by the unpaired electron; that is, the unpaired electron is not delocalized very much on the *p*-chlorophenyl ring. From the electron-nuclear double resonance (ENDOR) results for *p*-Cl-BDPA,[10] the unpaired electron-spin density on the carbon atom adjacent to the chlorine can be estimated to be about 0.01 at most. The unpaired electron could also be distributed slightly on the chlorine atom.

The broadening of the resonance line may be interpreted as indicating that the correlation time becomes longer because of the short-range magnetic ordering below the temperature of the susceptibility maximum (T_m=5.6 K). This result corresponds to the line broadening of the ESR and PMR in this temperature region.[1,2] The disappearance of the ^{35}Cl resonance line near the temperature of 3.2 K is attributable to a magnetic-phase transition to the antiferromagnetic state at T_N=3.25 K.[3] This fact is consistent with the disappearance of the ESR and PMR lines near the Néel temperature.[1,2] In the antiferromagnetic state, the time-averaged spin, $\langle S\rangle$, does not vanish even in the absence of an external magnetic field and is proportional to the sublattice magnetization, $M(T)$. Therefore, the pure NQR eigen values are affected by the internal field created by electron-spin through the hyperfine interaction of Eq. (1). Below the Néel temperature, a hyperfine splitting is expected in the ^{35}Cl NQR as a result of the weak hyperfine interaction between the chlorine nucleus and the unpaired electron, although the crystal structure of *p*-Cl-BDPA and the spin structure in the antiferromagnetic state are not determined. Unfortunately, however, new ^{35}Cl resonance lines could not be detected at 1.6 K in the 30—40 MHz frequency range. This result is probably due to the lack of spectrometer sensitivity, a line broadening in the antiferromagnetic state which has not been investigated in such a delocalized spin system, or some other effect. We hope to determine the crystal structure and the spin structure in the antiferromagnetic state in the future.

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