Proton Magnetic Resonance in Organic Free Radicals, BDPA-Bz and *p*-Cl-BDPA

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(Received August 20, 1973)

The proton NMR absorption spectra from 1.3 to 77 K in two organic free radicals, BDPA-Bz and *p*-Cl-BDPA, have been measured on powder samples which undergo a magnetic phase transition from a paramagnetic to an antiferromagnetic state at the temperatures of 1.695 and 3.25 K respectively. The behavior of the NMR absorption spectra associated with the magnetic phase transition has been studied for the first time in the organic free radicals and interpreted in terms of the hyperfine interaction. These results are then compared with those of the TANOL radical, which is a linear antiferromagnet with no magnetic phase transition down to 1.3 K.

Since the original preparation of an organic free radical BDPA (1,3-bisdiphenylene-2-phenyl-allyl) by Koelsch,[1] the magnetic properties of this radical and its derivatives have been studied on powder samples by several authors. For these radicals, especially in the cases of BDPA–Bz (the complex of 1,3-bisdiphenylene-2-phenyl-allyl with benzene) and *p*-Cl-BDPA (1,3-bisdiphenylene-2-[*p*-chloro-phenyl]-allyl), static magnetic susceptibility, magnetic resonance absorption, and specific heat measurements have been carried out.[2–7]

Anderson *et al.*[2] have observed the magnetic susceptibility from the paramagnetic shift, which exhibited a broad maximum at about 6 K. Hamilton and Pake[3] have pointed out the possibility of a long-range magnetic ordering of BDPA-Bz below 1.73 K, judging from the results of the specific heat and ESR measurements. One of the present authors (J.Y.)[4] has measured the magnetic susceptibility and ESR spectra of BDPA–Bz and *p*-Cl-BDPA. A broad maximum in the magnetic susceptibility was observed for both radicals at 5.6 K and a minimum for *p*-Cl-BDPA at 2.8 K; a divergence of the linewidth of the ESR absorption was also observed for BDPA-Bz and *p*-Cl-BDPA at 1.78 and 2.8 K respectively. Recently, Duffy *et al.*[5] have measured the specific heat of BDPA–Bz and observed a sharp peak in the magnetic contribution part at 1.695 K, while Yamauchi *et al.*[6,7] have observed a sharp peak in the magnetic specific heat of *p*-Cl-BDPA at 3.25 K and have also measured the antiferromagnetic resonance spectra below that temperature. Thus, it has become clear that BDPA-Bz and *p*-Cl-BDPA undergo a magnetic phase transition from a paramagnetic to an antiferromagnetic state at the Néel temperatures of 1.695 and 3.25 K respectively.

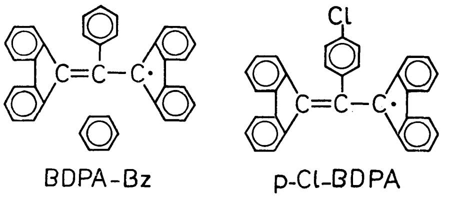

Fig. 1. The molecular structures of the radicals studied.

The behavior associated with the magnetic phase transition of the two BDPA derivatives is as follows: 1) a minimum in the magnetic susceptibility at the Néel temperature, 2) an abrupt increase in the ESR absorption linewidth and in the *g*-value in the vicinity of the Néel temperature, 3) an observation of the antiferromagnetic resonance absorption, and 4) an anomaly in the magnetic specific heat at Néel temperature. The behavior of the NMR absorption spectra associated with the magnetic phase transition, however, has not yet been clarified in organic free radicals. In this paper we would like to demonstrate the behavior associated with both the short-range and the long-range ordering of unpaired electron spins in these radical solids, whose molecular structures are as is shown in Fig. 1.

Experimental

The samples of BDPA-Bz and *p*-Cl-BDPA were prepared according to the procedure of Kuhn and Neugebauer[8] and were recrystallized from a benzene solution. The melting points and the results of the elementary analyses of carbon and hydrogen are in good agreement with those in the literature.

The proton NMR measurements were carried out using Pound-Watkins-type[9] and Robinson-type[10] spectrometers at the oscillation frequency, ν, of 18.0 MHz and at 27.0, 30.0, and 35.0 MHz. During the measurements the oscillation frequency and power level were kept constant. The magnetic field was modulated at 80 Hz, and the phase-sensitive detection was employed following the use of a narrow-band amplifier.

An ordinary cryostat was utilized, and the thermometer, an Allen-Bradley carbon resistor, was calibrated against the vapor pressures of liquid helium, hydrogen, and nitrogen.

Results

The proton NMR spectra of a powder sample of BDPA-Bz at 18.0 MHz are shown in Fig. 2. In addition to the central unshifted line, one more absorption line, shifted to the upper magnetic field and with a relatively small intensity, was observed from the temperature of liquid nitrogen down to about 2 K. The resonance field of the unshifted line corresponded to the magnetic field where the resonance of a free proton occurs at that frequency. The shift of the absorption line which appears at the high field

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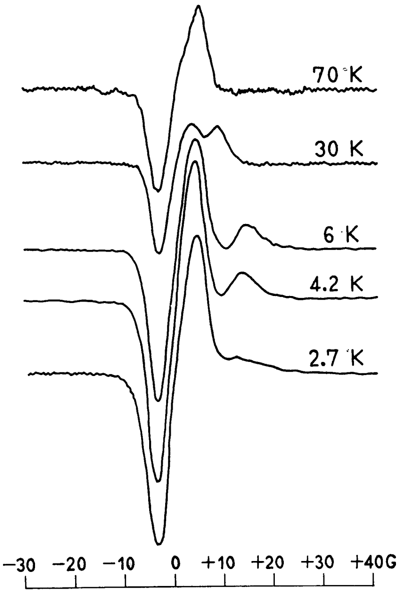


Fig. 2. NMR spectra of BDPA-Bz measured at 18.0 MHz.

is attributed to the paramagnetic shift of some protons attached to the carbon atoms with positive spin densities. The paramagnetic shift can be evaluated from the spacing between the unshifted and shifted absorption lines. Although these two resonance lines are not highly resolved, one may regard the resonance position of the shifted line as the center of the two peaks of the shifted absorption line. Thus, the paramagnetic shift, δH, the peak height of the unshifted line, h, and the half-width between the maximum slopes of the unshifted line, ΔH, were defined as is shown in Fig. 3. As the temperature was lowered to about 2 K, the shifted line became too broad to evaluate the δH, and the peak height of the unshifted line, h, decreased abruptly from 2.2 to 1.5 K, much as in the case of the spectra measured at 30.0 MHz. The curve of Fig. 4 indicates the temperature dependence of h for BDPA-Bz, which is normalized to 100% at 4.2 K.

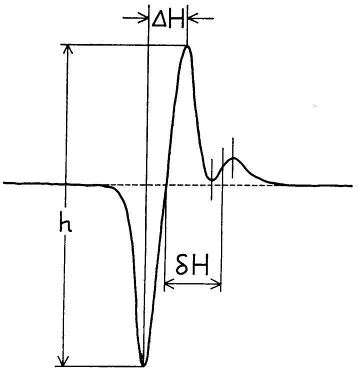


Fig. 3. Definition of δH, h and ΔH in the NMR spectra of the free radicals studied here. The δH stands for the paramagnetic shift to the high field. h and ΔH mean the peak height and the peak-to-peak linewidth of the unshifted absorption line respectively.

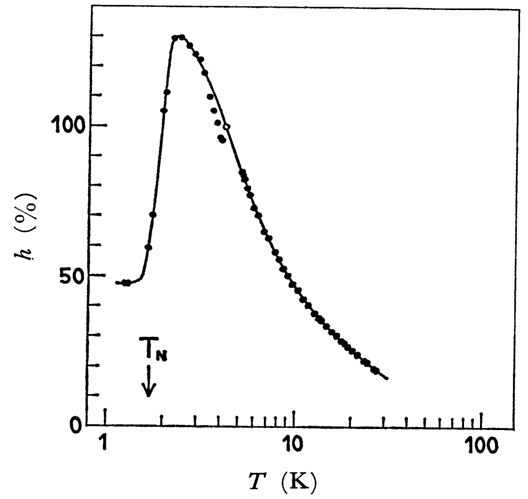


Fig. 4. Peak height of the unshifted line, h, of BDPA-Bz *vs.* temperature measured at 18.0 MHz. h is normalized to 100% at 4.2 K. T_N is the Néel temperature of this radical.

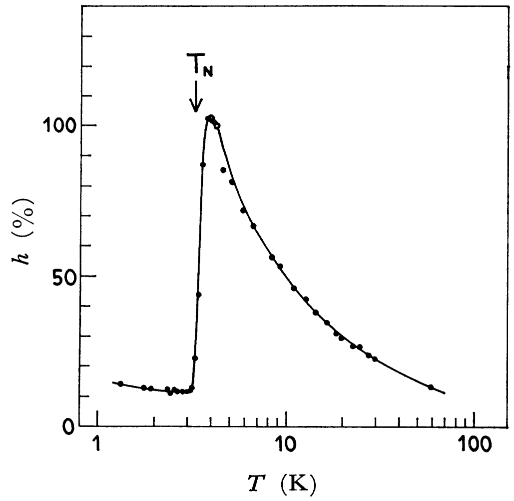


Fig. 5. h of *p*-Cl-BDPA *vs.* temperature measured at 18.0 MHz.

For the measurements of *p*-Cl-BDPA, spectra similar to those of BDPA-Bz were obtained except for one or two shifted lines observed above 4 K. The peak height, h, exhibited an abrupt decrease from 3.8 to 3.2 K, as is shown in Fig. 5.

For the sake of comparison, as will be discussed later, the temperature dependence of h for a powder sample of TANOL (2,2,6,6-tetramethyl-4-piperidinol-1-oxyl) was also obtained.

Discussion

Each proton in a radical molecule interacts with an unpaired electron which spreads over a whole molecular framework. In general, the Hamiltonian in the system where such a proton is located in a static magnetic field, H_0, along the z-axis may be given by:

$$\mathcal{H} = \mathcal{H}_{\text{Zeeman}} + \mathcal{H}_{\text{iso}} + \mathcal{H}_{\text{dip}}. \tag{1}$$

Here, $\mathcal{H}_{\text{Zeeman}}$ is the nuclear Zeeman term:

$$\mathcal{H}_{\text{Zeeman}} = -g_N\beta_N H_0 I_z. \tag{2}$$

$\mathcal{H}_{\rm iso}$ and $\mathcal{H}_{\rm dip}$ denote the hyperfine interaction; the former is the isotropic term, and the latter, the anisotropic dipolar term. $\mathcal{H}_{\rm Zeeman}$ decides the free proton resonance field, and $\mathcal{H}_{\rm iso}$ and $\mathcal{H}_{\rm dip}$ contribute to a shift from that field.

Paramagnetic Region. The electron spins fluctuate rapidly as a result of the exchange interaction between the unpaired electrons on neighboring radical molecules. Hence, a small time-averaged local magnetic field acts on a proton.[11] In a powder sample, therefore, the dipolar term does not contribute to the paramagnetic shift, and the isotropic hyperfine term is given by:

$$\mathcal{H}_{\rm iso} = a\boldsymbol{I}_z\langle\delta\boldsymbol{S}_z\rangle. \qquad (3)$$

where a is the isotropic hyperfine coupling constant and is proportional to the spin density on the carbon atom adjacent to the proton according to McConnell's relation,[12] and where $\langle\delta S_z\rangle$ denotes the z-component of a time-averaged value of an electron spin which is induced by the external magnetic field, H_0. The relation between $\langle\delta S_z\rangle$ and H_0 is:

$$\chi_{\rm M}H_0 = -Ng\beta\langle\delta\boldsymbol{S}_z\rangle. \qquad (4)$$

where $\chi_{\rm M}$ is the molar static magnetic susceptibility and N, Avogadro number. From Eqs. (2) and (3) the paramagnetic shift, expressed in Gauss, is obtained as:

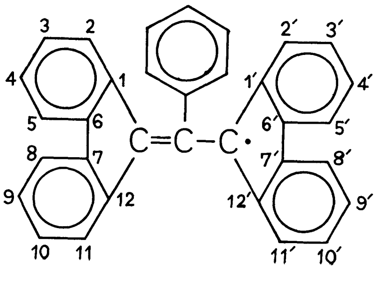
$$\delta H = \frac{a\langle\delta\boldsymbol{S}_z\rangle}{g_{\rm N}\beta_{\rm N}}\,. \qquad (5)$$

From Eq. (4) and the resonance condition $(h\nu = g_{\rm N}\beta_{\rm N}H_0)$, we obtain:

$$\delta H = \frac{a\chi_{\rm M}h\nu}{Ng\beta(g_{\rm N}\beta_{\rm N})^2}\,. \qquad (6)$$

Thus, δH is proportional to the hyperfine coupling constant (or the spin density on the adjacent carbon atom), the static magnetic susceptibility, and the resonance frequency.

According to McConnell's relation, a is negative for a proton attached to the carbon atom with a positive spin density. From the results of a simple molecular orbital calculation for BDPA, it is considered that the absorption line shifted to the high field is attributable to eight protons attached to the carbon atoms, with positive spin densities, situated at the 2-, 4-, 9-, and 11-positions on two diphenylene groups in a radical molecule. Since BDPA-Bz is a one-to-one complex of benzene, the absorption intensity ratio of the unshifted line to the shifted line should be 13+6 : 8 (observed 70 : 30). Hence, the line shape of BDPA-Bz in Fig. 3 is valid and also corresponds well with the results by Anderson *et al.* Since the intensity ratio for *p*-Cl-BDPA should be 12 : 8 (observed 60 : 40), the line shape of this radical is also valid.



One can recognize the frequency dependence of δH in Fig. 6 and can see quite a good agreement of the temperature dependence curve of δH with that of $\chi_{\rm M}$ as is shown in Fig. 7.

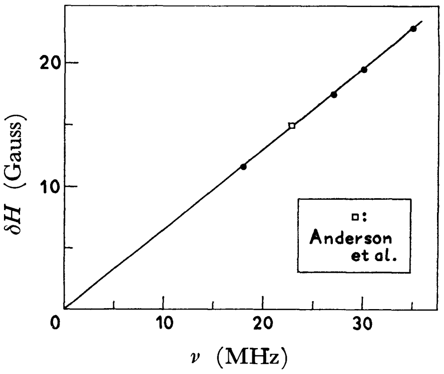


Fig. 6. Paramagnetic shift, δH, of BDPA-Bz *vs.* resonance frequency, ν, measured at 4.2 K. The value by Anderson *et al.* is also plotted for comparison.

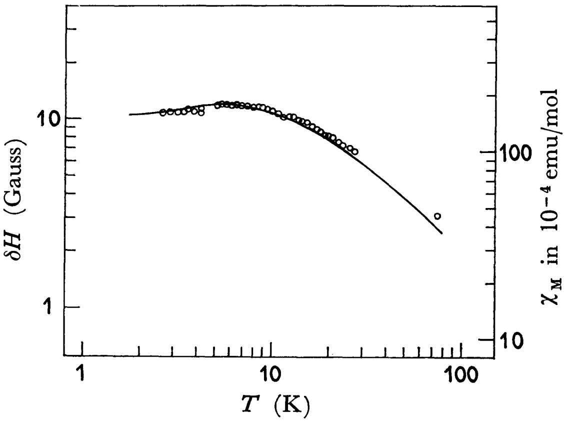


Fig. 7. δH of BDPA-Bz *vs.* temperature. The solid line is the curve of the molar magnetic susceptibility, $\chi_{\rm M}$, by Yamauchi[4] fitted at the maximum point.

As it is known that the width of the shifted line depends upon $\langle\delta S_z\rangle$,[13] Fig. 2 shows a broadening of that line associated with a rise in the paramagnetic susceptibility.

Critical Region and Antiferromagnetic Region. The electron spins do not fluctuate rapidly any longer. Hence, a spontaneous magnetization of the electron spins occurs and a large time-averaged local field acts on a proton, which is specified as:

$$\mathcal{H}_{\rm iso} = a\boldsymbol{I}_z\langle\boldsymbol{S}_z\rangle. \qquad (7)$$

where $\langle S_z\rangle$ denotes the time average of the z-component of the effective spontaneous magnetization of the electron spins which acts on that proton. In the paramagnetic state, $\langle S_z\rangle$ is nonvanishing only in a finite applied field. Though it would be difficult to express $\mathcal{H}_{\rm dip}$ in a simple form for a system where the electron spins are widely delocalized, it can be easily understood that this term also involves $\langle S_z\rangle$. Both the hyperfine terms contribute to the striking increase in the width of the shifted line shown in Fig. 2. The unshifted line originally consists of the absorption of each proton which is coupled weakly with the unpaired electron (or attached to the carbon atom with a very small spin density). The occurrence of the spontaneous magnetization, therefore, shifts the resonance field of each proton to a point far from the free-proton resonance field.

The temperature dependence of *h* can be regarded as that of the absorption intensity of the unshifted line, for ΔH does not show a large temperature dependence, as is shown in Fig. 8, and no saturation of the unshifted line[3] was observed. The rapid decrease in *h* near Néel temperature can, therefore, be ascribed to the long-range ordering of the unpaired electron spins in BDPA-Bz and *p*-Cl-BDPA. In TANOL a short-range ordering occurs, with a maximum susceptibility at 6.5 K,[4,14,15] but a long-range ordering does not occur down to 1.3 K; this radical is believed to be a good linear antiferromagnet.[4] Hence, *h* (or the absorption intensity) for TANOL is approximately inversely proportional to the temperature, as is shown in Fig. 9, and it may be considered that the absorption intensity is proportional to the "nuclear magnetic susceptibility" in the absence of a long-range ordering. On the other hand, in the presence of a long-range ordering, the absorption intensity of the unshifted line decreases abruptly in the critical temperature region, as is shown for BDPA-Bz and *p*-Cl-BDPA in Figs. 4 and 5 respectively, because of the spontaneous sublattice magnetization, which acts as a large local field on protons through the hyperfine interaction.

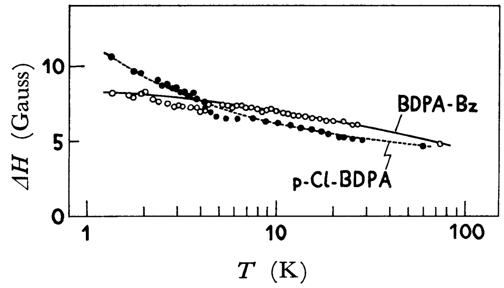


Fig. 8. Linewidth of the unshifted line, ΔH, of BDPA-Bz and *p*-Cl-BDPA *vs.* temperature measured at 18.0 MHz.

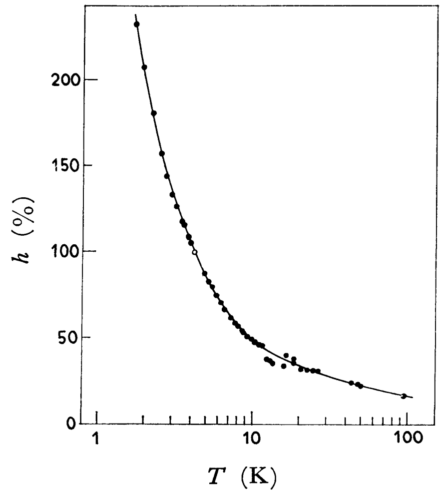


Fig. 9. *h* of TANOL *vs.* temperature measured at 30.0 MHz.

Thus, the results of the proton NMR measurements are consistent with the other information about the magnetic susceptibility, the ESR, and the specific heat measurements.

The shifted absorption lines in the antiferromagnetic region could not be found for powder samples of the two radicals. It is hoped that the magnetic properties of these radicals will be studied with single crystals in the future.

Conclusion

The proton NMR of the organic free radicals was studied in the paramagnetic and antiferromagnetic regions. The results are consistent with the other information on their magnetic properties; especially, it may be concluded that the intensity of the proton NMR absorption line decreases abruptly in the vicinity of the Néel temperature. This phenomenon illustrates the behavior associated with the long-range magnetic ordering of the two organic free radicals, BDPA-Bz and *p*-Cl-BDPA. Moreover, it may be concluded that the transition temperature in the organic free radicals can be foretold on the basis of the results of the proton NMR measurements of powder samples.

The authors would like to express their sincere thanks to Messrs. Teruaki Fujito and Toshio Yoshioka for their help in the measurements and also to Mr. Kohji Watanabe for his advice on the sample preparation.

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