PMR Studies of the Phase Transition in *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine (Wurster's Blue) Perchlorate

Motomichi INOUE, Hiroyoshi KURAMOTO, and Daiyu NAKAMURA

Department of Chemistry, Nagoya University, Chikusa, Nagoya 464

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The powder PMR spectra of $[TMPD]^+(ClO_4)^-$ were recorded in the temperature range 110—300 K. The spectra observed above 140 K consist of two widely separated simple absorption curves of intensity ratio approximately equal to 3 : 1. Spin densities on the carbon and nitrogen atoms of the cation radical were evaluated from the observed field shift ascribable to the Fermi contact interaction. The spin density distribution of the radical ion changes at the transition temperature of 189 K.

The phase transition of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) perchlorate attracts particular attention, because the crystals display phase transition at *ca.* 189 K accompanied by a novel magnetic behavior.[1,2] X-Ray crystal analysis carried out at 300 and 110 K has revealed that cation radicals, in the high-temperature phase, are stacked equidistantly to form a one-dimensional array, whereas radical ions are dimerized to construct alternating chains in the low-temperature phase.[3] The magnetic interaction between radical ions is closely related to the stacking of cations and also to the distribution of an unpaired electron within radicals.[4,5] The latter can be determined by observing the contact shift of PMR. Kawamori and Suzuki[6] have reported that the PMR absorption curve of TMPD-perchlorate powders consists of two component curves, and that the separation between the centers of the curves varies with temperature in proportion to the magnetic susceptibility of the compound. However, the authors failed to determine the absolute values of the PMR shifts. In the present investigation, we have precisely recorded the PMR spectrum of the radical salt at various temperatures between 110 and 300 K, and have determined the spin density distribution of the TMPD cations in crystals.

Experimental

TMPD perchlorate was prepared by the method of Michaelis and Granick.[7] Crystalline powders obtained were dried *in vacuo* for *ca.* 4 h to eliminate solvent molecules completely.

The PMR spectra were recorded by means of a JEOL JNM-MW-40 NMR spectrometer operating at 40 MHz with a field-modulation amplitude of 0.5 G.* Isohexane (isomeric mixture) was employed as an external standard. The temperature of the specimen was determined with a copper-constantan thermometer inserted directly in the specimen before and after recording each PMR spectrum. The temperature was automatically controlled within ±1° by the following method. Cold vapor evaporated from liquid nitrogen was conducted to the specimen through a transfer tube, in which a heater was mounted. The evaporation of liquid nitrogen was kept at a constant rate, and the temperature of flowing gas was controlled by use of the heater connected to a conventional PID temperature controller. The homogeneity of temperature in the specimen was difficult to keep within ±1°, because of a large volume of the specimen amounting to *ca.* 4 cm^3. The accuracy of the temperature was estimated to be within ±2° over the temperature range investigated.

* The unit corresponds to 10^{-4} T in the SI unit system.

Results

Figure 1 shows some typical derivative curves of PMR absorptions observed at various temperatures. Above *ca.* 140 K, each curve observed can be resolved into two component curves of intensity ratio equal to 3 : 1. The stronger component shifts to a low field, whereas the weaker one does to a high field. From the intensity ratio, the former can be assigned to *N*-methyl protons and the latter to the protons of benzene rings. The amount of the shifts from the external standard is plotted against the temperature for each component as shown in Fig. 2. The temperature dependence of the PMR shifts closely resembles that of the magnetic susceptibility. This is consistent with the results reported by Kawamori and Suzuki.[6]

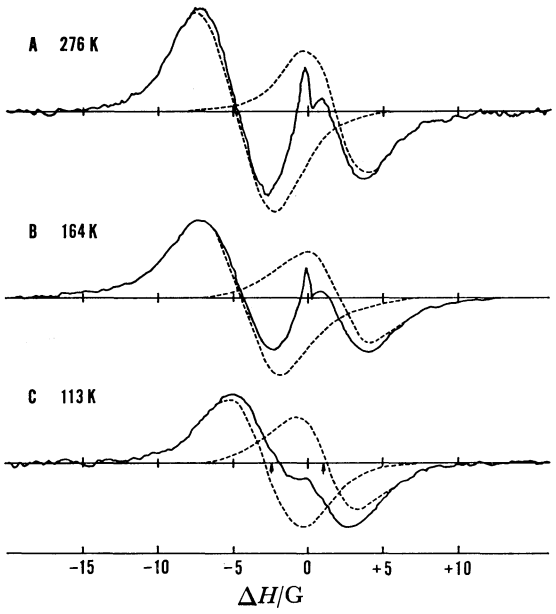


Fig. 1. PMR absorption derivative curves of $[TMPD](ClO_4)$ at various temperatures. Each curve can be resolved into two simple derivative curves (broken curves). Sharp components at $\Delta H=0$ in the spectra A and B are due to isohexane employed as an external standard. The spectrum C dispalys the curve recorded without the external standard to show the inherent curve clearly. The arrows in the spectrum C show the resonance fields estimated by use of the coupling constants of the low-temperature phase.

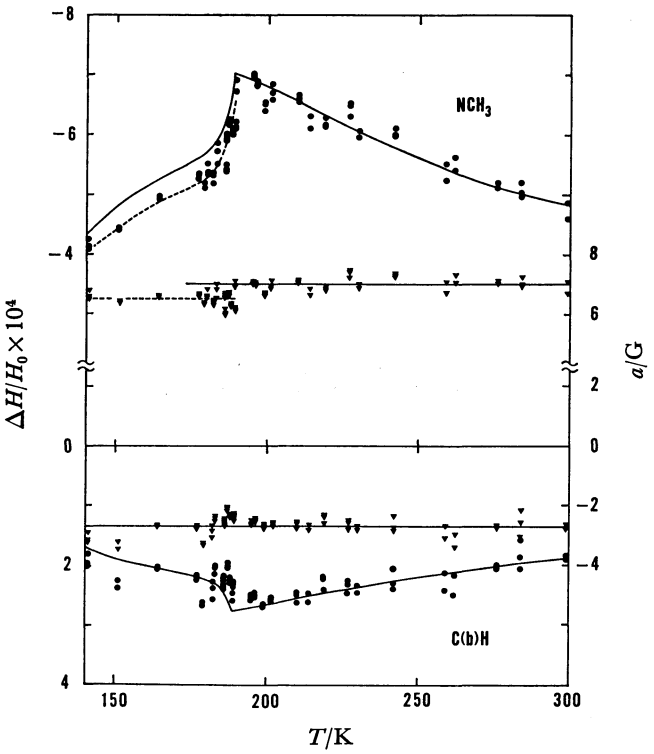


Fig. 2. Observed PMR shifts (●) and the coupling constants (▼) of *N*-methyl protons and ring protons. The straight lines show the respective averaged values of the coupling constants. The solid curves display the shifts evaluated with the coupling constants of the high-temperature phase. The a_{NCH_3} value averaged below T_c gives the broken curve reproducing well the shifts of *N*-methyl protons observed below T_c.

Each curve observed below 140 K can be decomposed into two simple derivative curves, the intensity ratio of which, however, varies with temperature. For example, the spectrum C in Fig. 1 observed at 113 K is made up of two components of intensity ratio nearly equal to 2 : 1. In this paper, the discussion is based solely on the data observed above 140 K.

Discussion

The PMR shift $\Delta H/H$ is attributable to the Fermi contact shift, which is proportional to magnetic susceptibility χ:[8]

$$\frac{\Delta H}{H_0} = -\frac{a_i}{g_N\mu_N}\cdot\frac{\chi}{cN}, \tag{1}$$

where, apart from the usual notations, a_i is the contact coupling constant in Gauss and c is the radical concentration determined from the Curie constant. Thus, the coupling constants, a_{NCH_3} for *N*-methyl protons and $a_{C(b)H}$ for ring protons, can be evaluated from the corresponding PMR shifts and the magnetic susceptibility which has been reported by Duffy, Jr.[1] and Okumura[2] in the temperature range 77—300 K. The temperature, at which the PMR shift shows a sharp decrease, agrees with the transition temperature T_c determined by Okumura rather than by Duffy, Jr. Therefore, the coupling constants were evaluated on the basis of Okumura's data (T_c=189 K and c=0.86$_7$). Each coupling constant is practically constant above T_c as shown in Fig. 2. The averaged values of the constants are listed in Table 1 along with estimated standard deviations. The shifts observed above T_c are well reproduced by the solid curves calculated using Eq. 1.

The coupling constant $a_{C(i)H}$ is proportional to spin density $\rho_{C(i)}$ localized on a carbon atom bonded to the proton:[8]

$$a_{C(i)H} = Q_{CH}\rho_{C(i)}, \tag{2}$$

where Q_{CH} is a proportionality constant. When the rotation of *N*-methyl groups is hindered in $>\dot{N}-CH_3$ systems, the contact coupling constant depends on the torsional amplitude ϕ as well as the equilibrium angle θ_j between an N–C–H(j) plane and the axis of the nitrogen p-orbital involving the unpaired electron:[9]

$$a_{NCH_3}(j) = B\langle\cos^2\theta_j\rangle_\phi\rho_N, \tag{3}$$

where j stands for the jth proton of an *N*-methyl group and B is a proportionality constant. For freely rotating methyl groups, all the protons are equivalent so that the coupling constant is simply proportional to the spin density ρ_N of nitrogen:

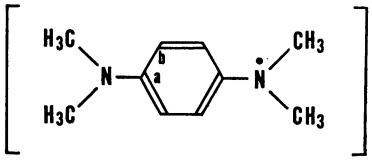
$$a_{NCH_3} = Q_{NCH_3}\rho_N. \tag{4}$$

The *N*-methyl groups of TMPD cations can be assumed to undergo a free rotation about the threefold axis in the high-temperature phase, because of the following facts: (1) the component curve attributable to *N*-methyl protons has a peak-to-peak width nearly equal to that of the curve due to the ring protons, and shows no appreciable structure, and (2) the absolute values of the coupling constants agree well with the corresponding values determined by an ESR experiment[10] carried out on the radical ions in solution (Table 1), in which *N*-methyl groups perform a free rotation. The proportionality constants have been estimated as Q_{CH}=−28 G and Q_{NCH_3}=25 G.[11] By using these values, the spin density can be evaluated as given in Table 1. All the carbon atoms in the benzene ring carry positive spin densities. The spin density distribution has been calculated on the basis of various MO models.[11,12] The distribution determined by McLachlan[11] yields the best fit to the present result.

Below the transition temperature, the observed shifts of *N*-methyl protons deviate systematically from the solid curve in Fig. 2 calculated with the value of a_{NCH_3} evaluated above T_c, while the broken curve shows the temperature dependence of the shift calculated with a_{NCH_3}=6.52 G, reproducing well the data observed below T_c. The a_{NCH_3} value of the low-temperature phase differs clearly from that of the high-temperature phase. Although the magnetic data reported by Duffy differ slightly from Okumura's data, the coupling constants evaluated on the basis of Duffy's data agree with the corresponding values based on Okumura's data over the whole temperature range except near T_c (180—190 K). Therefore, it can be concluded that the "a_{NCH_3} gap" accompanying the phase transition is inherent in the radical salt. Two interpretations are conceivable for the marked a_{NCH_3} gap: (a) the spin density on nitrogen atoms changes appreciably at the transition

Table 1. Contact coupling constant a_i and spin density ρ_i of a TMPD cation[a)]

	a_{NCH_3}/G	$a_{C(b)H}$/G	ρ_N	$\rho_{C(b)}$	$\rho_{C(a)}$[b)]
$T>189$ K	7.01±0.20	−2.71±0.22	0.28_0	0.09_7	0.02_6
$T<189$ K	6.52±0.21	−2.69±0.35	0.26_1	0.09_6	0.04_7
ESR[c)]	6.76	(−)1.97	0.27_0	0.07_0	0.09_0

a)  b) $\rho_{C(a)}=\{1-(2\rho_N+4\rho_{C(b)})\}/2$. c) Ref. 10.

temperature, and (b) a hindered rotation of *N*-methyl groups below T_c yields an apparent Q_{NCH_3} value different from that for freely rotating *N*-methyl protons. Equation 3 indicates that, in case (b), three protons within an *N*-methyl group display PMR shifts different from one another, and, hence, the component curve attributable to *N*-methyl protons is expected to display an incipient indication of structure. Contrary to expectation, the component curve obtained below T_c exhibits no appreciable change in shape and line width as compared with that above T_c, suggesting that the *N*-methyl groups practically perform a free rotation even below the temperature. The aforementioned value of Q_{NCH_3} gives a smaller spin density ρ_N in the low-temperature phase than that in the high-temperature phase. This indicates that a fraction of an unpaired electron, in the former phase, is delocalized from nitrogen onto the aromatic ring to a greater extent. X-Ray crystal analysis[3)] has shown that the C–N bond length 1.346 Å at 110 K is evidently shorter than the length of 1.359 Å at 300 K, suggesting a larger double-bond character in the C–N bonds below T_c. This gives support to the present conclusion. The $a_{C(b)H}$ values averaged above and below T_c agree with each other, although the constant is difficult to determine accurately owing to the small absolute value. Hence, it can be presumed that $\rho_{C(b)}$ remains almost unchaged with decreasing temperature through T_c, despite the discernible change of $\rho_{C(a)}$. In fact, X-ray crystal analysis has shown that the C(*a*)–C(*b*) bond distance increases by 0.005 Å at 110 K whereas the C(*b*)–C(*b*) distance remains unchanged, suggesting that there is no significant alteration in the charge distribution on C(*b*) atoms above and below T_c.

The present investigation presents a unique example showing that the phase transition is accompanied by spin-distribution change in a molecule as well as change of molecular arrangement.

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