On the Low Dimensionality in Organo-magnetic Material:
9-(α-Fluorenylidene-p-chlorobenzyl)-9-fluorenyl

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Synopsis.   The low-dimensional character in the organic free radical, p-Cl-BDPA, is discussed. The temperature dependence of the g-values can provide a method of discrimination between the short- and long-range-ordering effects, and the organic free radical can be regarded as a one-dimensional organo-magnetic material at first approximation, but its interchain interaction is appreciable, amounting to the order of $|J'/J|=0.2$; thus, $|J'|/k=0.88$ K.

Recently the magnetic interactions between unpaired electron spins in crystalline organic free radicals have been of great interest. Especially in the case of neutral organic free radicals, much information has been accumulated so far, and it is generally accepted that there are two regions characteristic of the magnetic interaction between unpaired electron spins in organic free radicals, that is, the short- and long-range-ordered regions.[1] One of the present authors (J.Y.) has discussed in detail the linear antiferromagnetic interaction and the possibility of long-range ordering in organic free radicals.[2]   Thus, organic free radicals have been classified as among low-dimensional magnetic materials, that is, low-dimensional organo-magnetic material. An organic free radical, 9-(α-fluorenylidene-p-chlorobenzyl)-9-fluorenyl (hereafter abbreviated as p-Cl-BDPA),
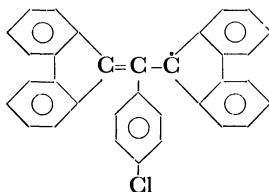
is a typical example, exhibiting magnetic low dimensionality in the short-range-ordered region and experiencing a magnetic phase transition to a long-range-ordered state.[2]

In order to clarify the magnetic interactions in organic free radicals and to obtain more information about low dimensionality and the magnetic structure, various kinds of experiments have been carried out on p-Cl-BDPA.[3-8] In the course of these investigations an important question has been arisen— to what extent does the organic free radical, p-Cl-BDPA, have a magnetic low dimensional character. This may be one question to which it is not possible to give a definite answer. In this paper, however, attention will be paid mainly to the low dimensionality of the organic free radical, p-Cl-BDPA.

It was shown in our previous papers that the low-dimensional character can be found in susceptibility,[2] magnetic heat capacity,[3] ESR linewidth,[2] and NMR intensity[4] as a function of the temperature and that p-Cl-BDPA has a nearly one-dimensional magnetic interaction with an exchange interaction parameter of $J/k=-4.4$ K, where k is Boltzmann's constant. In the
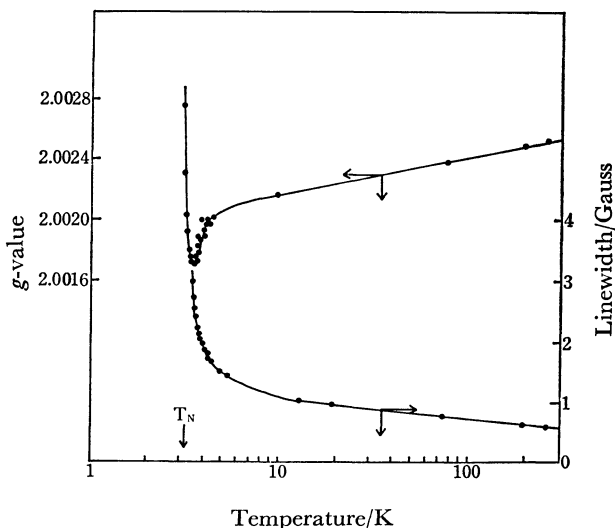

Fig. 1.   Temperature dependences of g-value and linewidth of p-Cl-BDPA. It should be noted that the linewidth is different from that published previously.[2]

microscopic information concerning the ESR linewidth or the NMR intensity, however, the low-dimensional effect could not be discriminated from the long-range-ordering effect.

The experimental results on the ESR g-values of polycrystalline p-Cl-BDPA as a function of the temperature are shown in Fig. 1, which indicates a g-value deviation from a room-temperature g-value as the temperature is lowered and its divergence after reaching a minimum at 3.6 K when the temperature approaches the magnetic-phase-transition temperature, 3.25 K. This deviation may be attributed to the magnetic short-range-ordering effect, and the divergence may be due to the magnetic long-range-ordering effect.

Nagata et al. classically estimated the simple relations between the anisotropies of the g-value and the susceptibility by introducing a small magnetic dipolar interaction and a single ion D-term, both of a uniaxial symmetry referred to the directions of the linear chain interaction.[9] The relationships were as follows:

$$\Delta g_{//}/g = (\chi_{//}-\chi_\perp)/\chi_{//}, \qquad (1)$$

$$\Delta g_\perp/g = (\chi_\perp-\chi_{//})/2\chi_\perp. \qquad (2)$$

When we assume the following relation for a powder sample:

$$\Delta g_{iso} = (\Delta g_{//}+2\Delta g_\perp)/3, \qquad (3)$$

equations 1 and 2 give this expression:

$$\Delta g_{iso}/g = -(\chi_{//}-\chi_\perp)^2/3\chi_{//}\chi_\perp. \qquad (4)$$

Equation 4 indicates that the g-value observed on the powder sample decreases with a decrease in the tem-

perature. The g-value deviation of p-Cl-BDPA is comprehensible from the theory and, therefore, implies a one-dimensional short-range ordering of unpaired electron spins in a linear chain. In the long-range-ordered region, ESR shows an antiferromagnetic resonance pattern, and the resonance shifts to the down-magnetic-field become much larger.[6] This leads to a large g-value anisotropy and to a divergence of the g-value in the short-range-ordered region near the long-range-ordering temperature. This may be the reason why the divergence of g-values can be observed in the case of p-Cl-BDPA.

It is generally accepted that one-dimensional magnetic interactions characterize ESR absorptions at room temperature; that is, the line shape is different from the usual Lorenzian or Gaussian line shapes, and the linewidth angular variation is different from that of the three- or two-dimensional magnetic interaction.[10] These facts are explained at present on the basis of a one-dimensional spin diffusion model. Although the line shape of p-Cl-BDPA was observed, we could not obtain any characteristic behavior such as is mentioned above, but it exhibits a Lorenzian line shape exactly. This fact indicates that p-Cl-BDPA is not a purely one-dimensional magnetic material and implies the presence of fairly large interactions between the magnetic linear chains. As for the angular variations in the linewidth, we can not draw any decisive conclusion because of the lack of the single crystal measurements.

The interchain interaction can not be estimated directly from the experimental results, but the relationship between the intrachain interaction, J, the interchain interaction, J', and the phase transition temperature can be anticipated. Oguchi deduced this relationship in the case of a two-dimensional interchain interac-

tion using the Green function method,[11] which gives the interchain interaction, J', of p-Cl-BDPA. In Table 1 the results obtained are listed, together with those of other organic free radicals for comparison. It can be seen there that $|J'/J|=0.2$ leads to $|J'|/k=0.88$ K and that the interchain interaction is fairly large and not negligible compared with that of the TANOL radical,[12] amounting to the same order of magnitude as in the BDPA-Bz radical.[2,13]

In conclusion, the temperature dependence of the g-values of the organic free radical, p-Cl-BDPA,can provide a method of discrimination between the short- and long-range-ordering effects, and p-Cl-BDPA can be regarded as a one-dimensional organo-magnetic material at first approximation, but its interchain interaction is appreciable, amounting to the order of $|J'/J|=0.2$; thus, $|J'|/k=0.88$ K.

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TABLE 1. INTRACHAIN- AND INTERCHAIN-EXCHANGE INTERACTION PARAMETERS OF SEVERAL ORGANIC FREE RADICALS

	J/k	$T_N{}^{c)}$	J/kT_N	$\|J'/J\|$	$\|J'\|/k$
p-Cl-BDPA	−4.4 K	3.25 K	−1.4	0.2	0.88 K
BDPA-Bz[a]	−4.4 K	1.695 K	−2.6	0.04	0.18 K
TANOL[b]	−5.0 K	0.49 K	−10.2	0.004	0.02 K

a) 1,3-Bisdiphenylene-2-phenyl-allyl and benzene complex. b) 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl. c) Antiferromagnetic phase transition temperature.