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Magnetic Phase Transition of the 1,3-Bis(2,2′-biphenylene)-2-phenylallyl (BDPA) Complex with Acetone

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The magnetic susceptibility of the 1,3-bis(2,2′-biphenylene)-2-phenylallyl (BDPA) complex with acetone exhibited a broad maximum at around 10 K, characterized by a linear Heisenberg-type magnetic interaction; a discontinuity in $d\chi/dT$ at ca. 2.8 K was observed, suggesting an antiferromagnetic spin-ordering. The magnetic behavior in the paramagnetic region is discussed in terms of the Weiss temperature, exchange interaction parameters, and a divergent character in the ESR linewidth and g-value. The spin-ordered state was ascertained by antiferromagnetic resonance, in which one of the resonance branches showed a rapid temperature dependence, indicating a transition temperature of 3.1 K. Compared with the magnetic data of the BDPA–benzene complex, it was concluded that the magnetic characteristics were greatly influenced by solvent complexation and that the magnetic parameters in both the paramagnetic and antiferromagnetic regions were enhanced by changing the incorporated solvent from benzene to acetone.

The magnetic properties of molecular materials have attracted considerable interest during the last few years.[1] Any unpaired electrons of magnetic molecular materials usually reside in π-orbitals, and are delocalized within the molecule. This situation makes magnetic interactions in these systems complicated, but characteristic. It has been pointed out that magnetic phase transitions take place in several organic free radicals at low temperature. In many cases although spin-ordered phases are antiferromagnetic, ferromagnetic spin-ordering, though uncommon, is observed.[1]

1,3-Bis(2,2′-biphenylene)-2-phenylallyl (BDPA)[2] is one of the typical organic free radicals which have many of the characteristics mentioned above. The magnetic susceptibility of BDPA fits well to a Heisenberg antiferromagnetic chain with $J/k=-8.5$ K,[3] where J is an exchange coupling constant between two neighboring molecules in a magnetic chain, as

$$\mathscr{H}=-2J\boldsymbol{S}_1\cdot\boldsymbol{S}_2. \qquad (1)$$

When BDPA is crystallized from a benzene solution, it yields a BDPA–benzene 1:1 complex (BDPA–Bz) which exhibits a weak intrachain exchange interaction, $J/k=-4.4$ K,[3] and orders as a three-dimensional Heisenberg antiferromagnet at $T_N=1.695$ K.[4] Spectroscopic evidence for a spin-ordered state was afforded from antiferromagnetic resonance (AFMR) spectra,[5] and an interchain exchange interaction, which induces magnetic phase transitions in the magnetic chain systems, was estimated to be $|J'|/k=0.18$ K.[6]

On the other hand, chloro-substituted BDPA, 1,3-bis(2,2′-biphenylene)-2-(p-chlorophenyl)allyl (p-Cl-BDPA),[2] showed the same order of an intrachain exchange interaction as that of BDPA–Bz. The antiferromagnetic phase transition, however, took place at a higher temperature $T_N=3.25$ K,[3,7] indicating a stronger interchain exchange interaction for p-Cl-BDPA. $|J'|/k$ was predicted to be 0.88 K.[6] Heat-capacity measurements under hydrostatic pressures disclosed that the Néel temperature is enhanced up to 5.03 K at 5.4 kbar.[8]

As these magnetic data indicate, BDPA is one of the interesting molecular materials which have been studied extensively from the point of view of a short-range spin ordering as well as of long-range one. In view of the variety of the magnetic properties of BDPA and its derivatives, we investigated BDPA complexes with other solvents, such as acetone (BDPA–Ac). Compared with the BDPA–Bz complex, BDPA–Ac exhibited enhanced intrachain and interchain exchange interactions and a higher phase-transition temperature.

Experimental

Sample Preparation. BDPA was prepared according to a procedure of Kuhn and Neugebauer.[9] We purified the radical through recrystallizing crude material from benzene a few times. When BDPA is crystallized from benzene, it forms a 1:1 solvent complex (BDPA–Bz). BDPA–Ac was obtained from the two methods as follows. First, BDPA–Bz was heated at about 90 °C in vacuo for several hours. The solvent-free BDPA thus obtained was recrystallized two times from its acetone solution. In the second method BDPA–Bz was directly recrystallized from its acetone solution. The process was repeated several times. Elemental analyses indicated a 1:1 acetone complex with BDPA; Found: C, 91.08; H, 5.68%. Calcd for $C_{36}H_{27}O$: C, 90.91; H, 5.72%. The radical concentration determined from magnetic susceptibility measurements was evaluated to be almost 100% based on the 1:1 complex molecule. The magnetic data of both samples were not substantially different.

Magnetic Susceptibility Measurements. Magnetic susceptibility measurements were carried out between 1.5—77 K by means of a magnetic torsion balance (described elsewhere[10]) on 76 mg powder samples in a magnetic field of 880 mT. The temperatures were measured with a germanium resistor and an AuCo–Cu thermocouple calibrated from the magnetic susceptibility of Mn(II) Tutton salt and/or the vapor pressures of liquid helium, hydrogen, and nitrogen. The diamagnetic correction of -2.95×10^{-4}

emu mol^{-1} was made using Pascal's constants.

ESR and AFMR Measurements. ESR and AFMR spectra were observed between 2—300 K using an X-band spectrometer (JEOL-ME-3X) with 80 Hz field modulation. The cavity of the TE_{102} mode was immersed in a liquid-helium bath. The temperatures were also measured with a germanium resistor and/or an AuCo–Cu thermocouple attached to the cavity wall. The magnetic fields and g-values were calibrated from the standard signals of Mn^{2+} diluted in MgO (1/2000) and of peroxylamine disulfonate ion.

Results and Discussion

Magnetic Susceptibility. The magnetic susceptibility of BDPA–Ac between 1.5—77 K is shown in Fig. 1, in which the plotting is logarithmic in both the abscissa and ordinate coordinates. The magnetic susceptibility starts to deviate from the Curie–Weiss law at about 20 K and shows a round maximum at 10.0 K. The maximum susceptibility was 140×10^{-4} emu mol^{-1}. After this maximum the susceptibility gradually decreases down to 2.8 K and then slightly increases again. This means a discontinuous change in the slope of the magnetic susceptibility ($d\chi/dT$) at 2.8 K. The reciprocal magnetic susceptibility vs. temperature depicted in Fig. 2 gives a Weiss constant of −13 K, which is larger in absolute value than any other BDPA compounds (−8 K for BDPA and BDPA–Bz and −6 K for p-Cl-BDPA). The broad maximum in the magnetic susceptibility took place at a temperature of 10.0 K, which is almost the same as that for BDPA (10.9 K). In the paramagnetic region above 2.8 K the magnetic susceptibility was analyzed on the basis of the linear Heisenberg chain model proposed by Bonner and Fisher.[11] The result is indicated in Fig. 1 using a dashed line. Agreement is good, especially above 6 K. According to the theory, the exchange interaction parameter (J) along the chain included in the Eq. 1 is related to the temperature (T_m) at which the maximum susceptibility appears, as follows:

$$kT_m/|J| = 1.282. \tag{2}$$

This relation yields $J/k=-7.8$ K for BDPA–Ac, which is slightly smaller in absolute value than $J/k=-8.5$ K for BDPA. The exchange interaction in the acetone complex, however, is greatly enhanced when compared with that in the benzene complex ($J/k=-4.4$ K). The exchange interaction parameter is summarized and compared with those for other organic free radicals in Table 1.

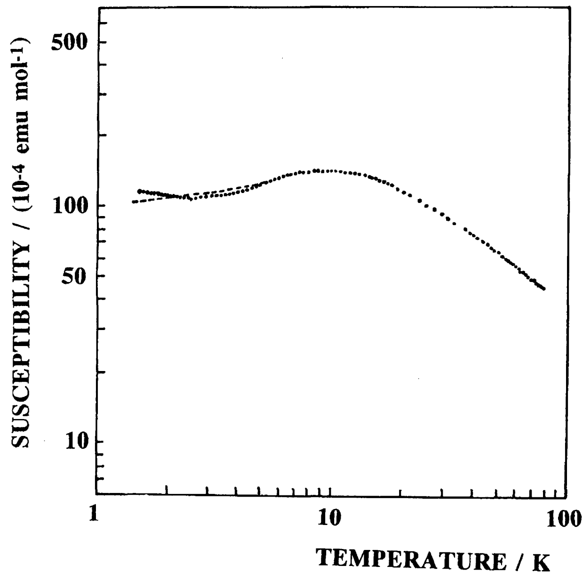

Fig. 1. Temperature dependences of the magnetic susceptibility of BDPA–Ac and the theoretical one (dashed line) based on the linear Heisenberg model.

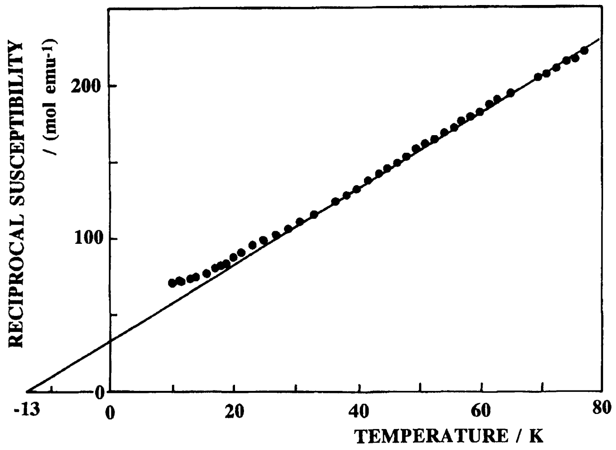

Fig. 2. Temperature dependence of the reciprocal magnetic susceptibility of BDPA–Ac. The straight line indicates a Weiss constant of −13 K.

The discontinuity in the slope of the magnetic susceptibility may suggest an antiferromagnetic phase transition at around 2.8 K, which could be confirmed from the spectroscopic experiment described below. The magnetic phase-transition temperature is also greatly enhanced from 1.695 K of BDPA–Bz. This considerable increase in the magnetic transition temperature may be attributed mainly to an enhanced exchange interaction within the magnetic chain. The interchain exchange in-

Table 1. Exchange Interaction Parameters and Magnetic Phase Transition Temperature for Several Organic Free Radical Antiferromagnets

Compound	J/k/K	T_N/K	$J/k/T_N$	$\|J'/J\|$	$\|J'\|/k$/K
BDPA–Ac	−7.8	3.0	−2.6	0.05	0.39
BDPA–Bz[a]	−4.4	1.695	−2.6	0.05	0.22
BDPA	−8.5	—	—	—	—
p-Cl-BDPA	−4.4	3.25	−1.4	0.2	0.88
TANOL[b]	−5.1	0.49	−10.2	0.004	0.02
TPV[c]	−6.0	1.70	−3.5	0.03	0.18

a) $|J'/J|=0.05$ is better than 0.04 listed in Ref. 6.
b) 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl. See Ref. 6.
c) 2,4,6-triphenylverdazyl. See Ref. 8b.

teraction, however, is also important for increasing the phase-transition temperature. This is discussed below.

ESR in the Paramagnetic Phase. The ESR spectra in the paramagnetic region comprised a single Lorenzian line with a narrow linewidth and an isotropic g-value (2.0024). We show temperature variations in the linewidth and g-value in Fig. 3. Below a temperature of T_m the linewidth increases rapidly, showing a divergent behavior towards 3.0 K. The g-value, on the other hand, decreased with decreasing temperatures down to 3.2 K. This behavior was discussed previously in the case of p-Cl-BDPA as being due to a short-range spin ordering within the magnetic chain.[6] The g-value starts to increase below 3.2 K, corresponding to the linewidth divergence toward 3.0 K. Both of the temperature variations in the vicinity of 3 K may be critical phenomena, indicating a sign of the magnetic phase transition predicted based on the magnetic susceptibility.

AFMR in the Antiferromagnetic Phase. The ESR spectra in the vicinity of the magnetic phase-transition temperature are shown in Fig. 4. The broad Gaussian-type absorption line (Fig. 4 (a) at 3.18 K) splits into two absorptions, one with a narrow linewidth and a small intensity and one with a remarkably broad linewidth. Moreover, the latter spectrum has a strong temperature dependence. The broad bump shifts to both sides, just like a powder pattern of the antiferromagnetic resonances for p-Cl-BDPA[12] and BDPA–Bz.[5] The component shifting downfield belongs to one of the principal branches, in which the magnetic field is applied along the hard axis of the orthorhombic anisotropy in the antiferromagnetically spin-ordered state.[13] The resonance equation is

$$(\omega/\gamma)^2 = H^2 + C_2, \tag{3}$$

where ω is the frequency of an applied oscillating field and γ is the magnetomechanical ratio. The parameter C_2 includes the orthorhombic anisotropy multiplied by the exchange field.[12,13] The resonance shift is therefore due to the internal magnetic field, which is relevant to the sublattice magnetization of antiferromagnets. This temperature deviation of the resonance positions is depicted in Fig. 5. By interpolation of the shift, the magnetic phase transition temperature can be determined, giving T_N=3.1 K. This phase-transition temperature is slightly higher than that determined from the magnetic susceptibility, but is in good agreement with the value predicted from the ESR measurements in the paramagnetic region.

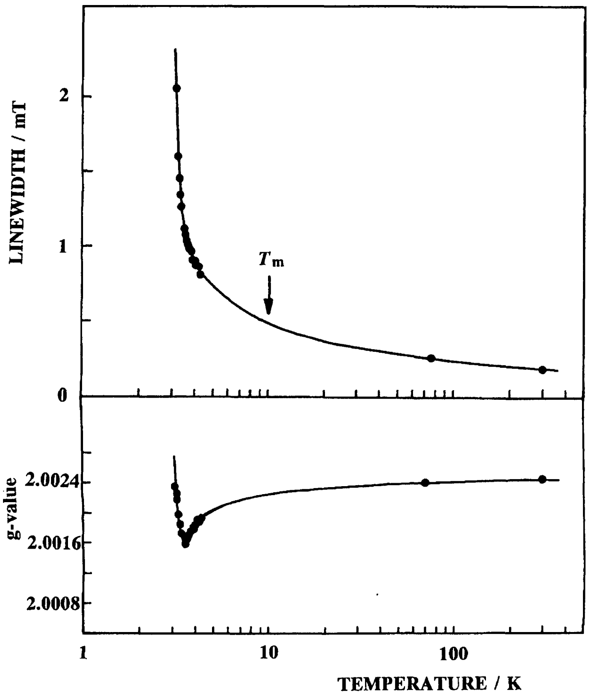

Fig. 3. Temperature dependences of the ESR linewidth and the g-value of BDPA–Ac in the paramagnetic region. Both of them are diverging at 3.0 K.

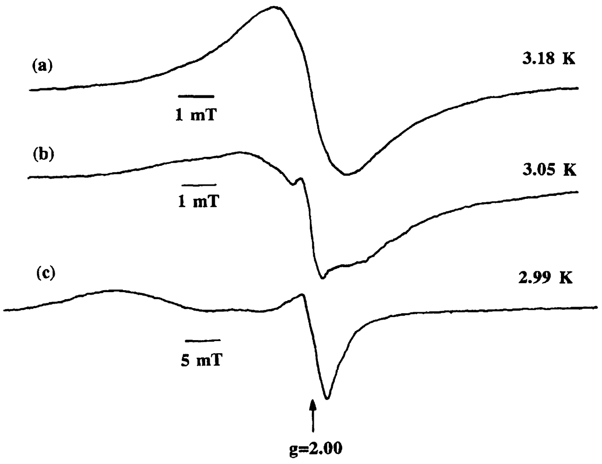

Fig. 4. ESR and AFMR spectra of BDPA–Ac in the vicinity of the magnetic phase transition temperature.

Magnetic Phase Transition. Both the magnetic susceptibility and the ESR measurements indicate an antiferromagnetic phase transition in BDPA–Ac. The determined transition temperatures are slightly different, depending on the experimental methods. The discontinuity in $d\chi/dT$ appears at lower temperature, whereas the internal magnetic field due to the long-range spin-ordering starts to be exerted on the electron spins at a higher temperature. The shift in the magnetic resonance due to the internal magnetic field also includes a contribution from the short-range spin ordering which occurs at around or below 10 K. The higher phase-transition temperature, therefore, may be predicted from the spectroscopic measurements. Heat capacity measurements are necessary to accurately determine the phase-transition temperature.

Above 5 K the magnetic susceptibility is well fitted to the linear Heisenberg model with the exchange coupling constant, J/k=−7.8 K, within the magnetic chain. It is

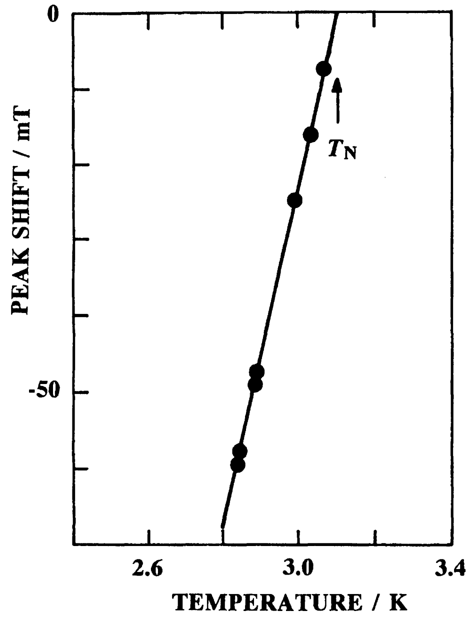

Fig. 5. Peak shift of the low-field branch in the AFMR of BDPA–Ac in the antiferromagnetic region.

well established that the interchain exchange coupling constant (J') can trigger a magnetic phase transition, and it is possible to speculate the value of J', if one assumes appropriate models.[14] We used Oguchi's relationship between J, J', and T_N deduced from the Green-function method,[15] as follows:

$$kT_N/|J| = 4S(S+1)/3I(\eta). \qquad (4)$$

Here, $I(\eta)$ is the following integral with $\eta=|J'/J|$:

$$I(\eta) = \frac{1}{\pi^3}\int\int_0^{\pi}\int \frac{dq_x dq_y dq_z}{\eta(1-\cos q_x)+\eta(1-\cos q_y)+\eta(1-\cos q_z)}. \qquad (5)$$

In the case of BDPA–Ac the left-hand side of the Eq. 4 is equal to 0.385 ($|J|/k/T_N=2.6$), assuming a phase-transition temperature of 3.0 K. Thus, $|J'/J|=0.05$ is predicted, giving $|J'|/k=0.39$ K. The ratio of these exchange interactions for BDPA–Ac is the same as that for BDPA–Bz, and is much smaller than that for *p*-Cl-BDPA (Table 1). By changing the solvent incorporated in the organic free radical (BDPA) the magnetic properties concerning J, T_N, and J' were varied, and all of these parameters for the acetone complex became large in the absolute magnitude. Interestingly, as can be seen from Table 1, the enhanced factor is almost the same: the exchange interactions (J and J') and the transition temperature (T_N) for BDPA–Ac increased by a factor of 1.77, compared with those for BDPA–Bz. A correlated enhancement like this would suggest the law of the corresponding states in the various solvent complexes with BDPA. Accordingly, the ratios $J/k/T_N$ and $|J'/J|$ remain constant (−2.6 and 0.05, respectively). This fact means no variation regarding the magnetic low-dimensionality in the exchange interaction schemes for these solvent-complexed organic free radicals. On the other hand, the enhanced magnetic interactions by a factor of 1.77 are remarkable, and would promise further investigations concerning other solvent incorporations as well as crystallographic analyses of these crystals.

In conclusion, we have shown the magnetic properties of the BDPA acetone complex based on magnetic susceptibility and ESR observations in the paramagnetic as well as in antiferromagnetic regions. By changing the incorporated solvent in the BDPA radical, the magnetic characteristics were remarkably changed. The intra- and inter-chain interactions (J and J') are increased by a factor of 1.77 for the acetone complex, as compared with those for the benzene complex. Accordingly, the magnetic phase transition temperature is also enhanced from 1.695 K (benzene) to ca. 3.0 K (acetone) by the same factor. On the other hand, the degree of magnetic low-dimensionality in the exchange interaction network was not significantly influenced, keeping the same ratio of $|J'/J|$. Judging from the same values of $J/k/T_N$, $|J'/J|$, or $|J'|/k/T_N$ for BDPA–Bz and BDPA–Ac, the law of the corresponding states is likely to hold for the BDPA–solvent complexes.

References

1) a) D. Gatteschi, O. Kahn, J. S. Miller, and F. Palacio, "Magnetic Molecular Materials," NATO ASI Series E: Applied Sciences, Kluwer Academic Publishers, The Netherlands (1991), Vol. 198; b) "The Proceedings of International Symposium of Molecular Based Magnetic Materials," Tokyo, 1992, *Mol. Cryst. Liq. Cryst.*, **232—233** (1993).

2) Abbreviated as BDPA which has been conventionally used following 1,3-bisdiphenylene-2-phenylallyl.

3) J. Yamauchi, *Bull. Chem. Soc. Jpn.*, **44**, 2301 (1971).

4) W. Duffy, Jr., J. F. Dubach, P. A. Pianetta, J. F. Deck, D. L. Strandburg, and A. R. Miedema, *J. Chem. Phys.*, **56**, 2555 (1972).

5) J. Yamauchi, *Phys. Lett. A*, **70**, 238 (1979).

6) J. Yamauchi and Y. Deguchi, *Bull. Chem. Soc. Jpn.*, **50**, 2803 (1977).

7) J. Yamauchi, K. Adachi, and Y. Deguchi, *J. Phys. Soc. Jpn.*, **35**, 443 (1973).

8) a) J. Yamauchi, K. Takeda, and M. Inoue, *Chem. Lett.*, **1990**, 1551; b) J. Yamauchi, K. Takeda, and K. Konishi, *Mol. Cryst. Liq. Cryst.*, **233**, 97 (1993).

9) R. Kuhn and A. Neugebauer, *Monatsh. Chem.*, **95**, 3 (1964).

10) M. Mekata, *J. Phys. Soc. Jpn.*, **17**, 796 (1962).

11) J. C. Bonner and M. E. Fisher, *Phys. Rev. Sect. A.*, **135**, A640 (1964).

12) J. Yamauchi, *J. Chem. Phys.*, **67**, 2850 (1977).

13) T. Nagamiya, K. Yoshida, and R. Kubo, *Adv. Phys.*, **4**, 1 (1955).

14) R. L. Carlin, "Magnetochemistry," Springer-Verlag, Berlin (1986).

15) T. Oguchi, *Phys. Rev. Sect. A.*, **133**, A1098 (1963).