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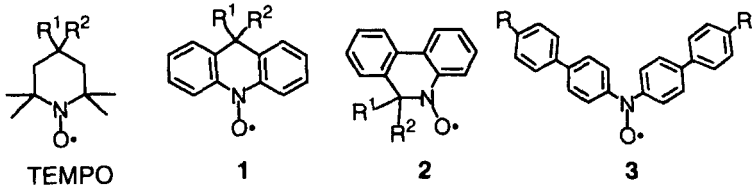
The crystal of 9,9-dipropyl-9,10-dihydroacridin-10-yloxyl exhibited a positive Weiss constant (+0.77 K) due to a 3-D network of ferromagnetic interactions. The crystal of 6,6-bis(*p*-ethylphenyl)-5,6-dihydrophenanthridin-5-yloxyl was revealed to possess a ferromagnetic dimer structure with $2J/k_B$= +3.5 K. Several bisbiphenylyl nitroxide radicals showed ferromagnetic interaction.

Keywords: organic radical; nitroxide; ferromagnetic interaction

INTRODUCTION

The research on purely organic magnetic materials has greatly progressed in recent years[1]. We have reported organic ferro- and metamagnets having a TEMPO radical group[2]. Although TEMPO radicals are extremely stable so that we could easily access the TEMPO-based materials, they are thought to have a few weak points bringing about low T_C or T_N. The sterically bulky substituents such as four methyl groups in a TEMPO moiety pull the N-O radical centers apart (typically 6 Å[2]), and the spin densities on aliphatic substituents are generally small, compared to those on aromatic substituents in π-conjugated radicals. The intermolecular exchange interaction is considered to be proportional to the polarized spin densities at contacting atoms[3]. For developing high-T_C organic magnets, we turn our attention to π-conjugated radicals, especially to aryl nitroxides[4].

We have recently reported that the magnetism of BTAO (**1**, $R^1 = R^2 = p$-tolyl) was analyzed by a ground triplet-state dimer model with $2J/k_B = +18$ K, which is consistent with the dimer structure determined by crystallographic analysis[5]. This interaction is much larger than those observed for TEMPO-based magnets. We report here the magnetic properties of the related systems, disubstituted dihydroacridinoxyls (**1**), dihydrophenanthridinoxyls (**2**), and bis(biphenylyl) nitroxides (**3**), and also discuss possible mechanisms of intermolecular magnetic interactions.



RESULTS AND DISCUSSION

Dihydroacridinoxyls

Since we reported the ferromagnetic dimer of BTAO[5], we have investigated its derivatives with less bulky substituents than *p*-tolyl in order to obtain stronger ferromagnetic interaction. Radical DPAO (**1**, $R^1 = R^2 = n$-C_3H_7; 9,9-dipropyl-9,10-dihydroacridin-10-yloxyl) was prepared by photochemical reaction of acridine and butanoic acid according to Noyori's method[6], followed by oxidation of the resultant amine with *m*-chloroperbenzoic acid. The sample was purified by recrystallization from a dichloromethane-hexane mixed solvent (red prisms, mp. 146-148 °C).

The static magnetic susceptibility (χ_{mol}) was measured on a SQUID magnetometer down to 1.8 K at 5 kOe. FIGURE 1 shows that, with decreasing temperature, the product $\chi_{mol}T$ of DPAO monotonously increased and reached 0.59 cm^3 K mol^{-1} at 1.8 K. The plot of the reciprocal magnetic susceptibility against temperature gave a positive Weiss temperature (θ) of +0.77 K. This finding indicates the presence of intermolecular ferromagnetic interaction. Furthermore, the $\chi_{mol}T$ value larger than 0.5 cm^3 K mol^{-1} at 1.8 K means that more than two molecules are ferromagnetically correlated, in contrast to the case of BTAO having a dimer structure.

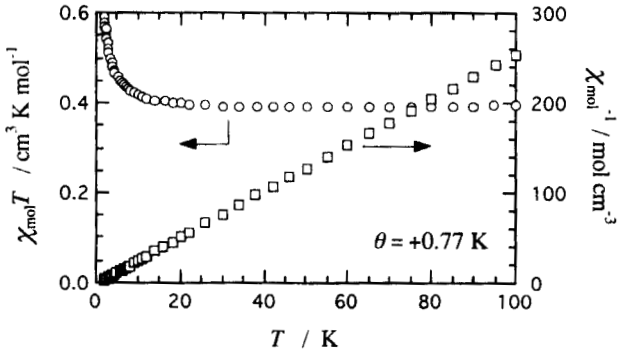


FIGURE 1 Temperature dependence of $\chi_{mol}T$ and χ_{mol}^{-1} of DPAO.

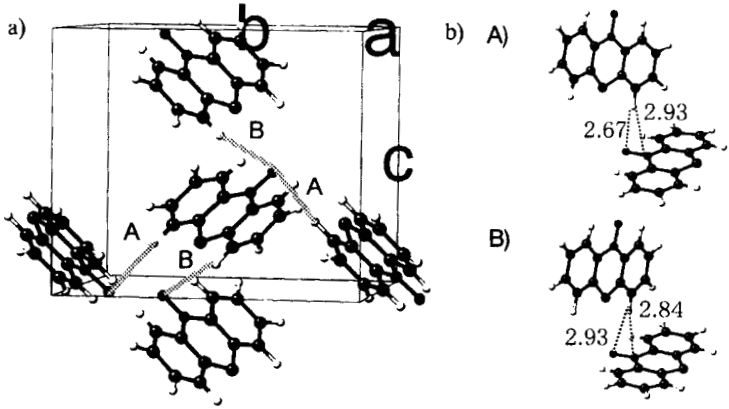


FIGURE 2 a) Molecular arrangement in the crystal of DPAO. Propyl groups are omitted for clarity. Dotted lines indicate relatively short distances between nitroxide O and aromatic H atoms. b) Detailed geometries for A and B types of the molecular locations. N···H and O···H distances are shown in Å with dotted lines.

We initially expected pancake-type stacking of aromatic rings which is favorable for strong magnetic interaction according to McConnell's model[3]. In fact, such stacking of acridine skeletons was found in the crystal of BTAO[5]. However, neighboring acridine skeletons of DPAO were not arranged to be parallel, as shown in FIGURE 2a[7].

The nearest O···O distance was 6.16 Å. There seems to be no direct interaction among the N-O sites, because the theoretical model calculations indicate that the through-space exchange and dipole interactions between two nitroxide radicals are negligible when the O···O distance is larger than 5 Å[2,8]. Rather short atomic distances were found between the N-O sites and aromatic hydrogen atoms. A possible interpretation of the ferromagnetic interaction is as follows.

FIGURE 2b shows intermolecular atomic distances of N···H and O···H for the first and second nearest locations between N-O groups and hydrogen atoms. For both locations A and B, three atoms H, O, and N approximately forms an isosceles triangle. The singly occupied molecular orbital of DPAO has a π^* character at the NO site, indicated by semi-empirical UHF/PM3 MO calculation (the coefficients of $2p_z$(O) and $2p_z$(N) were +0.44 and -0.60, respectively)[9]. The hydrogen 1s and nitroxide π^* orbitals can not have any appreciable orbital overlap due to the symmetrical orthogonality.

The solution ESR spectrum of DPAO (benzene, room temperature) indicated g = 2. 0050, a_N = 8.82, $a_{Ho,p}$ = 2.37, and a_{Hm} = 0.77 G, in good agreement with those of typical diphenyl nitroxides[5,10]. The sign of the hyperfine splitting constants or the spin densities could not be determined by ESR data alone. The through-bond spin polarization occurs from a radical center onto the conjugated benzene rings, giving alternating spin density[11]. The C and H atoms at a *meta*-position are known to possess negative and positive spin densities, respectively, in phenyl nitroxides[10]. Therefore, the H atom in the above triangle, which corresponds to a *meta*-H atom, have a positive spin density.

The exchange interaction J is generally expressed as the sum of a positive contribution J_F stabilizing the triplet state and a negative contribution J_{AF} stabilizing the singlet state [Eq. (1)][12]. The J_F term comes from the exchange integral k. The J_{AF} term approximately increases in proportion to both the overlap integral S and resonance integral β.

$$J = J_F + J_{AF} = k + 2\beta S \qquad (1)$$

When the second term is negligible due to the orbital orthogonality, the interaction should be ferromagnetic. Caneschi et al. reported the successful application to the transition metal complexes in which the nitroxide O atom was coordinated to the metal center[13]. The absence of the orbital overlap between the magnetic d-orbitals of the transition metal ion and the π* orbital of the nitroxide radical center causes ferromagnetic coupling between them. In the present case, the polarized spin density at the *meta*-H atom is positive, and the spin density at the NO site in a neighboring molecule should be positive by through-space ferromagnetic coupling. The interaction J was much smaller than those of the nitroxide-metal complexes, probably because the exchange occurs in a non-covalent manner, as well as because the polarized spin density at the H atom is small.

As FIGURE 2a shows, the contacts A and B run along the b and c axes, respectively, by 2_1 symmetry operation. A closer look at the molecular arrangement informs us that the crystal of DPAO has a three-dimensional network of ferromagnetic interactions.

The magnetic properties of other alkylated derivatives should be noted. The corresponding dimethyl (**1**, $R^1 = R^2 = CH_3$), diethyl (**1**, $R^1 = R^2 = C_2H_5$), and dibutyl (**1**, $R^1 = R^2 = n\text{-}C_4H_9$) derivatives showed intermolecular antiferromagnetic interaction, as indicated by θ = -13, -4.6, and -1.6 K, respectively. The crystals of alkyl phenyl derivatives (**1**, R^1 = Ph) with R^2 = CH_3, n-C_3H_7, n-C_5H_{11} showed ferromagnetic interaction, whereas those with $R^2 = C_2H_5$, n-C_4H_9 showed antiferromagnetic interaction.

Dihydrophenanthridinoxyls

Radical BEPPO (6,6-bis(*p*-ethylphenyl)-5,6-dihydrophenanthridin-5-yloxyl; **2**, $R^1 = R^2 = p\text{-}C_2H_5\text{-}C_6H_4$) was prepared according to the reported method[14] by using p-EtC_6H_4MgBr in place of PhMgBr, and purified by recrystallization from a dichloromethane-hexane mixed solvent in a refrigerator (red prisms, mp. 151-153°C).

As FIGURE 3 shows, the product $\chi_{mol}T$ of BEPPO monotonously increased with decreasing temperature, and reached 0.48 cm^3 K mol^{-1} at 1.8 K. The plot of the reciprocal magnetic susceptibility against temperature gave a

positive Weiss temperature of +0.42 K. The solid line in FIGURE 3 was drawn by a best fit to the Bleaney-Bowers equation [Eq. (2)][15] with $2J/k_B$ = +3.5 K. No inter-dimer interaction was obtained. The calculated line reproduced well the experimental data. This analysis is supported by the crystal structure analysis.

$$\chi = \frac{2N g^2 \mu_B^2}{k_B T} \frac{1}{3 + \exp(-2J/k_B T)} \qquad (2)$$

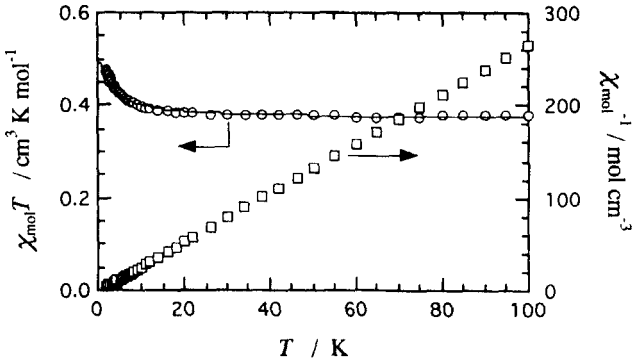


FIGURE 3 Temperature dependence of $\chi_{mol}T$ and χ_{mol}^{-1} of BEPPO. The solid line is a calculated $\chi_{mol}T$ curve based on the Bleaney-Bowers equation with $2J/k_B$ = +3.5 K.

The molecular arrangement in the crystal of BEPPO is shown in FIGURE 4a[16]. The first and second nearest O···O distances were 6.94 and 7.73 Å, respectively. FIGURE 4b shows two BEPPO molecules projected to an averaged phenanthridine plane. The crystal inversion center resides at the center of this dimeric structure. The separation between two averaged phenanthridine rings was 3.51 Å which is close to the sum of the van der Waals radii (3.4 Å). The nearest intermolecular atomic distance was 3.50 Å for C(1)···C(10b'). Rather short distances 3.51, 3.52, and 3.55 Å were found for C(1)···C(10a'), C(2)···C(10'), and C(1)···C(1'), respectively.

The solution ESR spectrum of BEPPO (benzene, room temperature) was reproduced by simulation with g = 2.0057, a_N = 10.73 G, $a_{H(2)} = a_{H(4)}$ = 2.72 G, $a_{H(1)} = a_{H(3)}$ = 0.98 G, and $a_{H(8)} = a_{H(10)}$ = 0.32 G. These values deviate

only slightly from those of the 6,6-diphenyl derivative[14]. The MacLachlan[17,18] and UHF/PM3 calculations[9] of BEPPO suggested the

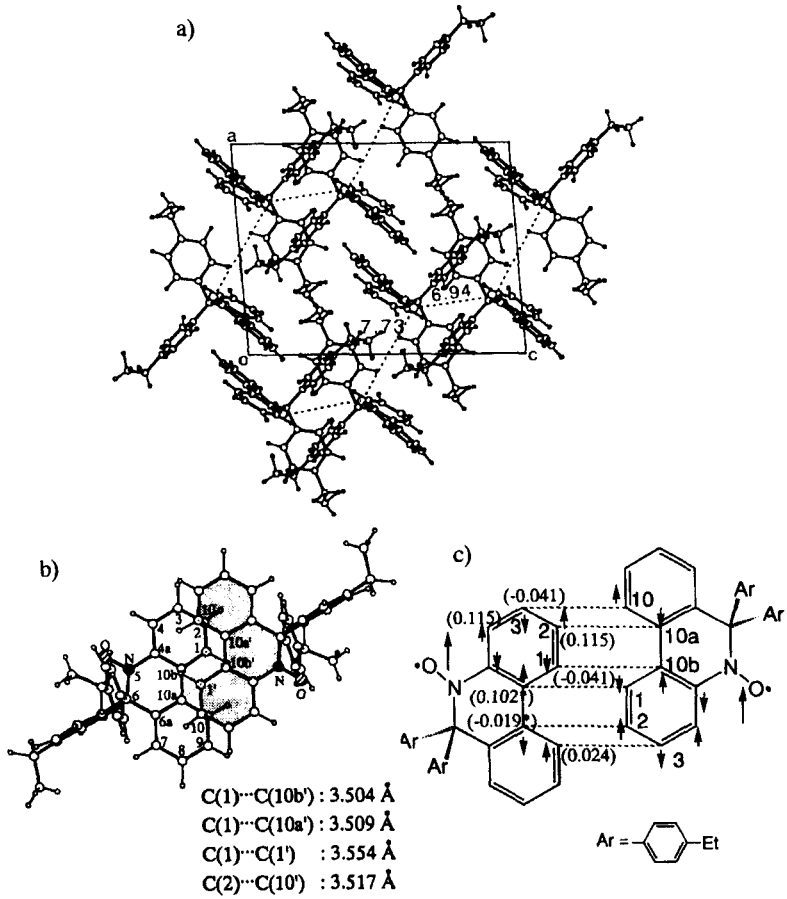


FIGURE 4 a) Crystal structure of BEPPO viewed along the *b* axis. Intermolecular O···O distances are indicated in Å with dotted lines. b) Molecular arrangement of two BEPPO molecules. One phenanthridine ring is shaded. Intermolecular atomic distances are indicated. c) Exchange mechanism in the dimeric structure of BEPPO based on the spin polarization. The spin densities determined by solution ESR spectra and MO calculation (asterisks) are shown in parentheses.

alternation of the sign on the π-conjugated skeleton. Thus, the McConnell equation with $|Q| = 23.7$ G[19] gave the spin densities (ρ_C) shown in FIGURE 4c. For further discussion, we use the values of the MacLachlan calculation for the quaternary carbon atoms C(10a) and C(10b) because of good agreement between the experiment and calculation[20].

The ferromagnetic interaction within the dimeric BEPPO molecules can be explained as follows. The exchange interactions through the shortest C(1)···C(10b) and through comparably short C(1)···C(10a), C(1)··· C(1), and C(2)···C(10) are expected to be ferromagnetic and antiferromagnetic, respectively. However, the former contribution should be dominant, because the interactions are determined not only by atomic distances but by the product of spin densities ρ_i and ρ_j at two interacting atoms [Eq. (3)[3]]; the product $|\rho_{C(1)}\rho_{C(10b)}|$ is the largest among them. Other ferromagnetic pathways through C(2)···C(10a) and C(3)···C(10) may play an auxiliary role (FIGURE 4c).

$$H^{AB} = -S^A \bullet S^B \Sigma J_{ij}{}^{AB} \rho_i{}^A \rho_j{}^B \qquad (3)$$

The slippage from an ideal atom-over-atom overlap is responsible for the rather small ferromagnetic interaction. In the present case, the balance is slightly in favor of ferromagnetic interaction.

Bis(biphenylyl) Nitroxides

Bis(biphenylyl) nitroxides (**3**) were revealed to have a high probability showing ferromagnetic interaction. All of the 4'-*n*-alkylated homologues investigated here showed ferromagnetic interactions.

The samples were prepared from 4'-alkylbiphenyl-4-yl magnesium bromide and pentyl nitrite according to the method reported by Berti[21]. They were recrystallized from a dichloromethane-benzene or -hexane mixed solvent to give reddish purple thin plates (**3**, R = n-C_nH_{2n+1}), mp. 232-234 (n = 0), 255-258 (n = 1), 221-223 (n = 2), 221-223 (n = 3), 243-245 (n = 4), 210-211 (n = 5), and 204-207 °C (n = 7).

The results of magnetic measurements summarized in FIGURE 5 clearly indicate that they showed ferromagnetic interaction. With decreasing temperature, the $\chi_{mol}T$ values monotonously increased for all of the alkylated

derivatives, except for **3** (R = Me) whose $\chi_{mol}T$ value had a maximum at 2.6 K. Ferromagnetic interactions were also found in the crystals of **3** (R = Br, CH_3O) and bis(*p*-phenoxyphenyl) nitroxide.

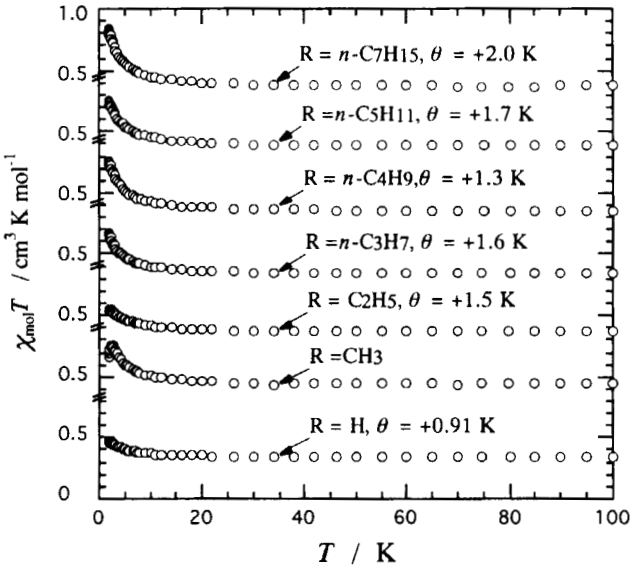


FIGURE 5 Temperature dependence of $\chi_{mol}T$ of **3** (R = n-C_nH_{2n+1}; n = 0 - 5, 7).

Although the crystal structures of these alkylated series could not been determined so far, an isostructure of these crystals is strongly suggested. More interestingly, the Weiss temperature roughly tends to increase with an increase of the length of the alkyl group. It may be pointed out that the "molecular fastener"[22] effect is operative; that is to say, the central skeletons were fastened with the attractive van der Waals interaction among the *n*-alkyl chain substituents.

References

[1] Special Issues on *"Proceedings of the Vth International Conference on Molecule-Based Magnets,"* ed by K. Itoh, J.S. Miller, and T. Takui, *Mol. Cryst. Liq. Cryst.*, **305–306** (1997).

[2] T. Nogami, T. Ishida, M. Yasui, F. Iwasaki, N. Takeda, M. Ishikawa, T. Kawakami, and K. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **69,** 1841 (1996); K Togashi, R. Imachi, K. Tomioka, H. Tsuboi, T. Ishida, T. Nogami, N. Takeda, and M. Ishikawa, *Bull. Chem. Soc.*

Jpn., **69,** 2821 (1996); T. Nogami and T. Ishida, *Mol. Cryst. Liq. Cryst.*, **296,** 305 (1997).
[3] H.M. McConnell, *J. Chem. Phys.*, **39,** 1910 (1963).
[4] For recent results on novel π-conjugated radicals, benzimidazole-based nitronyl nitroxides, see D. Shiomi *et al.*, this proceedings.
[5] R. Imachi, T. Ishida, M. Suzuki, M. Yasui, F. Iwasaki, and T. Nogami, *Chem. Lett.*, 743 (1997).
[6] R. Noyori, M. Kato, M. Kawanisi, and H. Nozaki, *Tetrahedron*, **25,** 1125 (1969).
[7] Crystallographic data of DPAO: orthorhombic, $P2_12_12_1$, a = 12.060(3), b= 12.466(3), c = 10.892(3) A, V = 1637.6(7) Å^3, Z = 4, D_{calc} = 1.137 g cm^{-3}, R = 0.049 for 2092 observed reflections.
[8] T. Kawakami, S. Yamanaka, W. Mori, K. Yamaguchi, A. Kajiwara, and M. Kamachi, *Chem. Phys. Lett.*, **235,** 414 (1995).
[9] *MOPAC ver 6.0*, J. J. P. Stewart, QCPE #455.
[10] A.R. Forrester, S.P. Hepburn, and G. McConnachie, *J. Chem. Soc., Perkin Trans. I*, **1974,** 2213; J. Goldman, T.E. Petersen, and K. Torssell, *Tetrahedron*, **29,** 3833 (1973); J. Yamauchi, K. Okada, and Y. Deguchi, *Bull. Chem. Soc. Jpn.*, **60,** 483 (1987).
[11] H. Iwamura and N. Koga, *Acc. Chem. Res.*, **26,** 346 (1993) and references cited therein.
[12] O. Kahn, *Molecular Magnetism*, Chapt. 8, Sect. 8.4, pp. 150–154 (VCH Publishers, 1993).
[13] A. Caneschi, D. Gatteschi, and R.Sessoli, *Acc. Chem. Res.*, **22,** 392 (1989).
[14] M. Colonna, L. Greci, and M. Poloni, *J. Heterocycl. Chem.*, **17,** 1437 (1980).
[15] B. Bleaney and K.D. Bowers, *Proc. R. Soc. London, Ser. A*, **214,** 451 (1952).
[16] Crystallographic data of BEPPO: monoclinic, $P2_1/n$, a = 13.174(2), b = 9.656(2), c = 17.230(4) A, β = 94.36(2)°, V = 2185.4(7) Å^3, Z = 4, D_{calc}= 1.230 g cm^{-3}, R = 0.086 for 2467 observed reflections.
[17] A.D. MacLachlan, *Mol. Phys.*, **3,** 233 (1960).
[18] The spin density was calculated by use of λ = 1.2 ignoring the $(p\text{-EtC}_6\text{H}_4)_2\text{C}$ moiety. For the Hückel parameters of heteroatoms, see T. E. Gough and R. Puzic, *J. Magn. Reson.*, **23,** 31 (1976).
[19] H.M. McConnell, *J. Chem. Phys.*, **24,** 632, 764 (1956).
[20] Calculated values[18,19]: ρC(1) = –0.048, ρC(2) = 0.105, ρC(3) = –0.053, ρC(4) = 0.126, ρC(8) = 0.021, and ρC(10) = 0.024.
[21] C. Berti, *Synthesis*, **1983,**793.
[22] H. Inokuchi, G. Saito, P. Wu, K. Seki, T.B. Tang, T. Mori, K. Imaeda, T. Enoki, Y. Higuchi, K. Inaka, and N. Yasuoka, *Chem. Lett.*, **1986,** 1263.