Ferromagnetic Dimer of π-Conjugated Organic Free Radicals 9,9-Bis(*p*-tolyl)-9,10-dihydroacridin-10-yloxyl

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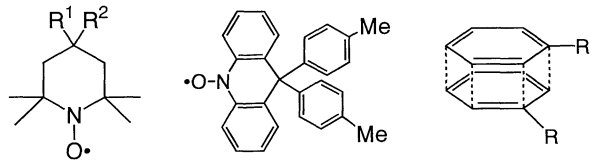
The magnetic property of the title radical crystals was analyzed by the Bleaney-Bowers equation with J/k_B = +8.85 K, which is consistent with the dimeric molecular arrangement with "pseudo-*ortho*" stacking determined by crystallographic analysis. The inter-dimer interaction was antiferromagnetic.

The research on organic/molecular magnetic materials has greatly progressed in recent years.[1,2] We have reported organic ferro- and metamagnets having a 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO) group.[3-5] Singly occupied molecular orbitals extended on π-conjugated systems are likely to overlap in crystal packing to give rise to intermolecular antiferromagnetic interactions, as exemplified by very recent results on 2,5,8-tri-*t*-butylphenalenyl reported by Nakasuji.[6] However, we have found ferromagnetic π-orbital-π-orbital interaction in the crystal of 6,6-bis(*p*-ethylphenyl)-5,6-dihydrophenanthridin-5-yloxyl.[7] A mechanism for ferromagnetic interaction in aromatic and olefinic radicals was proposed by McConnell in 1963,[8] and experimentally verified by Iwamura *et al.* in 1985[9] by using the [2.2]paracyclophane skeleton. In the course of our study on the magnetic properties of nitroxide radicals conjugated with aryl groups, we found fairly strong ferromagnetic interaction in the crystal of the title radical (abbreviated as BTAO hereafter), owing to pseudo-*ortho*[9] stacking of the acridine benzene rings.



Radical BTAO was prepared according to the reported method of the corresponding diphenyl derivative.[10,11] The sample was recrystallized from a dichloromethane-hexane mixed solvent (red prisms, mp 202-204 °C).

The solution ESR spectrum of BTAO (benzene, room temperature) was perfectly reproduced by the simulation with g = 2.0053, a_N = 8.94 G, $a_{o\text{-H}}$ = $a_{p\text{-H}}$ = 2.32 G, and $a_{m\text{-H}}$ = $a_{m'\text{-H}}$ = 0.78 G, where *o*, *m*, and *p*-positions are defined with respect to the N-O site. These values are typical of diphenyl nitroxide derivatives.[12] The ENDOR[13] and NMR measurements[14] and MO calculations[12,15] of phenyl nitroxide derivatives indicate the spin density at the *m*-carbon atoms to be negative. The McConnell equation with $|Q|$ = 23.7 G[16] gave the spin densities of +0.098 for *o*- and *p*-carbon atoms and -0.033 for *m*-carbon atoms in BTAO.

The molecular arrangement in the crystal of BTAO is shown in Figure 1a.[17] The acridine rings are arranged in a face-to-face fashion, which affords an intermolecular interactive pathway. Figure 1b shows two BTAO molecules projected to an averaged acridine plane. The crystal inversion center resides at the center of this dimeric structure. The shortest intermolecular C···C atomic distances were 3.63 Å for C(2)···C(6') and 3.65 Å for C(3)···C(7'). The benzene rings are arranged to give two sets of pancakes, and the two radical centers are related as pseudo-*ortho* stacking via both acridine benzene rings in BTAO. The magnetic coupling is expected to be ferromagnetic based on the spin polarization mechanism and McConnell's theory;[8,9] atoms with positive spin density are exchange-coupled to atoms with negative spin density in neighboring molecules to give ferromagnetic coupling ($H^{AB} = -S^A \cdot S^B \Sigma J_{ij}^{AB} \rho_i^A \rho_j^B$). The sign of spin polarization is qualitatively drawn in Figure 1b.

The shortest inter-dimer atomic distance was found to be 2.48 Å for O···H(6") which is shorter than the sum of the van der Waals radii (2.6 Å), as indicated in Figure 1a.

The static magnetic susceptibility was obtained on a SQUID magnetometer down to 1.8 K at 0.5 T. As Figure 2 shows, with decreasing temperature, the effective magnetic moment of BTAO once increased, reached a maximum 1.87 μ_B at 9 K, and

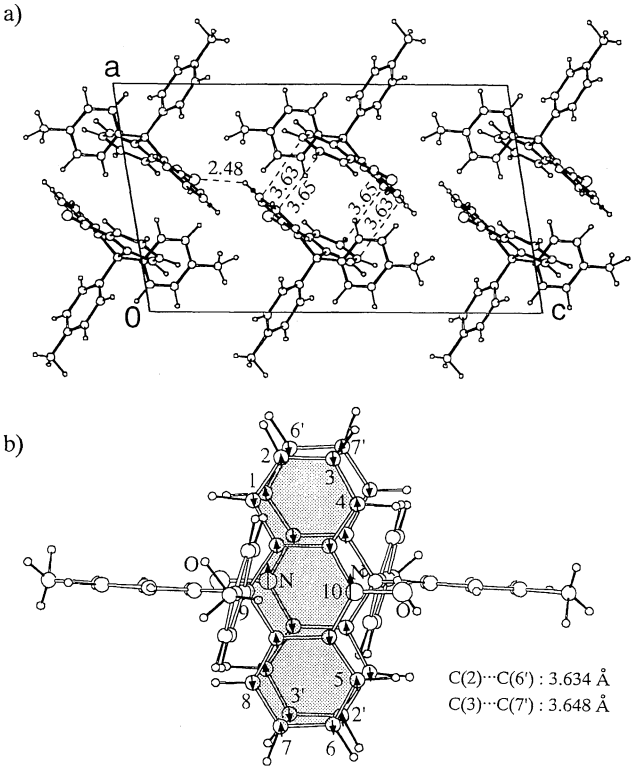


Figure 1. a) Crystal structure of BTAO viewed along the *b* axis. Intermolecular atomic distances are indicated in Å with dotted lines. b) Molecular arrangement of two BTAO molecules projected to an averaged acridine plane (defined by 14 atoms of the acridine skeleton). One acridine ring is shaded. The signs of spin density are qualitatively indicated with small arrows. Atomic numbering is also drawn.

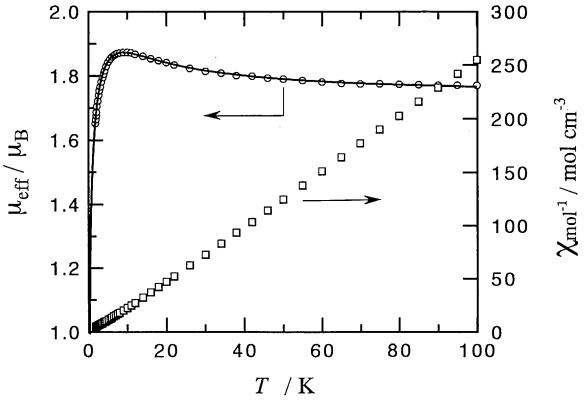


Figure 2. Temperature dependence of the effective magnetic moment (μ_{eff}) and the reciprocal molar magnetic susceptibility (χ_{mol}^{-1}) of BTAO. The solid line is a calculated μ_{eff} curve based on the modified Bleaney-Bowers equation with J/k_B = +8.85 K and θ = -0.86K (see the text).

then decreased. The solid line in Figure 2 was drawn by a best fit to Equation 1, which is modified from the Bleaney-Bowers equation[18] with a Weiss mean field parameter θ. The optimized values were J/k_B = +8.85 K, θ = -0.86 K, and g = 2.01. The crystal structure analysis of BTAO suggested that the ferromagnetic J and antiferromagnetic θ could be attributed to intra- and inter-dimer interactions, respectively.

$$\chi = \frac{2Ng^2\mu_B^2}{k_B(T-\theta)} \frac{1}{3+\exp(-2J/k_BT)} \quad (1)$$

The ferromagnetic stacking of aromatic rings could be obtained, avoiding synthetic labor such as in the case of the preparation of [2.2]paracyclophanes.[9] Whereas through-bond interactions via two ethano-bridges could not be excluded in that case, through-space interactions were essentially observed in the present work.[19] The ferromagnetic interaction is fairly large for organic radicals, in spite of the separation between the phenyl rings (3.63 Å) which is longer than the sum of the van der Waals radii (3.4 Å). The study on derivatives possessing less bulky substituents than the tolyl group is now underway. Although the approach based on McConnell's theory[8] is confirmed to be a hopeful strategy, ferromagnetic polymeric stacking is more desired than dimeric one for development of molecular magnetic materials.

The inter-dimer antiferromagnetic interaction is much weaker than the intra-dimer ferromagnetic interaction, so that the origin of the former is rather delicate. However, we propose one of possible explanations as follows. The inter-dimer atomic distance of 2.48 Å was found for O···H(6";*m*). Since the *m*-hydrogen atom has a positive spin density,[14] the positive spin density should polarize a negative spin density at the contacting N-O site through intermolecular orbital overlap (Figure 3). In other words, the antiferromagnetic coupling occurs through γ-hydrogen atoms, which we call "γ-hydrogen mechanism" as an extension of the ferromagnetic β-hydrogen mechanism.[3,4]

Assuming the presence of the coupling via *m*-hydrogen contacts, the dimers were 2-dimensionally related within a sheet parallel to the *bc* plane. In order to estimate the inter-dimer exchange parameter J', $\theta = 4zJ'/[k_B\{3+\exp(-2J/k_BT)\}]$ is

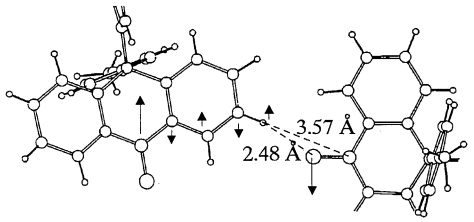


Figure 3. Possible mechanism for inter-dimer antiferromagnetic exchange interaction in the crystal of BTAO based on the spin polarization.

introduced[20] to Equation 1 with the number of nearest neighboring dimers z = 4. The best fit with varying J gave J/k_B = +8.43 K, J'/k_B = -0.16 K, and g = 2.01.

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