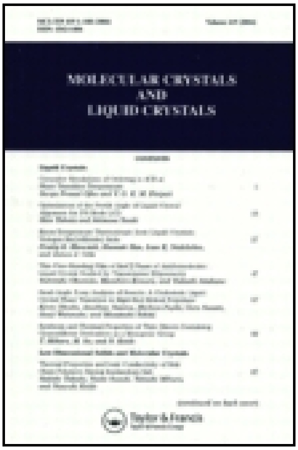

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Possible Superhigh-Spin Cluster in the Crystals of a Novel Nitronyl Nitroxide Radical as Studied by FT Pulsed ESR

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Syntheses and magnetic properties of novel nitronyl nitroxide derivatives are reported. In the derivatives under study, the bulky tetramethylethylene group of the conventional nitronyl nitroxide has been replaced by aromatic rings, giving planar π-conjugation systems. The first half of the paper is devoted to the syntheses and characterization of new derivatives of such radical, 2-phenylbenzimidazol-1-yl-*N,N'*-dioxide (PBIDO). Chemical stability, π-spin density distribution, and solid state magnetic properties have been examined from solution ESR and static susceptibility measurements. In the latter half, we discuss an anomaly of paramagnetic relaxation found in crystals of PBIDO by pulsed ESR spectroscopy. The origin of the anomaly is attributed to a possible formation of paramagnetic species with huge S, or "superhigh-spin cluster" at lattice defects in the crystal.

Keywords: nitronyl nitroxide; imidazole-1-oxyl-3-oxide; pulsed ESR; lattice defect; relaxation time; T_1 and T_2

INTRODUCTION

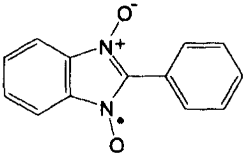
Organic molecule-based magnetism and magetics have been the focus of current topics in an interdisciplinary area of physics and chemistry[1]. Many stable open-shell molecules have been found in nitronyl nitroxide radical derivatives[1].

The high stability of the derivatives in crystalline solid states underlies the recent development in the research field of molecule-based magnetism.

In designing new stable radical molecules as building blocks of organic magnetic materials, the bulky tetramethylethylene group of the conventional nitronyl nitroxide is worth applying chemical modification[2]. The bulky group of sp^3-carbons disturbs the planarity of the imidazole ring of nitronyl nitroxide. When the bulky group is replaced by a planar aromatic ring of sp^2-carbons, new features of intramolecular spin density distribution and molecular packing are expected, leading to a variety of intermolecular magnetic interactions. In this context, the isolation of a nitronyl nitroxide radical with a benzene ring fused with the imidazole ring, 2-phenylbenzimidazol-1-yl-*N*,*N*'-dioxide (abbreviated as PBIDO; **1**)[2], makes an epoch in magnetics of the molecular crystals.

The first part of the present study deals with new derivatives of PBIDO. One category of chemical modification is substitution at the 2-phenyl group of PBIDO. The other is extension of π-conjugation to an aromatic ring fused with the imidazole ring of PBIDO. Syntheses and characterization by ESR spectroscopy are presented for the new derivatives. For some derivatives isolated as stable solids, intermolecular magnetic interactions are examined by magnetic susceptibility measurements.

In the second part of this paper, we elucidate electron spin relaxation properties of PBIDO from pulsed ESR spectroscopy in a crystalline solid state. We propose the possible occurrence of paramagnetic species with huge spin *S*, or superhigh-spin cluster, formed at lattice defects in the crystal of PBIDO. The spatial topology of the lattice defects are discussed in view of a quantum nature of isotropic spin systems in the organic solids.

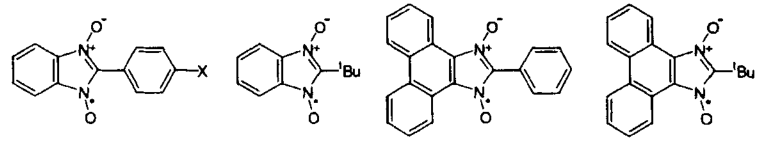


PBIDO, **1**

PREPARATION AND CHARACTERIZATION OF NEW DERIVATIVES OF PBIDO

Syntheses

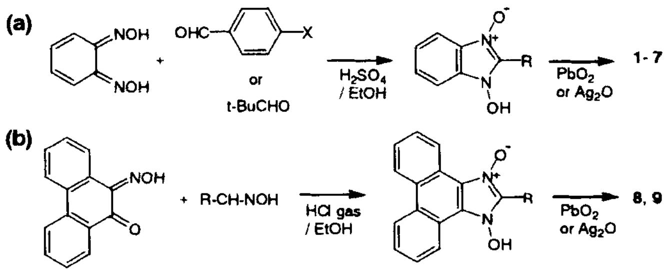
The novel derivatives of PBIDO synthesized in the present study are shown in Scheme I. The radicals **2** - **6** have substituents at the 2-phenyl group of PBIDO. The derivatives **8** and **9** are expected to have extended π-conjugation on the aromatic rings.



X = H (**1**), NO_2 (**2**), CO_2Et (**3**), OMe (**4**), Cl (**5**), Me (**6**)

7 **8** **9**

Scheme I Derivatives of PBIDO.



Scheme II Synthetic routes for (a)benzo and (b)phenanthreno derivatives.

The synthesis of PBIDO **1** is based on the coupling of *o*-benzoquinone dioxime and benzaldehyde (Scheme II-a)[2]. The derivatives **2** - **6** were synthesized by the similar procedure and isolated as stable solids. The 2-*t*-butyl derivative **7** was also obtained by coupling of the dioxime and pivalaldehyde. However, this coupling did not succeed for 9,10-phenanthrenequinone dioxime. Instead, the coupling of phenanthrenequinone monooxime and benzaldoxime in ethanol with dry HCl yielded the precursor of the target radical **8** (Scheme II-b). The white precipitate obtained by this coupling was oxidized by PbO_2 or Ag_2O to yield a blue solution of **8** in benzene. Using pivalaldoxime we obtained a purple solution of **9** in benzene.

Magnetic Properties of the Derivatives with *p*-Substituted Phenyl Groups

The magnetic susceptibilities of the radicals **2** - **6** were measured for polycrystals with an applied field of 0.5 T over a temperature range of 1.8 K to 100 K on a Quantum Design SQUID magnetometer. The results are summarized in Table I. Rather strong antiferromagnetic interactions were obtained in several derivatives of PBIDO; for example, χ_p of *p*-NO_2 derivative **2** showed a broad maximum at 110 K.

Singly occupied molecular orbitals extended on π-conjugated systems are supposed to overlap with those of neighboring molecules in crystals, giving rise to intermolecular antiferromagnetic interactions. However, we have found ferromagnetic interactions in the crystals of **3**. With decreasing temperature, the product χ_pT increases as shown in Fig. 1, indicating the presence of intermolecular ferromagnetic interaction. The $1/\chi_p$ vs. T plot gave a positive Weiss constant of +1.0 K.

The *p*-substituted PBIDO derivatives have been found to be good building blocks with high stability for the organic molecule-based magnetic materials. In order to elucidate magneto-structural relationship, crystal structure analyses for **2** - **6** are now under way.

TABLE I Summary of magnetic susceptibility data for **2**-**6**.

Radical	Substituent X	Weiss constant θ (K)[†]
2	NO_2	-[‡]
3	$CO_2C_2H_5$	+1.0
4	OCH_3	-7.5
5	Cl	-11
6	CH_3	-6.9

[†] In the Curie-Weiss approximation for $S=1/2$.

[‡] A maximum of χ_p was observed at 110 K.

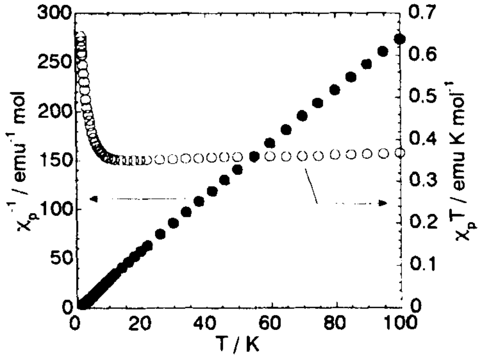


FIGURE 1 Temperature dependence of $1/\chi_p$ and χ_pT measured for the polycrystalline sample of **3** with an applied field of 0.5 T.

Extension of π-Conjugation in PBIDO

New derivatives of PBIDO **8** and **9** have been synthesized aiming at further extension of π-conjugation: the benzene ring has been replaced by phenanthrene moiety. We expect that this extension may lead to a new molecular packing motif in a solid state and delocalization of π-spin may afford additional stability in spite of the increasing number of chemically reactive sites.

The radicals **8** and **9** retained their color in solutions for ca. 30 min. and for ca. 3 h., respectively. Evaporation of the solutions of **8** and **9** caused decomposition of the radicals to give yellow ESR-silent materials; these radicals could not be isolated. Although **7** is more stable than **8** and **9** as indicated by a lifetime of about 2 days in benzene, evaporation of the solution gave only a diamagnetic oily mixture.

The π-spin density distributions in **8** and **9** are examined from ESR spectra recorded in benzene solutions at room temperature and compared with those of benzo derivatives **1** and **7**. All the spectra exhibit 1:2:3:2:1 five-split lines due to the hyperfine coupling with the two equivalent ^{14}N nuclei. For the radical **7**, an additional hyperfine splitting due to the four ^{1}H nuclei on the benzo group was superposed onto the five-split lines. The g-factor and the ^{14}N hyperfine coupling constants a_N are summarized in Table II. It is found from the a_N values that the spin density on nitrogen decreases with the extension of the π-system; the spin density seems to flow into the benzo groups. We suspect that this distribution of the spin density may reduce the chemical stability of the phenanthrene-based radicals, because enhanced spin density on the planar ring may raise a reactivity of the ring toward another radical molecule.

TABLE II ESR parameters and π-spin density at nitrogen for phenanthrene-based derivatives **8** and **9** as compared with PBIDO (**1**) and **7**.

Radical	g-value	hfc a_N (mT)	π-spin density ρ_N[†]
1	2.0068	0.438	0.208
7	2.0069	0.437	0.207
8	2.0070	0.381	0.181
9	2.0071	0.387	0.183

[†] a_N (mT) = 2.11 ρ_N.

PARAMAGNETIC RELAXATION OF PBIDO

Low Temperature Magnetic Anomaly of PBIDO Crystal

Let us summarize here the anomalous low temperature magnetic properties of

PBIDO crystals[2]. The susceptibility χ_p exhibited a round maximum at ca. 40 K, which was explained on the basis of the antiferromagnetically coupled radical dimers. This seems consistent with the crystal structure; the PBIDO molecules form dimers with the molecular planes facing to each other within the dimer[2]. However, χ_p increased again below ca. 10 K, followed by another small peak at 3 K. Cw-ESR spectra in this low temperature range showed angle-dependent fine structures and $|\Delta m_s| = 2$ transitions, indicating formation of high-spin states. The magnetic specific heat of PBIDO crystals measured down to 1 K in zero magnetic field exhibits a broad maximum at 2 K[3], which can be related to the low temperature magnetic anomaly. From this, the molar magnetic entropy change below 5 K was estimated to be ΔS = 0.18 JK^{-1} mol^{-1}, which amounts only to 3 % of the total entropy of a spin-1/2 system, $R\ln 2$ = 5.8 JK^{-1} mol^{-1}. Therefore, it is impossible to relate the low temperature anomaly to the bulk property of the crystal.

Temperature Dependence of Relaxation Times, T_1 and T_2

In attempting to give a solution to the anomaly described above, paramagnetic relaxation behavior of PBIDO was examined by pulsed ESR spectroscopy. The spin-lattice relaxation time T_1 was measured for the polycrystalline samples by an FID-detected inversion recovery method with π- and $\pi/2$-pulses on a Bruker X-band FT-ESR spectrometer ESP380E. The spin-spin relaxation time T_2 was measured from the time-profile of FID.

Figure 2(a) shows temperature dependence of T_1 and T_2. From room temperature down to 20 K, T_1 and T_2 coincide with each other within the experimental accuracy, indicating that the spin correlation rate is much larger than the microwave frequency of 9 GHz owing to the intermolecular exchange interaction. At lower temperature, however, T_2 exhibits downward divergence†. Quantitative analysis of spin-spin relaxation time T_2 is quite difficult particularly for exchange-coupled many-spin systems. We note at present that the drop in T_2 on lowering the temperature is indicative of enhanced fluctuation of local field in the crystal. Such enhancement would result from growth of effective magnetic moments in the exchange-coupled spin system. Since the

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†An anomaly in FID intensity was observed below 10 K: Transiently acquired FID signal gradually increased in intensity to its maximum in a few minutes. Our discussion is limited to the data above 10 K, because we have no plausible physical explanation for the anomalous slow dynamics at the present time.

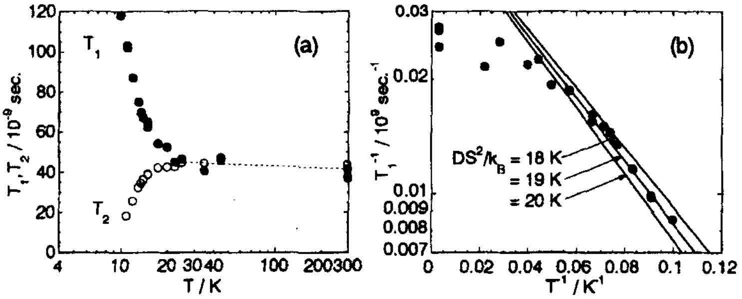

FIGURE 2 (a)Temperature dependence of the relaxation times, T_1 and T_2. (b)$\ln(T_1^{-1})$ vs. T^{-1} as compared with the generalized Orbach model (the activation energy: $DS^2/k_B = 19 \pm 1\,\mathrm{K}$).

assemblage of the radical dimers with a singlet ground state never gives rise to the enhancement of local field at low temperature, some specific, local structure instead of the bulk crystal structure should be taken into account to explain the relaxation anomaly as suggested from the specific heat experiment.

The spin-lattice relaxation time T_1 diverges upward below 20 K. The relaxation rate T_1^{-1} in logarithmic scale is proportional to T^{-1} below 20 K as shown in Fig. 2(b), indicating a thermally controlled mechanism in the spin-lattice relaxation with the activation energy of $\varepsilon/k_B = 19 \pm 1\,\mathrm{K}$. When there is an energy barrier due to magnetic anisotropy *D* of the fine structure interaction

$$H = DS_z^2, \tag{1}$$

the rate of phonon-mediated spin-lattice relaxation T_1^{-1} is calculated within the second order perturbation of the spin-phonon interaction as given by[4]

$$T_1^{-1} \propto \exp(DS^2/k_BT), \tag{2}$$

where S is the spin quantum number of the paramagnetic species contributing to the observed FID signal. Equation (2) means that the spin-lattice relaxation, *i.e.*, the rotation of the magnetization toward the thermal equilibrium needs the thermal energy $k_BT = |D|S^2$: The molecules in the state of $m_S = S$ have to climb to those of $m_S = S-1, S-2, \cdots$ and so on, untill they reach the top of the energy barrier of zero-field splitting $|D|S^2$ and then go down to the state $m_S = -S$. This process is regarded as a generalized Orbach process[4] involving $2S-1$ of intermediate states. The observed divergence of T_1 is explained by the model of Eq.(2) with $|D|S^2/k_B = 19\,\mathrm{K}$. Considering that D/k_B originating from the intermolecular dipole-dipole interaction is in the order of 1 mK, paramagnetic species with huge S composed of exchange-coupled spin-1/2 molecules is expected to dominate the relaxation process. The sign of D, which should be negative, is discussed below in connection with the spatial topology of the huge-spin paramagnetic species.

High-Spin Cluster at Edge Dislocation in the Crystals of PBIDO

Numerical calculation of Heisenberg spin Hamiltonian

The picture of the huge-spin paramagnetic species, which is deduced from the relaxation data in terms of the generalized Orbach mechanism, conflicts with the bulk structure of the molecular packing. We take account of lattice defects as possible sources of the huge-spin species. From the molecular packing and the space group of PBIDO[2], three patterns of edge dislocations are expected to appear in the {002}, {202}, and {200} planes. We take account of the dislocation running parallel to the {002} plane. This brings about "dangling spins" free from the antiferromagnetic interaction in the dimer as shown in Fig. 3(a). The dangling spins are arrayed along the *a*-axis, which is the principal axis of the fine structure found in the cw-ESR[2]. We suppose the {002} dislocation would dominate the relaxation anomaly, if it produces high-spin assemblages along the *a*-axis.

The appearance of the huge-spin species at the {002} dislocation is verified by calculating the Heisenberg spin Hamiltonian

$$H_{ex} = -2J_1 \sum_{i,j} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - 2J_2 \sum_{k,l} \boldsymbol{S}_k \cdot \boldsymbol{S}_l, \qquad (3)$$

where J_1 and J_2 denote the intra- and inter-dimer nearest-neighbor exchange interactions, respectively. S in Eq. (3) is the spin-1/2 operator at a molecular site. The Hamiltonian is schematically illustrated in Fig.3(a). The product of susceptibility and temperature $\chi_p T$ was calculated by exact numerical diagonalization of the Hamiltonian (3). The calculated $\chi_p T$ is plotted in Fig.3(b) for the two-dimensional (2-d) lattice of 14 $(= 4 \times 4 - 2)$ sites possessing two "dangling spins". When J_2 is small ($|J_2/J_1|<1/4$), the low-temperature limit of $\chi_p T$ corresponds to a pair of apparently decoupled spin-1/2 spins. On the other hand, when $|J_2/J_1|>1/4$, $\chi_p T$ approaches 0.071 emu K mol^{-1}, corresponding to one spin-1 in the lattice. A larger lattice with three "dangling spins"

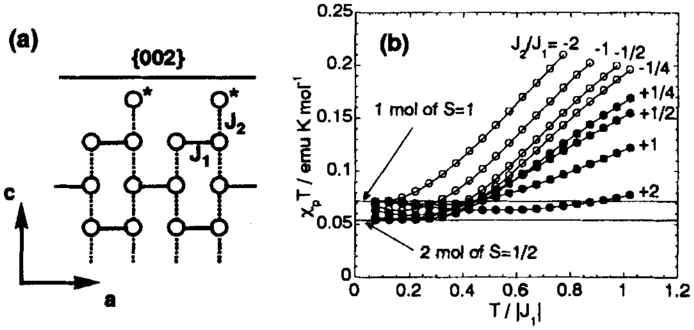

FIGURE 3 (a)Schematic drawing of the spin Hamiltonian. The circles represent the spin-1/2 sites which are coupled by the intra-dimer (J_1) and inter-dimer (J_2) exchange interactions. The starred circles are "dangling spins" at the {002} dislocations. (b)Calculated $\chi_p T$ for the Hamiltonian of the 14-spin system (o:$J_2>0$; •:$J_2<0$). The horizontal lines denote the low-temperature limits of $\chi_p T$ expected for $S=1$ and decoupled $S=1/2$ spins.

was found to have a spin-3/2 ground state from calculations of spin states using Lanczos algorithm[5]. From these results, it is suggested that the huge-spin species with $S=N/2$ appears in the 2-d system with N of "dangling spins" at low temperature. It is concluded that the huge-spin species, which is termed superhigh-spin cluster, grows along the {002} dislocations and the energy barrier due to the zero-field splitting of the cluster brings about the thermally activated T_1.

Fine structure of the superhigh-spin cluster

The spin Hamiltonian of the superhigh-spin cluster with a spin quantum number S is given by

$$H_S = \mu_B \boldsymbol{S} \cdot \boldsymbol{g} \cdot \boldsymbol{B} + \boldsymbol{S} \cdot \boldsymbol{D} \cdot \boldsymbol{S}, \tag{4}$$

where $\boldsymbol{g}$ and $\boldsymbol{D}$ are the g-tensor and the fine structure tensor of the entire cluster, respectively. The principal zz component of $\boldsymbol{D}$ is related to the fine structure parameter D in Eq.(1) as

$$D_{zz} = \frac{2}{3} D. \tag{5}$$

The principal value D_{zz} of $\boldsymbol{D}$ is negative with z // a, when it originates from the intermolecular dipole-dipole interaction along the dislocation axis. This finding is consistent with the thermal activation behavior of T_1 described by Eq.(2).

The size of the superhigh-spin cluster, *i.e.*, the spin correlation length along the dislocation, fluctuates at a given temperature, whereas the size of the dislocation has a macroscopic scale in length as large as the crystal. Therefore, we observe in the pulsed ESR experiments a thermal average of the clusters which have a size distribution. The fine structure parameter D is an effective one referring to the assemblage of the size-varying clusters. The satellite signals of the fine structure found in the cw-ESR[2] is thus regarded as a superposition of the signals from the clusters. We give only a rough estimate of the $|D|$ value from the satellites, $|D|/g\mu_B \approx 3\,\text{mT}$.

Lattice defects as novel physical model systems for quantum spin systems

One of the most salient features of organic open-shell molecules as building blocks of magnetic materials is the isotropic nature of intermolecular exchange interactions[6]. For antiferromagnetic spin systems, the isotropic nature underlies large quantum fluctuation of the spins which favors a singlet (S=0) pair more than an antiparallel alignment of neighboring spins. When $|J_2|$ is negligibly small, the coverings of nonmagnetic singlet pairs over the 2-d lattice is favorable in energy, resulting in the apparently decoupled S=1/2 spins at the dislocations. On the other hand, when $|J_2| \geq |J_1|$, spin-spin correlation is expected to survive along the dislocation, giving rise to the superhigh-spin cluster.

The finite-size Hamiltonian (3) predicted the high-spin ground state for the 2-d spin system with free-edges and the existence of the high-spin species with large DS^2 was clarified from the relaxation experiments. However, the small maximum of χ_p at 3 K[2] and the change in entropy below 5 K[3] indicate that the ground state of the entire lattice of the PBIDO crystal is not of high-spin nature. The full understanding of the genuine ground state of the crystal, which may be obtained in connection with another relaxation anomaly, *i.e.*, the slow dynamics of FID below 10 K, is expected to lead to further insight into low-dimensional exchange-coupled quantum spin systems.

CONCLUSION

New derivatives of PBIDO with various substituents on the phenyl ring have been synthesized and isolated as stable solids. Both ferromagnetic and antiferromagnetic intermolecular interactions have been found in these derivatives, indicating the potentiality of the derivatives with the fused aromatic rings as building blocks of molecule-based magnetic materials. The phenanthrene-based derivatives have also been generated in solutions, but are not isolable. The enhanced spin density on the aromatic ring may cause a chemical reaction between the radicals to hamper the stability.

For PBIDO, the divergence of T_1 and T_2 has been found at low temperature. From the analysis of T_1 in terms of the thermally activated spin-lattice relaxation mechanism, the formation of the superhigh-spin cluster at dislocations in the crystals was elucidated. Lattice defect such as dislocation is not a trivial problem in molecule-based magnetics but a novel physical model system in which the spatial topology of intermolecular magnetic interactions is essential to solid-state magnetism in view of the quantum nature of exchange coupled spins.

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