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Phenol-substituted nitronyl nitroxide biradicals with a triplet ($S=1$) ground state†

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The crystal structures of two kinds of nitronyl nitroxide biradical with a phenolic substituent, 2,4-bis(1-oxyl-3-oxido-4,4,5,5-tetramethyl-2-imidazolin-2-yl)phenol (**1a**) and 4-methyl-2,6-bis(1-oxyl-3-oxido-4,4,5,5-tetramethyl-2-imidazolin-2-yl)phenol (**2a**) have been solved. The biradical **1a** belongs to the monoclinic system with space group $P2_1/n$, $a=11.806(4)$ Å, $b=25.330(5)$ Å, $c=7.337(7)$ Å, $\beta=104.65(4)^\circ$, and $Z=4$, while the biradical **2a** to the orthorhombic system with *Pbca*, $a=20.206(4)$ Å, $b=40.405(4)$ Å, $c=11.888(3)$ Å, and $Z=8$. >From the magnetic susceptibility in the crystalline solid state, both **1a** and **2a** are found to have a triplet ($S=1$) ground state with the intramolecular ferromagnetic interaction of $2J/k_B=26.0\pm0.5$ K for **1a** and 12 ± 1 K for **2a**. The triplet ground states are confirmed by the EPR measurements on the isolated molecules in diluted glassy solutions. The singlet–triplet energy gaps of the biradicals with a phenolic hydroxy substituent are found to be reduced as compared with a parent non-substituted biradical.

Introduction

Extensive studies have been carried out on organic molecule-based ferromagnets and other molecular functionality magnetics in recent years.[1] Together with organic ferromagnetics (with purely ferromagnetic intermolecular interactions), ferrimagnets have been attracting attention as one of the facile approaches to organic ferromagnets after Buchachenko's research in 1979.[2] Magnetic phase transitions to a ferrimagnetic ordered state, however, have not been documented in organic molecular crystalline solids. This presents a remarkable contrast to the discovery of the organic molecular ferromagnets (with purely ferromagnetic intermolecular interactions),[1,3] and transition metal-based molecular ferrimagnets.[4] Only one molecular complex of an organic biradical with $S=1$ and a radical with $S=\frac{1}{2}$ has been reported as a model system of organic ferrimagnets.[5] Although the complex has an alternating molecular aggregation of the $S=1$ and the $S=\frac{1}{2}$ molecules with intermolecular antiferromagnetic interactions, no long-range magnetic order has been found.[5] In view of the magneto–structural correlation in molecule-based magnetic materials, different types of molecular complexes as models for organic ferrimagnetics are required in order to establish principles of ferrimagnetic spin alignment in alternating molecular aggregation.

A practical difficulty in the construction of the model compounds for organic ferrimagnets lies in co-crystallization of two kinds of organic molecules with different spin quantum numbers. In general, two distinct molecules, *e.g.*, one with $S=1$ and the other with $S=\frac{1}{2}$, crystallize separately from a solution unless some attractive force is operative between them.[6] Although intermolecular interactions such as hydrogen bondings have already been applied to the crystal engineering of doublet ($S=\frac{1}{2}$) molecules,[7] approaches to heteromolecular assemblages have not been established. We have proposed a novel crystal engineering approach to molecule-based ferrimagnetics.[8] An attractive coulombic interaction between a charged biradical with $S=1$ and a monoradical ($S=\frac{1}{2}$) with an opposite charge is a promising driving force which is utilized for co-crystallization. This crystal engineering approach is referred to as "organic salt ferrimagnetics".[8,9]

In general, two unpaired electrons linked by *m*-phenylene afford the preference for a triplet ($S=1$) ground state.[10] Heteroatomic substitution which is necessary for a ground-state triplet biradical to carry a charge, would affect the ground-state spin multiplicity and the spin density distribution in the molecule. Chemical modifications are found to affect heterocyclic derivatives of carbene[11] and trimethylenemethane,[12] and a substituted *m*-phenylene bis(α-nitronyl nitroxide) biradical.[13] Molecular conformation has also been shown to affect the ground-state spin multiplicity.[14] For heteroatomic substituted *m*-phenylene derivatives, the preference for a triplet ($S=1$) ground state is not guaranteed. Therefore, the effects of substituents in biradicals should be thoroughly examined as a step toward organic salt ferrimagnetics based on charged biradicals. In the present study, we have designed two kinds of anionizable stable biradicals based on nitronyl nitroxide[15] 2,4-bis(1-oxyl-3-oxido-4,4,5,5-tetramethyl-2-imidazolin-2-yl)phenol (**1a**) and 4-methyl-2,6-bis(1-oxyl-3-oxido-4,4,5,5-tetramethyl-2-imidazolin-2-yl)phenol (**2a**) (Fig. 1). The phenolic hydroxy group is introduced into 1,3-bis(1-oxyl-3-oxido-4,4,5,5-tetramethyl-2-imidazolin-2-yl)benzene [*m*-phenylenebis(α-nitronyl nitroxide)] (**3**), which has been shown to have a triplet ground state with the intramolecular exchange interaction of $J/k_B\sim20$ K.[16,17] We have made careful and elaborate experiments to examine the ground-state spin multiplicities and the intramolecular exchange interactions of **1a** and **2a** with the heteroatomic substituent. >From magnetic susceptibility measurements in crystalline solid states, the intra- and inter-molecular exchange interactions are elucidated on the basis of crystal structure analyses. EPR spectra in glassy solutions are invoked to clarify the ground states of the isolated molecules, **1a** and **2a**, and support the results of the magnetic susceptibility in the solid state.

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†ORTEP diagrams for crystals **1a** and **2a** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/jm/b0/b007316o/

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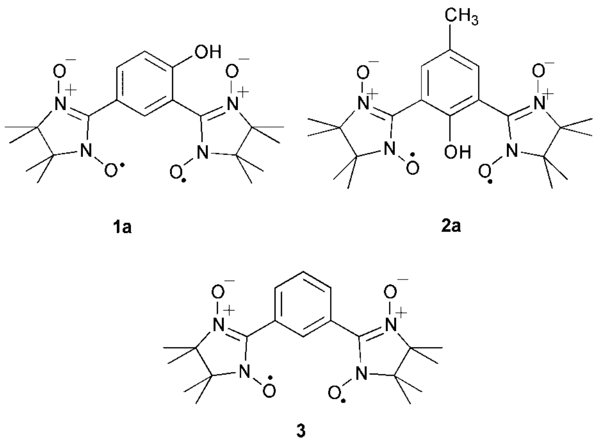


Fig. 1 Nitronyl nitroxide biradicals **1a**, **2a**, and **3**.

Experimental

Synthesis

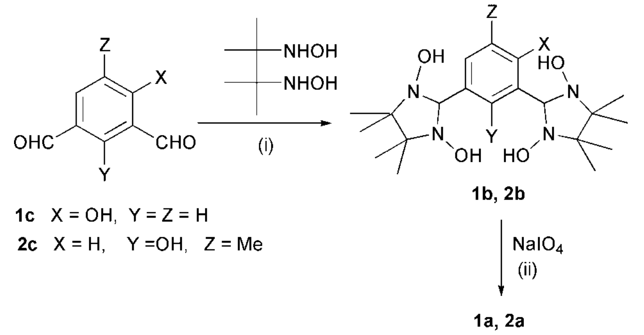
The biradicals **1a** and **2a** were synthesized from isophthalaldehydes (**1c**, **2c**) and 2,3-bis(hydroxylamino)-2,3-dimethylbutane following the method reported by Ullman *et al.*[18] (Scheme 1). Compound **1a** was purified by recrystallization from a saturated methanol solution at −21 °C, while **2a** was chromatographed on silica gel with acetone : diethyl ether = 1 : 5 as an eluent and recrystallized from a saturated methanol solution at −21 °C. Single crystals of **1a** and **2a** suitable for X-ray diffraction experiments were obtained by slow evaporation of acetone solutions at room temperature; thin dark-blue parallelepipeds for **1a** and purple needles for **2a**.

X-Ray crystallography‡

The X-ray diffraction data were collected on a Rigaku four-circle diffractometer AFC7R with graphite monochromated Cu-Kα radiation up to $2\theta_{max} = 120°$. The structure was solved by direct methods (SIR92[19]) and subsequent Fourier syntheses followed by the full-matrix least-squares refinement with the anisotropic approximation for non-hydrogen atoms. Positions of the hydrogen atoms were calculated and included in the final refinement. All the calculations were made using the program package *teXsan* (Single Crystal Structure Analysis Package, Version 1.10 (1999), Molecular Structure Corporation, The Woodlands, TX77381, USA).

EPR measurements

The EPR spectra in solution were measured in toluene for **1a** at 323 K and in CH_2Cl_2 for **2a** at 293 K using a JEOL X-band spectrometer JES-FE2XG with a concentration of 1×10^{-5} mol dm^{-3}. Glassy EPR spectra were measured in a 2-methyltetrahydrofuran solution or a 2-methyltetrahydrofuran : methanol = 1 : 1 solution (**1a**) and in a methanol solution (**2a**) with a final concentration of 1×10^{-3} mol dm^{-3} using a Bruker X-band spectrometer ESP300 in the temperature range of 5–50 K. All the solvents were chosen so as to avoid decomposition of the biradicals. The solutions were degassed by a freeze–pump–thaw cycle and sealed *in vacuo*. The simulation of EPR spectra was carried out with a Bruker program *SimFonia*, which is based on a second-order perturbation treatment. The perturbation treatment of a spin Hamiltonian was enough to reproduce the observed spectra satisfactorily.



Scheme 1 (i) Refluxed for 21 h in benzene to give the precipitate of the precursors **1b** (96%) and **2b** (85%). (ii) Stirred at room temperature for 41 h in H_2O–CH_2Cl_2 emulsion to yield 70% of **1a**, for 2 h to yield 26% of **2a**.

Magnetic susceptibility measurements

The static magnetic susceptibility was measured for the randomly oriented polycrystals recrystallized from acetone for **1a** and from methanol for **2a** using a Quantum Design SQUID magnetometer MPMS2 with an applied field of 0.1 T in the temperature range 1.8–300 K.

For **2a**, the solvent used in the preparation of single crystals for the X-ray crystallographic experiments was different from that for the susceptibility measurement. From powder X-ray diffraction experiments, the crystal structure of **2a** obtained from acetone has been found to be identical to that from methanol, and therefore the possibility that polymorphism in **2a** depends on the solvents for crystallization is eliminated.

Results and discussion

EPR spectra in solutions: ^{14}N hyperfine splitting

EPR spectra recorded for the solutions of the biradicals **1a** and **2a** exhibit nine lines with an equal spacing, which are attributed to the hyperfine splitting of four equivalent nuclei of ^{14}N (nuclear spin number $I = 1$). The spectral simulation using the hyperfine Hamiltonian of $S = 1$ and $I = 1$, as given by eqn. (1), gave the hyperfine coupling constants of $|A|/g\mu_B = 0.367$ mT and the averaged g-factor $g = 2.008$ for **1a** and $|A|/g\mu_B = 0.373$ mT and $g = 2.007$ for **2a**, respectively. The hyperfine coupling constants are almost the same as that of **3**.[16,18] In nitronyl nitroxide derivatives, the spin density ρ is concentrated on the nitroxide groups. The effects of the hydroxy group and the possible intramolecular hydrogen bonding between the nitroxide and the hydroxy groups[7,20] on ρ(NO) is negligibly small in the experimental resolution referred to hyperfine splitting.

$$H = g\mu_B B S_z + A S_z \sum_{i=1}^{4} I_z^i \qquad (1)$$

EPR spectra of allowed transitions in glassy solution

The fine-structure EPR spectrum of allowed transitions ($\Delta m_s = \pm 1$) of **1a** measured in the glassy solution of methanol at 50 K is shown in Fig. 2. The weak central peak is attributed to a small amount of monoradical ($S = \frac{1}{2}$) impurity. The observed spectrum is simulated by using the spin Hamiltonian of $S = 1$ with the fine structure parameters D and E, as given by eqn. (2).

$$H = \mu_B S\cdot \mathbf{g}\cdot B + D\{S_z^2 - S(S+1)/3\} + E(S_x^2 - S_y^2) \qquad (2)$$

In eqn. (2) μ_B, **g**, and **B** are Bohr magneton, the g-tensor, and the static magnetic field, respectively. Our best spectral simulation with $|D|/hc = 7.59 \times 10^{-3}$ cm^{-1}, $|E|/hc = 0.28 \times$

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‡CCDC reference number 1145/270. See http://www.rsc.org/suppdata/jm/b0/b007316o/ for crystallographic files in .cif format.

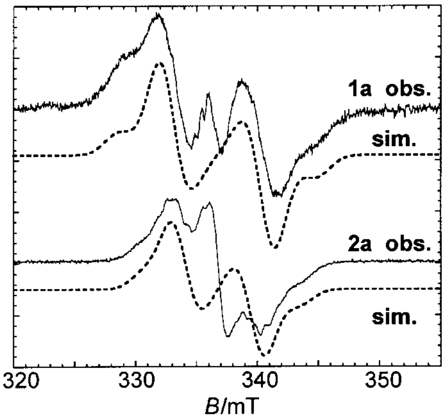

Fig. 2 Allowed EPR transitions in glassy solutions at 50 K. The dashed lines represent the simulation spectra calculated from eqn. (2). Microwave frequency: 9.44918 GHz (**1a**), 9.46775 GHz (**2a**).

10^{-3} cm^{-1}, $g_x=g_y=2.0051$, $g_z=2.0049$ is shown in Fig. 2. The $|D|$ value is a little smaller than that of the non-substituted biradical **3**, $|D|/hc=8.3\times10^{-3}$ cm^{-1}.[16,18] The decrease of 9% in $|D|$ is attributed to a perturbation effect of the hydroxy group on the π-conjugation and/or to a change in molecular conformation.

The fine structure parameters for **2a** are also estimated using eqn. (2) to be $|D|/hc=5.89\times10^{-3}$ cm^{-1} and $|E|/hc=0$ with the principal g-values of $g_x=2.0090$, $g_y=2.0080$ and $g_z=2.0066$. The simulated spectrum is compared with the observed one in Fig. 2. The biradical **2a** is less stable in solution than **1a**, and results in a larger central peak assignable to $S=\frac{1}{2}$ impurities. The $|D|$ value of **2a** is the smallest of the three biradicals. The electronic-structural origin of the smallest $|D|$ value is not clear at present. The intramolecular spin density distribution both over the phenyl and the nitronyl nitroxide groups is influenced by the hydroxy group.

Crystal structure

The X-ray crystallographic data of the biradical **1a** are summarized in Table 1.[21] The molecular structure with the atom numbering scheme is given in Fig. 3(a). The biradical **1a** forms a dimer with an inversion center.[22–24] A positional disorder of the oxygen atoms (O5 and O6) is found at the hydroxy group. The atomic occupancy is 0.25 at O5 and 0.75 at O6. The dihedral angles between the best-fit planes of the phenyl ring and the ONCNO groups are 39.9° (C3–C7) and 36.2° (C5–C14), which are a little larger than those of **3** (32.3° and 35.9°),[16] presumably reducing the intramolecular exchange interactions in **1a** as compared with that of **3**.

Table 1 Crystallographic data of **1a** and **2a**

	1a	**2a**
Formula	$C_{20}H_{27}N_4O_5$	$C_{45}H_{66}N_8O_{11}$
Formula weight	403.46	895.06
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (no. 14)	$Pbca$ (no. 61)
a/Å	11.806(4)	20.206(4)
b/Å	25.330(5)	40.405(4)
c/Å	7.337(7)	11.888(3)
β/degrees	104.65(4)	
V/Å^3	2122(2)	9705(3)
Z	4	8
T/K	296	296
μ(Cu-Kα)/cm^{-1}	7.61	7.28
Reflections measured	3257	7230
Reflections used ($I>3\sigma(I)$)	2959	3310
R_{int}	0.013	0.159
R_1[a]	0.062	0.059
R, R_w[a]	0.084, 0.192	0.087, 0.143

[a]The function minimized is $\sum w(F_o^2-F_c^2)^2$, where $w=1/\sigma^2(F_o^2)$. The residuals are defined as $R_1=\sum||F_o|-|F_c||/\sum|F_o|$, $R=\sum(F_o^2-F_c^2)/\sum F_o^2$, $R_w=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{\frac{1}{2}}$.

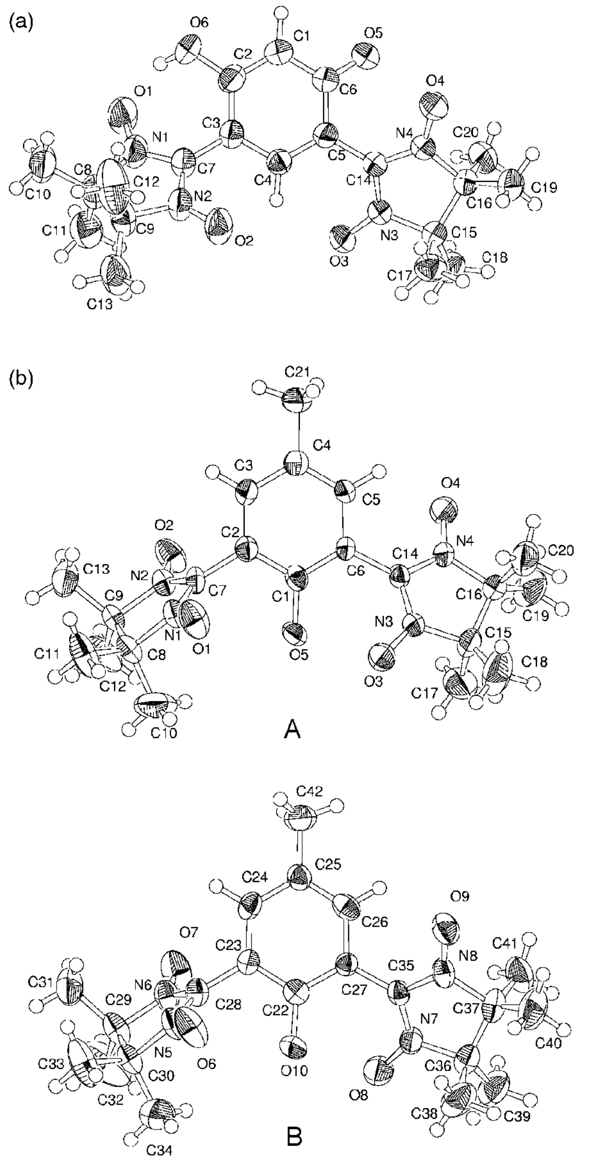

Fig. 3 Molecular structures of **1a** (a) and **2a** (b) with 50% thermal ellipsoids.

The crystallographic data of **2a** are also listed in Table 1. The crystal lattice of **2a** contains acetone molecules as crystal solvent. The solvation and molar ratio (biradical : solvent = 2 : 1) were confirmed by an infrared spectrum and an elemental analysis. We applied restraints to the molecular conformation of acetone in least-squares calculations in order to avoid divergence due to a disorder of the acetone molecules. We are not allowed to discriminate between oxygen and carbon atoms in the difference density map; four carbon atoms are allocated to the acetone molecule with bond angles of 120°. The thermal parameters for acetone are quite large, reflecting the disorder. The thermal parameters for the biradical molecules are within a satisfactory region.

There are two crystallographically independent molecules of **2a**, A and B, the atom numbering schemes of which are given in Fig. 3(b).[22–24] The dihedral angles between the best-fit planes of the phenyl ring and the ONCNO groups in **2a** are larger than those of **1a** and **3**: 72.1° (C2–C7) and 38.7(2)° (C6–C14) in A, and 58.6(2)° (C23–C28) and 38.6° (C27–C35) in B, respectively. The large dihedral angles are likely to weaken the intramolecular exchange interactions through the π-conjugation in **2a** as compared with those of **1a** and **3**. Short intermolecular atom–atom distances are found between the ONCNO groups of nearest-neighbor molecules A and B; 3.12 Å (O4–C35) and 3.19 Å (O4–N8).[22–24] The two neighboring ONCNO planes, however, are almost perpendicular to each other.[23] Magnetic interactions through the overlap of the π-SOMO's would be small, which is discussed below on the basis of magnetic susceptibility measurements.

Magnetic susceptibility in crystalline solid states

The temperature dependence of paramagnetic susceptibility χ_p measured for the polycrystalline sample of **1a** is shown in the χ_pT *vs.* T plot in Fig. 4. The χ_pT value of 0.75 emu K mol^{-1} at 300 K corresponds to 2 moles of free $S=\frac{1}{2}$ spins with the *g*-factor of 2.0, indicating that the purity of the biradical is satisfactory and that the intra- and inter-molecular exchange interactions are much smaller than the thermal energy k_BT of 300 K. The χ_pT value increases gradually as the temperature is lowered and rapidly decreases below 20 K, indicating that both ferromagnetic and antiferromagnetic interactions exist in the crystal. An estimate of the intra- and the inter-molecular exchange interactions is acquired using the modified Bleany–Bowers model in eqn. (3)[25,26] where $2J$ denotes the singlet–triplet energy gap in the biradical molecule. The intermolecular antiferromagnetic interaction is approximated by a mean-field signified by the Weiss constant θ. N_A and k_B in eqn. (3) are Avogadro constant and Boltzmann constant, respectively. The observed χ_pT is well reproduced by assuming $2J/k_B=26.0\pm0.5$ K, $\theta=-3.0\pm0.1$ K. The ground state of the molecule **1a** is found to be triplet ($S=1$).

$$\chi_p=\frac{2N_Ag^2\mu_B^2}{k_B(T-\theta)}\times\frac{1}{3+\exp(-2J/k_BT)} \qquad (3)$$

As the temperature lowers, the χ_pT value of **2a** increases from 0.75 emu K mol^{-1} at 300 K to 0.97 emu K mol^{-1} at 5 K[27] as depicted in Fig. 4, almost reaching the value of one mole of $S=1$. The observed temperature dependence of χ_pT indicates that the ground state of the molecule **2a** is triplet ($S=1$). A decrease in χ_pT found below 3 K implies that weak antiferromagnetic interactions are operative between the triplet molecules. This is consistent with the molecular packing as mentioned above. The intramolecular ferromagnetic interaction in **2a** is determined by using the Bleany–Bowers model, eqn. (3). The curve in Fig. 4 is our best fit with the interaction parameters $2J/k_B=12\pm1$ K with $\theta=0$ K and the purity of 98.5%. A fitting of χ_pT *vs.* T using two independent exchange parameters J's, which correspond to the two crystallographically inequivalent molecules, resulted in almost identical J values within the experimental accuracy. Non-zero Weiss constant θ did not improve the fit. The fitting to the observed data is not satisfactory. This is presumably because the modified Bleany–Bowers model, eqn. (3), is too crude to describe the intermolecular magnetic interactions in the crystal of **2a**. The model gives only an estimate of the intramolecular exchange interaction. The larger dihedral angles between the phenyl ring and the ONCNO groups or the electronic-structural perturbation of the hydroxy group would be responsible for the weaker intramolecular exchange interaction, $2J/k_B\sim12$ K, as compared with those of **1a** and **3**.

EPR spectra of forbidden transitions

In order to confirm the existence of the intramolecular ferromagnetic interactions in the biradical molecules, forbidden EPR transitions ($\Delta m_s=\pm2$) of the isolated triplet molecules were examined in the glassy solutions at various temperatures. The temperature dependence of the integrated signal intensity I_{EPR} of **1a** and **2a** is depicted in Fig. 5. The temperature dependence of I_{EPR} is reproduced by the Bleany—Bowers model in eqn. (4) with the energy gap of $\Delta E/k_B=26$ K for **1a** and $\Delta E/k_B=12$ K for **2a**, which have been estimated from the magnetic susceptibility. The antiferromagnetic interaction of $\Delta E/k_B=-6$ K, which has been considered as the intermolecular interaction for **1a**, does not reproduce the observed intensity. These results rule out the misinterpretation of the signs of intra- and inter-molecular exchange interactions in the analyses of the magnetic susceptibility in the solid state, and confirm the triplet ground states for **1a** and **2a**.

$$I_{EPR}\propto\frac{1}{T}\times\frac{1}{3+\exp(-\Delta E/k_BT)} \qquad (4)$$

For the biradical **2a**, both the fine structure parameter $|D|$ and the intramolecular exchange interaction J are significantly reduced compared with those of **1a** and **3**, which is partly attributed to the large dihedral angles between the phenyl ring and the nitronyl nitroxide moieties. In order to elucidate the possible effect of the electronic perturbation of the hydroxy group on the intramolecular exchange interaction, ENDOR experiments to afford the information on intramolecular spin density distribution and molecular orbital calculations are now under way.

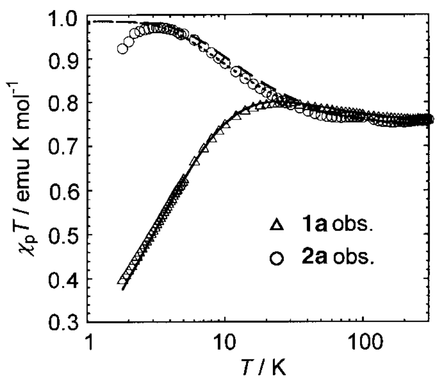

Fig. 4 Magnetic susceptibility of **1a** and **2a** in the χ_pT *vs.* T plots measured for the randomly oriented polycrystalline samples. The triangles and the circles represent the observed χ_pT values. The solid line for **1a** is calculated from eqn. (3) with $2J/k_B=26.0$ K, $\theta=-3.0$ K, while the dashed and dotted lines for **2a** are calculated with $2J/k_B=13$ K and 11 K, respectively.

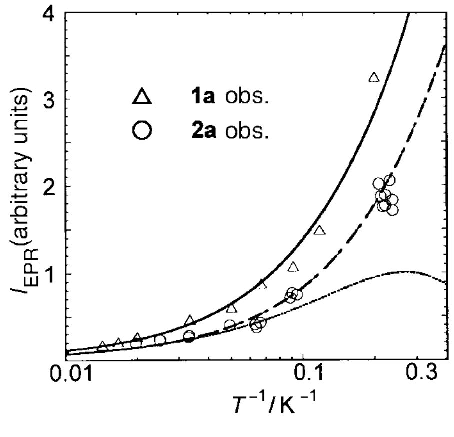

Fig. 5 Integrated intensity of forbidden EPR transitions for **1a** (triangles) and **2a** (circles) as a function of temperature. The solid, the dash-dotted, and the dotted lines represent the calculated temperature dependence of intensity assuming the singlet–triplet energy gap of $\Delta E/k_B=26$ K, 12 K, and -6 K, respectively.

Conclusion

We have synthesized the nitronyl nitroxide biradicals **1a** and **2a** as building blocks of organic salt ferrimagnetics. The magnetic properties of the molecules have been examined by EPR spectroscopy in the frozen solutions and the magnetic susceptibility measurements in the crystalline solid states. From the analyses of the EPR spectra and the susceptibility on the basis of the crystal structures, the molecular ground states of the molecules are found to be triplet ($S=1$) with the singlet–triplet energy gaps of $\Delta E/k_{\mathrm{B}}=26$ K for **1a** and $\Delta E/k_{\mathrm{B}}=12$ K for **2a**. Although the singlet–triplet energy gaps of the biradicals with a phenolic hydroxy substituent are reduced as compared with a parent non-substituted biradical **3**, functionalized stable biradicals with a triplet ground state have thus been obtained. Anionization of the biradicals as building blocks of organic salt ferrimagnets is now in progress.

Acknowledgements

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22 The relative arrangement of the nearest-neighbor molecules and the molecular packing in the unit cell are deposited as supplementary information.

23 M. Deumal *et al.* have proposed that the relative arrangement of radical molecules should be described by six geometrical parameters referring to the atom–atom distances and angles in the two nearest-neighbor ONCNO groups (Ref. 24). Geometrical parameters which define the relative positions of the two neighboring ONCNO groups in **1a** and **2a** are as follows; O3–O3′: 3.55 Å, O3–O3′-N3′ (N3–O3–O3′): 79.2°, N3′–O3′–O3–N3: 180°, C14–N3–O3–O3′ (O3–O3′–N3′–C14′): 67.2° for **1a**. O4–O9: 3.37 Å, O4–O9–N8: 71.1°, N4–O4–O9: 129.1°, N4–O4–O9–N8: −166.5°, O4–O9–N8–C35: 68.7°, C14–N4–O4–O9: −171.8° for **2a**. Geometrical parameters similar to those for **1a** and **2a** as above have been found in nitronyl nitroxide derivatives exhibiting intermolecular antiferromagnetic interactions (Ref. 24). As pointed out in Ref. 24, however, there has been no statistically significant correlation between the relative disposition of NO–NO contacts and the sign of intermolecular exchange interactions. We restrict ourselves to attributing qualitatively the weak antiferromagnetic interactions observed in the susceptibility measurements to the contacts between the nearest-neighbor molecules.

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27 A small enhancement of $\chi_{\mathrm{P}}T$ is found around 90 K, which is not reproducible and is dependent on the powder samples used. The $\chi_{\mathrm{P}}T$ values at room temperature are always 0.75 emu K mol^{-1}, indicating the satisfactory purity. The enhancement is probably due to triplet oxygen molecules absorbed in the samples..