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Galvinoxyl-inspired dinitronyl nitroxide: structural, magnetic, and theoretical studies[†]

A novel galvinoxyl-inspired dinitronyl nitroxide (1) has been synthesized. Structural analysis revealed that $\mathbf{1}$ exhibited a resonance structure, resulting from *p*-benzoquinonediimine *N*,*N*'-dioxide and *N*-phenyl nitr-

oxide moieties. The magnetic study revealed an intramolecular exchange-coupling constant $J/k_{\rm B}$ of -761

(3) K in $H = -J(S_1 \cdot S_2 + S_2 \cdot S_3)$, indicating a ground doublet state. Theoretical calculations suggested not

only the strong intramolecular antiferromagnetic coupling but also a unique electron configuration owing

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Takuya Kanetomo, (10) * Sayaka Ono, Yusuke Fukushima, Yuta Takenouchi and Masaya Enomoto (10) *

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Introduction

Organic radicals have many uses in the fields of spin trapping,^{1,2} spin labeling,^{3,4} dynamic nuclear polarization,^{5,6} organic catalysts,^{7,8} photochromic materials,^{9,10} and molecular magnetic materials.^{11–16} An understanding of not only the physical properties but also the chemical stability of these unique radical-based materials is required. There are two approaches to stabilize radical species: (i) delocalization of the radical spin on the π -conjugated system and (ii) steric protection around the radical centre with bulky substituents.¹⁷

to a remarkable spin polarization effect.

Galvinoxyl reported by Coppinger is well known as a stable radical (Fig. 1a).¹⁸ The unpaired electron is delocalized throughout the molecule, and the tert-butyl groups play a role in steric protection. These factors impart both thermodynamic and kinetic stabilities to the molecule. As shown in Fig. 1a, galvinoxyl can be illustrated as a triradical, but it behaves as a monoradical species due to strong intramolecular antiferromagnetic coupling. Such triradicals with a doublet ground state (S = 1/2) have been reported several times.^{19–22} Interestingly, galvinoxyl exhibits a difference in the spin polarization of the α and β spins owing to the strong intramolecular antiferromagnetic coupling; namely, the β-HOMO level is elevated to the α -SOMO level, where the SOMO and HOMO represent singly and doubly highest occupied molecular orbitals, respectively.^{23,24} This electron configuration is known as a partial SOMO-HOMO inversion (SHI),²⁴ as shown in Fig. 1b.

Owing to the thermal stability and the unique electron structure, several galvinoxyl analogues have been reported where the chemical modification is mainly at the methine position.^{25–36}

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In this study, we have synthesized a galvinoxyl-inspired dinitronyl nitroxide, 2,7-bis(*N*-tert-butyl-*N*-oxylamino)-10'-methyl-9,9'(10H,10'H)spirobiacridin-10-oxyl (1). The *N*-oxy-acridine side of 1 is an isoelectronic structure with galvinoxyl (Fig. 1c); namely, two oxygen and methine sites in galvinoxyl are replaced by nitroxides/nitrones. The NO site is more thermodynamically stable than phenoxy (>C-O`) due to a local



Fig. 1 Resonance and equilibrium schemes of (a) galvinoxyl and (c) dinitronyl nitroxide **1**. (b) Illustration for three electronic configurations, non-SHI, partial SHI, and SHI.

Department of Chemistry, Faculty of Science Division 1, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo, 162-8603, Japan.

E-mail: kanetomo@rs.tus.ac.jp

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resonance structure of the $>N-O^{\bullet}$ and $>N^{\bullet+}-O^{-}$ forms. This allows the removal of the tert-butyl substituents used in galvinoxyl, and a six-membered ring can be created in the central moiety. The latter improves the planarity of the whole molecule, resulting in strong intramolecular antiferromagnetic coupling. For 1, the formation of the spiro structure with N-methyl-9(10H)acridine not only forms the central six-membered ring but also introduces steric protection. According to Iwamura's work, the 1,4-phenylene bisnitroxide moiety could be stabilized as a quinoid form, p-benzoquinonediimine N,N'dioxide.³⁷ Therefore, 1 should favour the dinitronyl nitroxide monoradical structure (the left side in Fig. 1c). In fact, magnetic and theoretical studies of 1 exhibited the ground doublet state (S = 1/2). The MO diagram exhibited the partial SHI state as well as galvinoxyl, owing to the remarkable spin polarization effect.

Results and discussion

Synthesis and characterization

Compound **1** was synthesized by following the procedure shown in Scheme S1.[†] Black platelet polycrystals of **1** were obtained by recrystallization from CH_2Cl_2 and *n*-hexane. Product **1** was characterized through spectroscopic and X-ray crystallographic analyses. The decomposition temperature of **1** was 168 °C, where the thermal stability of **1** is similar to that of galvinoxyl (153 °C).¹⁸

The X-band electron spin resonance (ESR) spectrum of **1** in a toluene solution at room temperature (rt) is shown as a red line in Fig. 2. The spectrum was a major triplet splitting with several minor ones, indicating the hyperfine structures for one ¹⁴N and three ¹H atoms. This pattern indicates that **1** in solution exhibits dinitronyl nitroxide as shown in Fig. 1c. It was also found that the radical spin could be localized in one benzenoid moiety. This finding is also reported in the study of galvinoxyl.^{26,38,39} When bulky substituents such as *tert*-butyl or 1-adamantyl are introduced at the methine site of galvinoxyl, two phenyl rings are twisted, resulting in the unpaired electron



Fig. 2 X-Band ESR spectrum of **1** in a degassed toluene solution at 298 K. The top and bottom spectra represent the experimental and simulation, respectively. For the optimized parameters in the simulation, see the text.

being confined to one phenoxy ring. By means of simulation using the EasySpin software,⁴⁰ the hyperfine constants, *g* values, and the linewidth of peak-to-peak (lwpp) were determined as $a_N = 1.17$ mT, $a_{H1} = 0.252$ mT, $a_{H2} = 0.182$ mT, $a_{H3} =$ 0.087 mT, $g_{xx} = 2.0037$, $g_{yy} = 2.0069$, $g_{zz} = 2.0096$, and lwpp = 0.164 mT. The simulation spectrum (a black line in Fig. 2), derived from the above parameters, well reproduced the experimental one. For **1**, two N–O sites could be twisted along a single bond relative to the acridine ring, leading to a situation similar to that of the galvinoxyl derivative with bulky substituents.

Time-dependent ESR measurements were performed under ambient conditions to assess the stability of **1** in solution (Fig. S1a[†]). The time dependence of the maximum intensities in the central peak is shown in Fig. S1b.[†] Fitting of the data shows an exponential decay of the ESR intensity, but the intensities did not reach zero for the measurement times. The hyperfine structure ($a_{\rm H}$) gradually disappeared, resulting in a simplified triplet splitting pattern. This finding can be attributed to the infiltration of O₂ into the solution during storage.

Single-crystal X-ray crystallography

The crystal structure of **1** was evaluated at 93 K, and it crystallized in a monoclinic $P\bar{1}$ space group (Table S1†). There were two crystallographically independent molecules in a unit cell (Fig. 3a). Two independent molecules (**1a** and **1b**) are represented in Fig. 3b and c, respectively. There were disordered CH_2Cl_2 crystal solvents, which were accounted for in the SQUEEZE/PLATON program, and the electron count was 72 electrons per formula unit. This value is close to the 1.7 CH_2Cl_2 solvents (71 electrons). The N1–O1, N2–O2, and N3–O3



Fig. 3 Crystal structures of (a) asymmetry units in the unit cell and molecular structures of (b) **1a** and (c) **1b**. Thermal ellipsoids for non-hydrogen atoms are drawn at the 50% probability level. The H atoms and solvent molecules are omitted for clarity.

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bond lengths of 1a are 1.285(2), 1.295(2), and 1.281(2) Å, respectively, and the N5-O4, N6-O5, and N7-O6 bond lengths of 1b are 1.285(3), 1.287(3), and 1.284(2) Å, respectively. These bond lengths are shorter than the average of about 1.45 Å for hydroxylamine compounds,41-47 indicating successful oxidation. Three N-O sites in 1 show either nitroxides or nitrones, as shown in Fig. 1b. However, since both nitrones and nitroxides have an N-O length of about 1.3 Å,^{16,19,37,48-85} the bond length between the N and neighbouring sp² carbon atoms is important to determine the electron state of the N-O site. In fact, there is a difference in the N-C_{sp²} length; the average lengths for nitrones are 1.31 Å (N–O: 1.29 Å),^{48–53} those for aryl tert-butyl nitroxides are 1.43 Å (N-O: 1.29 Å),^{16,19,37,45,54-71} and those for 10-oxy-9(10H)acridines are 1.41 Å (N–O: 1.29 Å).72-75 The compound 4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl, known as nitronyl nitroxide, has both nitrone and nitroxide moieties and thus an N-C_{sp2} length of 1.34 Å (N-O: 1.28 Å), $^{41,54,55,76-85}$ which is intermediate between those of nitrone and nitroxide species. For 1a and 1b, the N-C_{sn²} lengths are 1.380(3)-1.387(3) and 1.373(3)-1.396(4) Å, respectively. These values are close to those of nitronyl nitroxides, indicating a dinitronyl nitroxide structure (the left-side structures in Fig. 1b).

Dinitronyl nitroxide **1** possesses benzenoid and quinoid substructures, and the quinoid one shows bond alternation and reduction of aromaticity. In fact, 1,4-phenylene bis(*tert*-butyl nitroxide) (2) shows alternating C–C bond lengths (Table 1).³⁷ On the other hand, chemical modifications shifted the equilibrium in favour of the benzenoid form due to (i) linker elongation and (ii) steric hindrance. For example, the former are 4,4'-biphenyl- and 4,4"-1,1':4',1"-terphenylene bis (*tert*-butyl nitroxide) compounds (3 and 4, respectively),⁸⁶ and the latter is 2,3,5,6-tetramethoxy-1,4-phenylene bis(*tert*-butyl nitroxide) (5).³⁷ Selected bond lengths and torsion angles of **1a** and **1b** are summarized in Table 1. For comparison purpose, the data of 2–5 are also listed. A harmonic oscillator model for aromaticity (HOMA) value is useful for clarifying comparisons of bond lengths.^{87,88} Four phenyl rings, C1–C6 (A) and C7–C12

(B) for **1a** and C35–C40 (C) and C41–C46 (D) for **1b**, show HOMA values of 0.844, 0.853, 0.806, and 0.922, respectively. For **1a**, the values are intermediate between those of the quinoid form **2** and the benzenoid forms **3–5**, indicating the delocalized radical spin throughout the acridine moiety. On the other hand, the HOMA values of the C and D rings in **1b** are smaller and larger, respectively, compared to **1a**. This finding implies that the C and D rings favour the quinoid and benzenoid forms, respectively. This situation is also supported by the large torsion angle between the D ring and the N–O site.

The nearest intermolecular NO···NO distance is 3.943(2) Å of O2···O2^{*a*}. This value is larger than the sum of the van der Waals radii of O/O of 3.04 Å,⁸⁹ indicating no direct radical-radical contact. On the other hand, three O atoms, O2, O5^{*b*}, and O6^{*c*}, face each other around the C5 atom, as shown in Fig. S2.† The O2···O5, O5···O6, and O6···O2 distances of 4.007 (3), 4.055(3), and 4.330(2) Å, respectively, are larger than the sum of vdW radii (O/O; 3.04 Å), while the O2···C5, O5···C5, and O6···C5 distances of 2.700(2), 3.058(3), and 3.237(2) Å, respectively, are smaller than it (C/O; 3.22 Å). These contacts between three O atoms through an H atom on the C5 atom could induce magnetic interaction.

Magnetic properties

Magnetic susceptibility was measured for the polycrystal sample **1** at 2–350 K (Fig. 4a). Note that the molecular weight is calculated excluding the crystalline solvent because the exact amount of solvent cannot be calculated due to the gradual desorption of the solvent during storage. Upon cooling from 350 K, the $\chi_m T$ value gradually decreased to a plateau at 100–10 K. This antiferromagnetic behaviour implies a depopulation from the quartet excited state (S = 3/2) to the doublet ground state (S = 1/2). On the other hand, the plateau value of about 0.32 cm³ K mol⁻¹ was smaller than the calculated $\chi_m T$ value of 0.378 cm³ K mol⁻¹ derived from S = 1/2 and g = 2.0067, where the g value is from the ESR study. This difference implies the presence of the residual crystal solvents in



	1a		1b		$\frac{2 (n = 1)^{a,b}}{3 (n = 2)^{c}}$			4 $(n = 3)^c$	5 ^b
о. С.	A	В	С	D	а	b			• OMe
O–N/Å	1.285(2)	1.281(2)	1.285(3)	1.284(2)	1.290(5)	1.287(6)	1.284(1)	1.291(1)	1.269(5)
N–C _a /Å	1.384(2)	1.380(3)	1.373(3)	1.386(4)	1.353(6)	1.362(7)	1.411(1)	1.413(2)	1.428(5)
$C_{\alpha}-C_{\beta}/Å$	1.412(2)	1.413(3)	1.407(4)	1.411(4)	1.422(6)	1.417(6)	1.406(1)	1.404(2)	1.393(7)
$C_{\beta}-C_{\gamma}/Å$	1.367(3)	1.368(3)	1.364(3)	1.362(4)	1.360(7)	1.358(7)	1.380(1)	1.385(2)	1.397(5)
$C_{\gamma} - C_{\delta} / Å$	1.411(2)	1.406(2)	1.416(3)	1.405(3)	1.424(6)	1.423(6)	1.416(1)	1.405(2)	1.384(6)
$ \angle O - N - C_{\alpha} - C_{\beta} /^{\circ}$	7.4(3)	2.8(3)	6.4(3)	24.3(3)	1.2(6)	3.3(7)	7.3(1)	15.3(2)	84.5(5)
HOMA ^d	0.844	0.853	0.806	0.922	0.722	0.745	0.925	0.955	0.990

^a Compound **2** has two crystallographically independent molecules in the unit cell (molecules *a* and *b*). ^b Ref. 37. ^c Ref. 86. ^d Ref. 87 and 88.



Fig. 4 (a) Temperature dependence of $\chi_m T$ for **1**, measured at B = 0.5 T. A solid line shows the fitting curve. The inset shows an enlarged view of the 280 to 350 K region. (b) *M* vs. *B* at 2.0 K. The solid line shows the Brillouin function with S = 1/2 and g = 2.0067. The dashed line is multiplied by 0.8668.

the sample. Upon further cooling from 10 K, the $\chi_{\rm m}T$ value decreased sharply, indicating intermolecular antiferromagnetic coupling. The experimental data of **1** were analysed with eqn (1) based on the linear three S = 1/2 centre model, $\hat{H} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3)$.⁹⁰

$$\chi_{\rm m}T = \frac{N_{\rm A}\mu_{\rm B}^2 g^2}{4k_{\rm B}} \frac{1 + \exp(J/k_{\rm B}T) + 10\exp(3J/2k_{\rm B}T)}{1 + \exp(J/k_{\rm B}T) + 2\exp(3J/2k_{\rm B}T)} \frac{T}{T - \theta} f \quad (1)$$

A Weiss mean-field parameter θ and a parameter f are introduced in order to estimate the intermolecular interaction in the low-temperature region and the amount of the residual CH_2Cl_2 as a crystal solvent, respectively. The g value was set at 2.0067. The best-fit curve was achieved with $J/k_{\rm B} = -761(3)$ K, θ = -1.22(3) K, and f = 0.8668(9) (a black line in Fig. 4a). The J value was negative, indicating the doublet ground state arising from the through-bond antiferromagnetic interaction, while the magnitude of J is discussed in the theoretical calculations below. The θ value was negative and small due to indirect contacts (Fig. S4^{\dagger}). From the *f* value of 0.8668(9), we estimated the amount of the CH₂Cl₂ crystal solvent required for the calculated molecular weight, resulting in 0.991 molecules. This value is less than the 1.7 molecules observed in the above structural study, suggesting desorption of the solvent during storage. Above 330 K, the experimental $\chi_{\rm m}T$ deviated from the fitting line (the inset of Fig. 4a), and this may be triggered by the desorption of the residual crystal solvents.

The field-dependence of the magnetization curve at 2 K is shown in Fig. 4b. The *M* value was not saturated and reached $0.814\mu_{\rm B}$ at 7 T. Compared to the black solid line in Fig. 4b, which is derived from the Brillouin function with *S* = 1/2 and *g* = 2.0067, there is a difference in the scale of the experimental and simulation curves. Therefore, the black dashed line in Fig. 4b is drawn, considering the purity factor *f* = 0.8668. The magnitude of *M* in the simulation is well in agreement with the experimental curve, whereas the experimental curve is within the simulation. This result indicates an antiferromagnetic interaction, supporting the negative θ constant.

Theoretical studies

The density functional theory (DFT) calculations on 1a and 1b were performed using the atomic coordination determined from the crystallographic study. For reducing calculation cost, the N-methyl acridine ring and tert-butyl groups were replaced with H atoms and methyl groups, respectively. The calculated spin densities of the doublet (d) and quartet (q) states for 1a and 1b have been mapped onto the molecular skeleton shown in Fig. 5. There is a difference in the maps of the doublet state in 1a and 1b. For 1a, the red and blue lobes, which represent positive and negative spin densities, appeared alternately along the π -conjugation system owing to the spin polarization (Fig. 5a). On the other hand, for 1b, two-coloured lobes appeared alternately only on the left-hand six-membered ring, while on the right-hand one, the spin density is strongly localized at the N-O site. The quartet and doublet energy states for 1a were $E_q = -969.95114196$ au with $\langle S^2 \rangle_q = 3.7501$ and $E_d =$ -969.97229443 au with $\langle S^2 \rangle_d = 0.8284$, respectively. Those parameters for **1b** were $E_q = -969.94969131$ au with $\langle S^2 \rangle_q =$ 3.7501, and the E_d energy was -969.96185149 au with $\langle S^2 \rangle_d =$ 0.8112. The ΔE_{a-d} values of **1a** and **1b** were determined to be +0.5756 and +0.3309 eV, respectively. The exchange-coupling constant $J/k_{\rm B}$ values for **1a** and **1b** are also -1589 and -908 K, respectively, calculated by the approximate spin-projection method, ${}^{91}J = (E_d - E_q)/(\langle S^2 \rangle_q - \langle S^2 \rangle_d)$. These findings indicate that both 1a and 1b show the ground doublet state.

The molecular orbitals (MOs) of the doublet state for **1a** and **1b** are shown in the left and right columns of Fig. 6, respectively. The α - and β -MO1–3 levels in **1a** and **1b** are obviously separated from the other MO levels, and thus these MOs play the key role in determining the spin state. For **1a**, α -MO2 and β -MO2 (-5.53 and -2.94 eV), α -MO1 and β -MO3 (-2.79 and -5.42 eV), and α -MO3 and β -MO1 (-5.77 and -2.42 eV) are paired, respectively, according to the comparison of



Fig. 5 Spin-density maps illustrating the DFT results for the (a) doublet and (b) quartet states of **1a** and the (c) doublet and (d) quartet states of **1b**. Those atomic positions were taken from the crystallographic study. Blue and red lobes indicate positive and negative spin densities, respectively, with the isocontour of $0.002 \text{ e} \text{ Å}^{-3}$.



Fig. 6 Molecular-orbital (MO) energy-level diagram for α and β spins in the doublet state of (left) **1a** and (right) **1b** (isovalue = 0.03). Blue and red colours represent unoccupied and occupied orbitals, respectively. Selected MO images are superposed.

those MO maps shown in Fig. 6. The orbital lobes of β -MO3 are positioned to avoid those of α-MO2, reducing electron repulsion; namely, there is a remarkable effect of spin polarization. This situation implies intramolecular antiferromagnetic coupling between the terminal and central N-O sites, providing a partial SHI state like galvinoxyl. On the other hand, there is a difference in the MO diagram of 1b and 1a. According to the structural study, the unpaired electron of 1b is localized on the N7-O6 site with the C42-C47 (D) ring. Those MO maps shown in Fig. 6 imply that α -MO1 and β -MO3 (-2.73 and -5.61 eV), α -MO2 and β -MO1 (-5.03 and -2.19 eV), and α -MO3 and β -MO2 (-6.10 and -3.24 eV) are paired. For the occupied MOs, α -MO2, α -MO1, and β -MO3, the arrangement of the molecular lobes on the left-side ring is affected by spin polarization, which is supported by the quinoid form observed in the structural study. However, only the α spin exists on the right-side ring. These results suggest that the radical spin is localized at the N-O site on the right-side ring. The differences in spin densities and MOs of 1a and 1b were caused by the degree of tilt of the N-O site to the acridine ring.

Conclusions

We have prepared the novel galvinoxyl-inspired dinitronyl nitroxide **1**, which shows a ground doublet state (S = 1/2) as confirmed by magnetic measurements. Compound **1a** shows high coplanarity between the acridine and N–O sites. The unpaired electron is delocalized throughout the acridine ring, resulting in thermodynamic stability similar to that of galvinoxyl. DFT calculations reveal strong intramolecular antiferromagnetic coupling and a remarkable spin polarization effect. On the other hand, in **1b**, one N–O site is twisted relative to the acridine ring, and the radical spin is localized to one phenyl ring. According to the ESR study, in solution, the radical spin localizes either on the phenyl rings due to the configuration of the N–O sites or the *N*-methyl acridine sites. Therefore, these studies on **1** reveal that the SOMO and HOMO electronic configurations are highly responsive to the conformation of the N–O sites. This highly responsive electronic structure makes it possible to produce a switching material that is triggered by the external environment.

Conflicts of interest

There are no conflicts to declare.

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