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Syntheses and Magnetic Properties of Stable Organic Triradicals with Quartet Ground States Consisting of Different Nitroxide Radicals

Megumi Tanaka, Kenji Matsuda,[†] Tetsuji Itoh, and Hiizu Iwamura*,[‡]

Contribution from the Institute for Fundamental Research in Organic Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

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Abstract: Bis[*p*-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl] nitroxide (**3**) was synthesized via desilylation of *O*-protected diradical followed by autoxidation. By deoxgenation of **3**, *p*-(1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl)phenyl-*p*-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl nitroxide (**4**) and bis[*p*-(1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl)phenyl] nitroxide (**5**) were prepared. X-ray analysis of a dark brown needle single crystal for **4** confirmed that **4** consisted of three different kinds of nitroxide radical centers, which showed three reversible redox waves at +0.42, +0.82, and +1.01 V (vs Ag/Ag^+) in CH_3CN solution. The temperature dependence of the molar magnetic susceptibilities for microcrystalline samples of triradicals **3**−**5** was measured by a SQUID susceptometer, showing the intramolecular ferromagnetic and intermolecular antiferromagnetic interactions. Experimental data were fitted to the equation derived from an asymmetric linear three-spin model ($H = -2(J_{12}\mathbf{S}_1\cdot\mathbf{S}_2 + J_{23}\mathbf{S}_2\cdot\mathbf{S}_3)$). The best fit parameters were $J_{12}/k_B = J_{23}/k_B = 231 \pm 4$ K for **3**, $J_{12}/k_B = 349 \pm 26$ K, $J_{23}/k_B = 130 \pm 3$ K for **4**, and $J_{12}/k_B = J_{23}/k_B = 127 \pm 3$ K for **5**. Triradicals **3**−**5** thus have quartet ground states. These exchange coupling parameters are mutually compared in reference to their molecular structures.

Introduction

Due to the valence electrons in organic molecules being paired, organic compounds are typically insulators and diamagnetic. The electron spin of the unpaired electrons is needed for developing strong magnetic properties in organic compounds. It has been established that (1) a strong inter- and/or intramolecular exchange coupling among the spins and (2) their high dimensional arrangement in space are required to order them at finite temperature.[1] From the first point of view, intramolecular ferromagnetic interaction among the electron spins in polyradicals is of great interest in connection with the design of molecular ferromagnets. Poly(*m*-phenylenecarbenes) **1** have been most systematically studied inter alia and are accepted to represent the highest spin organic molecules.[2] The high spin state of **1** is based on the ferromagnetic exchange coupling between the one-center π- and σ-unpaired electrons at the divalent carbons and among the topologically polarized π-spins. However, carbene species lack the stability for characterization under ambient conditions and have an inherent drawback for further extension to usable magnetic materials. To overcome the problems of *m*-phenylenecarbene units, Ishida et al. designed and synthesized bis[3-*tert*-butyl-5-(*N*-oxy-*tert*-butylamino)phenyl] nitroxide **2**, and showed that **2** was stable under ambient temperature and had a large ferromagnetic exchange coupling of $J/k_B = 240$ K.[3] The oxygen atom of nitroxide radicals is known to have enough basicity for coordination with transition metal ions. When three nitroxide radical centers are arranged trigonally within a triradical molecule, it can serve as bridging ligands for making high dimensional metal coordination complexes, satisfying the above condition (2).[4] From these points of view, stable polyradicals bearing high-spin ground states such as **3** were deemed very attractive to us as the coupling units for highly structured molecular magnets. However, stable quartet triradicals having multiple ligating sites are still quite limited.[5]

Results and Discussion

Molecular Design and Synthesis. In place of *tert*-butyl nitroxide for the terminal spin sources in **2**, Ullman's nitronyl nitroxide was selected in this work as in **3** which is more stable than *tert*-butyl nitroxide and modifiable to other organic radicals

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[†] Present address: Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.

[§] Present address: National Institution for Academic Degrees, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-0026, Japan.

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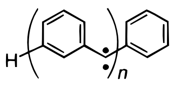

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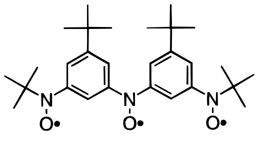

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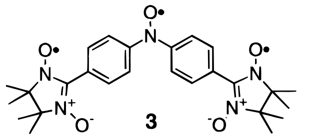

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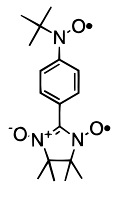

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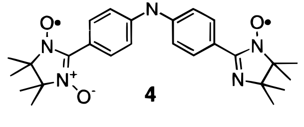

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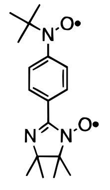

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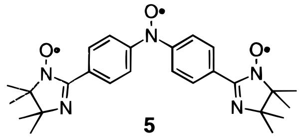


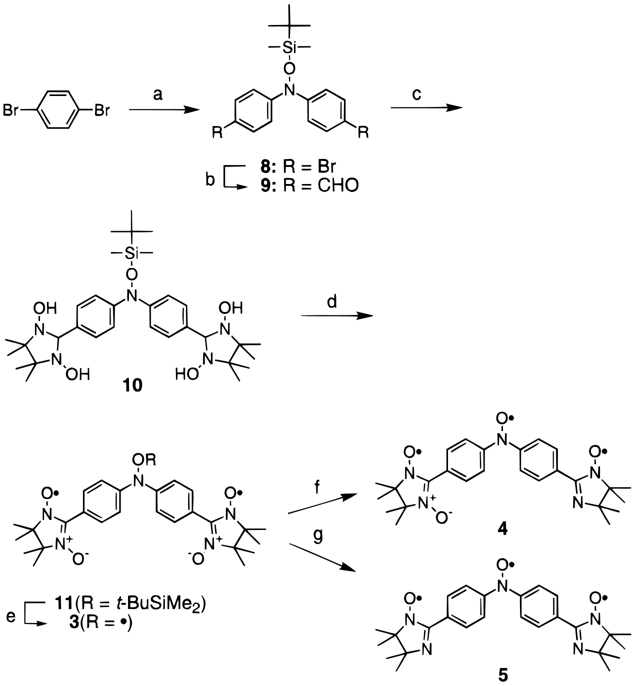
5

such as imino nitroxide as **4** and **5**, thus enabling the construction of organic radicals having three different kinds of nitroxide radicals. Such organic heterospin systems have a number of interesting aspects. The singly occupied MOs (SOMOs) have different spatial distribution and energy levels, and the magnitude of the exchange coupling between any of them should be different. The difference of the ionization potential or shape of the orbital contributing to the coordination bond may produce various coordination patterns to transition metals. Thus, for the construction of a molecular magnet, it is important to investigate the intramolecular interaction of a polyradical consisting of different spins and reflect to a later molecular design. Triradicals **3**−**5** are expected to have five ligating sites for transition metal ions.

In **1** and **2**, atoms carrying the positive spin density are directly attached to the aromatic ring, and therefore the latter has to be *m*-phenylene to have a high-spin ground state as in *m*-quinodimethane. The 2-imidazolinyl radical has a negative spin density at the carbon atom attached to the phenylene ring, and therefore the topology of the π-system changes by one carbon atom and the substitution pattern has to be *p*-phenylene as in triplet **6** and **7**.[6]

The synthesis of **3** was performed as summarized in Scheme 1. In this synthesis, diphenylhydroxylamine is not stable sufficiently; it had to be protected by a silyl group without isolation in situ.

Scheme 1[a]



[a] Reagents and conditions: (a) *n*-BuLi, THF, isopentyl nitrite, *tert*-butyldimethylchlorosilane, triethylamine; (b) *n*-BuLi, THF, DMF, 27.1%, 2 steps; (c) 2,3-dimethyl-2,3-bis(hydroxyamino)butane, methanol, 73%; (d) $NaIO_4$, H_2O, CH_2Cl_2, 72.4%; (e) tetrabutylammonium fluoride, THF, 0 °C, 62.5%; (f) *p*-toluenesulfonyl isocyanate, CH_2Cl_2, 39%; (g) $NaNO_2$, acetic acid, H_2O, CH_2Cl_2, 73%.

Table 1. Crystallographic Parameters for **4**

formula	$C_{26}H_{32}N_5O_4$	c/Å	19.01(1)
fw	478.57	V/Å^3	2468(3)
crystal color, habit	dark brown, needle	Z	4
		D_c/(g cm^{-3})	1.288
crystal system	orthorhombic	no. of reflections	2681
space group	$Pna2_1$	R	0.066
a/Å	21.211(4)	R_w	0.096
b/Å	6.1216(8)		

p-Dibromobenzene was monolithiated and allowed to react with isopentyl nitrite. *N*,*N*-Bis(*p*-bromophenyl)hydroxylamine salt thus formed was treated with *tert*-butyldimethylsilyl chloride and triethylamine. The *O*-protected hydroxylamine (**8**) was dilithiated and reacted with DMF to give the diformyl compound (**9**). Pentakis(hydroxylamine) derivative (**10**) was obtained by reaction with 2,3-dimethyl-2,3-bis(hydroxyamino)butane[7] and oxidized with $NaIO_4$. Desilylation followed by autoxidation of *O*-protected diradical (**11**) gave **3** as a purple powder. If autoxidation was not enough, oxidation by Ag_2O was effective.

By deoxygenation of **3** with *p*-toluenesulfonyl isocyanate,[8] **4** was prepared as a main product together with a few percents of **3** and **5**. With $NaNO_2$ and acetic acid as a catalyst,[9] only **5** was obtained.

Crystal Structure. The crystal structure of **4** was determined by X-ray crystallographic analysis. Crystallographic parameters are summarized in Table 1. An ORTEP drawing of the essential part of **4** is shown in Figure 1 with the numbering scheme. The selected bond distances and angles with their estimated standard deviations are listed in Table 2.

Figure 1 shows that **4** consists of three different kinds of nitroxide radicals just by comparing the bond lengths. Judging from the bond lengths of the benzene ring, to which the nitronyl nitroxide group is attached, we note a contribution of the

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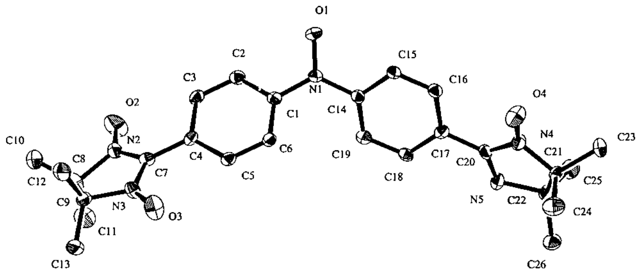

Figure 1. An ORTEP drawing of the essential part of **4** with a thermal ellipsoid plot (50% probability) with the numbering scheme. The hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **4**

Bond Distances (Å)			
N(1)−O(1)	1.289(5)	N(1)−C(1)	1.413(8)
N(1)−C(14)	1.433(8)	C(1)−C(2)	1.400(8)
C(2)−C(3)	1.374(8)	C(3)−C(4)	1.403(7)
C(4)−C(5)	1.431(7)	C(5)−C(6)	1.374(8)
C(6)−C(1)	1.417(7)	C(14)−C(15)	1.398(7)
C(15)−C(16)	1.382(8)	C(16)−C(17)	1.411(7)
C(17)−C(18)	1.392(7)	C(18)−C(19)	1.389(8)
C(19)−C(14)	1.395(7)	C(4)−C(7)	1.472(8)
C(7)−N(2)	1.341(7)	C(7)−N(3)	1.358(7)
N(2)−O(2)	1.270(6)	N(2)−C(8)	1.534(8)
N(3)−O(3)	1.261(6)	N(3)−C(9)	1.513(8)
C(17)−C(20)	1.469(8)	C(20)−N(5)	1.308(8)
C(20)−N(4)	1.384(7)	N(4)−O(4)	1.288(6)
N(4)−C(21)	1.490(7)	N(5)−C(22)	1.522(8)
Bond Angles (deg)			
O(1)−N(1)−C(1)	116.7(5)	O(1)−N(1)−C(14)	118.6(5)
C(1)−N(1)−C(14)	124.6(4)	C(4)−C(7)−N(2)	125.4(5)
C(4)−C(7)−N(3)	125.4(5)	C(7)−N(2)−O(2)	128.6(5)
C(7)−N(3)−O(3)	127.5(5)	N(2)−C(7)−N(3)	109.2(5)
C(17)−C(20)−N(4)	123.3(5)	C(17)−C(20)−N(5)	124.2(5)
C(20)−N(4)−O(4)	126.0(5)	N(4)−C(20)−N(5)	112.5(5)

quinonoid resonance structure; bond lengths C(2)−C(3) and C(5)−C(6) are 1.374 Å, shorter than the other C−C bonds, and similar to that of *p*-benzoquinone *N*-*tert*-butylimine (1.36 Å)[10] {*p*-benzoquinone (1.344 Å)}. All bond lengths are similar in the other benzene ring, to which imino nitroxide is attached, suggesting there is no significant contribution of a quinonoid resonance. It is also observed that the bond lengths C(7)−N(2) and C(7)−N(3) and N(2)−C(8) and N(3)−C(9) in the five membered ring of nitronyl nitroxide differ by only less than 0.02 Å, while C(20)−N(4) and C(20)−N(5) in the imino nitroxide are different by 0.08 Å.

Electrochemical Properties. The cyclic voltammograms of triradicals **3**−**5** are shown in Figure 2, and the numerical data are summarized in Table 3.

The cyclic voltammogram of **3** and **5** showed two reversible waves, and that of **4** showed three. From a comparison of the oxidation potential of each triradical, the oxidation was assumed to proceed as follows: first the terminal nitronyl nitroxide (NN), second the terminal imino nitroxide (IM), and finally diaryl nitroxide (Ar_2NO) at the center. The potential value +0.82 V of **4** is higher than the corresponding value +0.68 V of **5**, because **4** has a positive charge, and is therefore harder to oxidize than **5** by Coulombic repulsion.

ESR Measurements. ESR spectra of triradicals **3**−**5** were measured in degassed 2-methyltetrahydrofuran fluid solution. The spectra of **3** and **4** at 210 K and **5** at room temperature consisted of a multiplet due to nitrogen hyperfine coupling with broadening. The broadening was due to intramolecular dipole−dipole and exchange interactions among the unpaired electrons and also probably due to overlap of different resonances of conformational isomers.

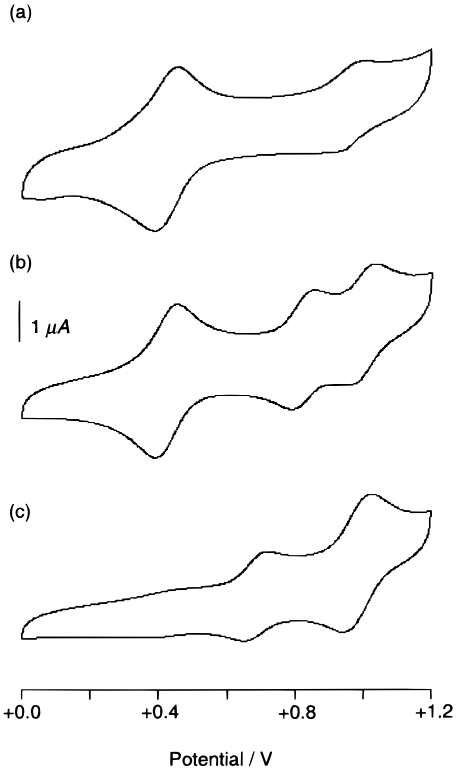

Figure 2. Cyclic voltammograms of (a) **3**, (b) **4**, and (c) **5** in acetonitrile (0.1 M TBAP) on a platinum electrode (vs Ag/Ag$^+$).

Table 3. Electrochemical Data for Triradicals in Acetonitrile (V vs Ag /Ag$^+$)

triradical	$NN^{\bullet}/NN^{+}$ $E_{1/2}$	$IM^{\bullet}/IM^{+}$ $E_{1/2}$	$Ar_2NO^{\bullet}/Ar_2NO^{+}$ $E_{1/2}$
3	+0.42		+0.97
4	+0.42	+0.82	+1.01
5		+0.68	+0.99

In frozen solution, **3** and **4** showed a large main peak with weak outside shoulder signals, and **5** showed only a main peak, suggesting small zero-field splitting parameters; $|D|$ and $|E|$ (Figure 3).

The temperature dependence of the $g = 2$ main peak followed a Curie law in the range 20−70 K for **3** and 12−100 K for **4**. This result suggests that the observed radicals of **3** and **4** are in the ground state in this temperature range (inset of Figure 3). Additionally, the $\Delta m_s = 2$ peak was detected, but $\Delta m_s = 3$ was not observed for all three radicals. Thus, whereas the quartet was concluded to be either a ground state or fully degenerate with lower spin states, it was not possible to determine how close the thermally accessible lower spin states lie above the ground state.

Magnetic Measurements. Magnetic measurements of three triradicals were carried out on a SQUID susceptometer from 2 to 300 K. The temperature dependence of the magnetic susceptibilities (χ) of the microcrystalline samples of three triradicals were measured at 5000 Oe, and are shown in Figure 4.

The χT values of three triradicals at 300 K were 1.37 for **3**, 1.35 for **4**, and 1.27 emu·K·mol^{-1} for **5**, which were close to a theoretical value of 1.125 for three isolated spins. As the temperature was increased, the magnetic susceptibilities of **4** increased from 0.54 emu·K·mol^{-1} at 2 K, reached a maximum of 1.55 emu·K·mol^{-1} at around 65 K, and gradually decreased

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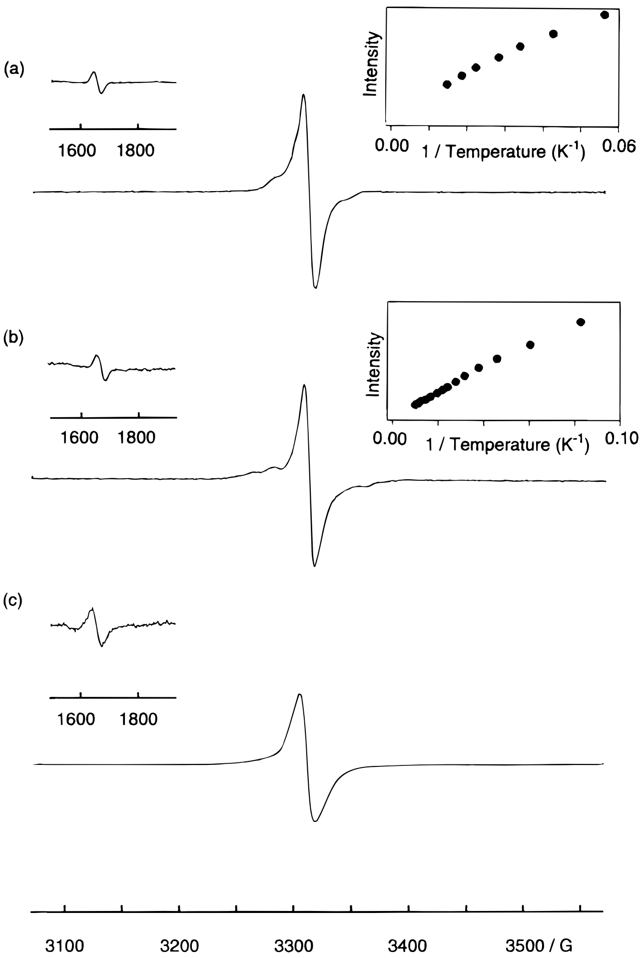

Figure 3. ESR spectra of triradicals in glass (9.31 GHz): (a) for **3** in MTHF/CH_2Cl_2 (1:1) glass at 12.0 K; (b) for **4** in MTHF glass at 11.5 K; (c) for **5** in MTHF glass at 7.0 K. The inset shows the temperature dependence of the ESR signal intensities (Curie plot).

to 1.35 emu·K·mol^{-1} at 300 K. The latter decrease is due to the thermal population of the spins from a quartet ground state to exited doublet state, and the initial attenuation of the χT values at lower temperature is due to intermolecular antiferromagnetic couplings.

The magnetic interactions in an asymmetric linear triradical system can be written as in eq 1, where J_{12} is the exchange

$$H = -2(J_{12}\mathbf{S}_1\cdot\mathbf{S}_2 + J_{23}\mathbf{S}_2\cdot\mathbf{S}_3) = -2J_{12}(\mathbf{S}_1\cdot\mathbf{S}_2 + a\mathbf{S}_2\cdot\mathbf{S}_3) \quad (1)$$

coupling parameter between $\mathbf{S}_1$ and $\mathbf{S}_2$, and a is the ratio of J_{12} and J_{23}, which is the exchange coupling parameter between $\mathbf{S}_2$ and $\mathbf{S}_3$; for symmetric **3** and **5**, $a = 1$ (see Figure 5). Equation 1 neglects intramolecular coupling (J') between two terminal radicals. For polyradicals like **3**−**5**, J' is assumed to be 2 orders of magnitude smaller than J.[11]

The molar susceptibility is given by eq 2, where all symbols have their usual meaning. The temperature correction factor ($T - \theta$) is introduced to represent the Weiss molecular field approximation. The best fitting parameters are summarized in Table 4.

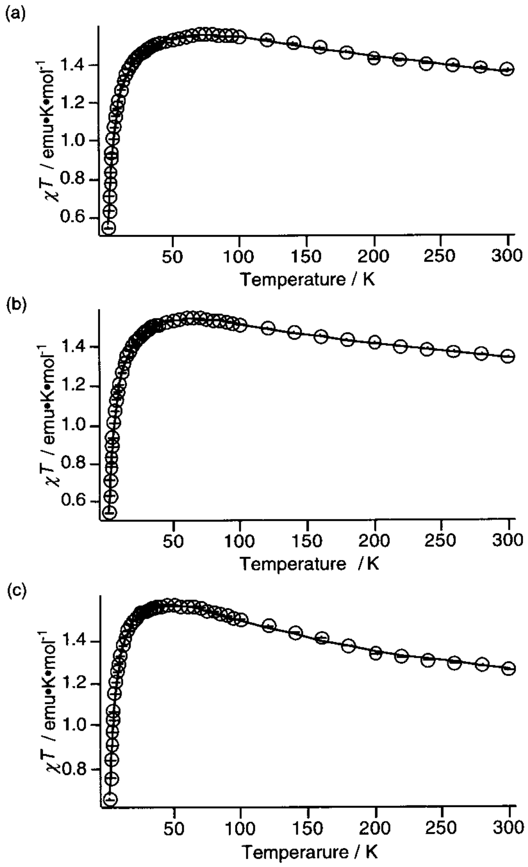

Figure 4. $\chi T - T$ plot for triradicals measured at 5000 Oe. The solid line indicates a theoretical curve (see text): (a) for **3**; (b) for **4**; (c) for **5**.

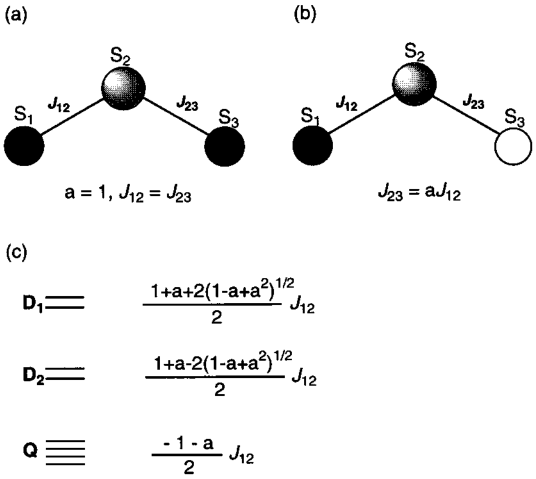

Figure 5. Illustrations to understand magnetism: (a) spin alignment for **3** or **5** and (b) for **4** and (c) energy levels of **3**−**5**.

$$\chi = f\frac{N_A g^2 \mu_B{}^2}{4k(T-\theta)} \times \{10 + \exp[(-1 - a - \sqrt{1 - a + a^2})(J/kT)] + \exp[(-1 - a + \sqrt{1 - a + a^2})(J/kT)]\}/\{2 + \exp[(-1 - a - \sqrt{1 - a + a^2})(J/kT)] + \exp[(-1 - a + \sqrt{1 - a + a^2})(J/kT)]\} \quad (2)$$

The following explanation is possible for the magnitude of exchange coupling (Scheme 2). Quinonoid resonance structure **3q** contributes to two terminal nitronyl nitroxide radicals to give $J_{12}/k_B = J_{13}/k_B = 231$ K. Since the contribution of the quinonoid structure is not conspicuous in **5**, the three spins are more or less localized at two terminal imino nitroxides and the

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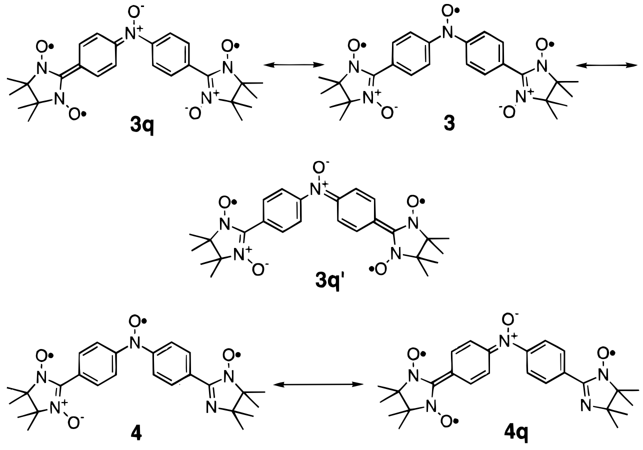
Table 4. Fitting Parameters of the Magnetic Data for Triradical **3**−**7**

triradical	(J_{12}/k_B)/K	(J_{23}/k_B)/K	θ/K	f
3	231 ± 4	231 ± 4	−3.99 ± 0.03	0.89
4	349 ± 26	130 ± 3	−4.09 ± 0.03	0.90
5	127 ± 3	127 ± 3	−3.08 ± 0.03	0.92
6[6]	319			
7[6]		108		

Scheme 2. A Schematic Illustration of the Contribution of Quinonoid Structures **3q** and **4q**



central nitroxide, resulting in relatively small exchange coupling (J/k_B = 130 K). The magnitude is ca. 60% of that in **6**. As revealed by the X-ray structure analysis the molecular structure is asymmetric and there are two exchange couplings, J_{12} and J_{23}, in **4**. The smaller one (J/k_B = 130 K) agrees nicely with that of **5** for the exchange coupling between imino nitroxide and central nitroxide. As concerns the larger one, however, the problem is not so straightforward since J_{12} is greater than that of **3** (J/k_B = 231 K). The contribution of quinonoid structure **4q** must be much greater than that of **3** to produce a larger exchange coupling (J/k_B = 350 K).

Recently, Hosokoshi et al. reported a very strong exchange coupling between nitronyl nitroxide or imino nitroxide on one hand and *tert*-butyl nitroxide on the other in **6** and **7**,[6] respectively (see Table 4); J_{12} of **4** is in good agreement with that of **6**.

Conclusion

In this work we have described a systematic synthesis of three trinitroxide radicals having quartet ground states. A heterospin system **4** which contains diphenyl nitroxide, nitronyl nitroxide, and imino nitroxide was one of them. Synthesis was effected by the protection of the hydroxyl group of bis(bromophenyl)-hydroxylamine and the transformation of nitronyl nitroxide to imino nitroxide by *p*-toluenesulfonyl isocyanate. The structure of **4** was determined by X-ray analysis, showing that whereas the nitronyl nitroxide moiety had a resonance contribution of quinonoid form **4q**, the imino nitroxide moiety appears not to have such a resonance. Cyclic voltammetry of triradicals revealed that oxidation took place consecutively and reversibly in the order the terminal nitronyl nitroxide (NN), the terminal imino nitroxide (IM), and finally diaryl nitroxide (Ar_2NO) at the center. By the measurement of the temperature dependence of magnetic susceptibility, these triradicals were confirmed to have quartet ground states. The exchange interactions between the heterospins were determined, showing the contribution of quinonoid resonance forms is important in strengthening the magnitude of exchange coupling. Triradicals **3**−**5** can have five ligating sites of different basicity and different steric effects. Our work on isolating metal complexes of interesting magnetic properties is in progress.

Experimental Section

A. Materials. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-270 instrument. IR spectra were obtained on a Hitachi I-5040 spectrometer. UV−vis spectra were recorded on a Hitachi U-3300 spectrophotometer. Mass spectra were obtained by JEOL JMS-HX110A instruments. Melting points are not corrected.

Tetrahydrofuran (THF) used in the reactions was distilled, from sodium−benzophenone ketyl under a dry nitrogen atmosphere, just before use. 2-Methyltetrahydrofuran (MTHF) used in the magnetic measurements was purified by distillation from sodium−benzophenone ketyl under a dry nitrogen atmosphere, just before use. IR spectra were obtained on a Hitachi I-5040 spectrometer. All reactions were performed under an atmosphere of dry nitrogen unless otherwise specified.

All reactions were monitored by thin-layer chromatography carried out on 0.2-mm E. Merck silica gel plates (60F-254) using UV light as detector. Column chromatography was performed on silica gel (E. Merck, 70−230 mesh) or alumina (Nacalai, Alumina Activated 200, 200 mesh) inactivated with 6% H_2O.

***N*,*N*-Bis(*p*-bromophenyl)-*N*-(*tert*-butyldimethylsiloxy)amine (8).** *p*-Dibromobenzene (20 g, 85 mmol) was monolithiated with 1.6 M *n*-butyllithium (55 mL) in THF (250 mL) at −78 °C. Into the solution was dropped isopentyl nitrite (5.7 mL, 43 mmol), and the mixture was gradually warmed to room temperature. After addition of *tert*-butyldimethylsilyl chloride (15 g, 100 mmol) and triethylamine (13 mL, 94 mmol), it was stirred for 3 days. A dilute aqueous solution of NH_4Cl and ether was added, and the organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was passed through a column (SiO_2/hexane), and the first fraction was collected. However, it was found to be the mixture of two products by ^{1}H NMR, the several measurements confirmed to produce dibromo compound **8**. The mixture was used in the next step without furthermore purification: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.05 (s, 6 H, Si−CH_3), 0.95 (s, 9 H, *t*-Bu), 7.05 (d, J = 8.91 Hz, 4 H, Ar), 7.40 (d, J = 8.91 Hz, 4 H, Ar); ^{13}C NMR($CDCl_3$, 67.8 MHz) δ −5.0, 18.0, 25.9, 117.5, 122.4, 131.7, 150.4; FAB HRMS (m + 1)/z calcd for $C_{18}H_{24}NOBr_2Si$ 455.9994, found 455.9974.

***N*,*N*-Bis(*p*-formylphenyl)-*N*-(*tert*-butyldimethylsiloxy)amine (9).** To a solution of the mixture of **8** in THF (150 mL) was added 1.6 M *n*-butyllithium (33.6 mL), and the mixture was stirred for 1 h at −78 °C. After addition of DMF (30 mL, excess), it was stirred for 1 h and gradually warmed to room temperature. After aqueous workup as described above, the residue was chromatographed on silica gel with hexane and CH_2Cl_2. By evaporation of the solvent under reduced pressure, the diformyl compound **9** (4.09 g, 11.5 mmol, 27%, 2 steps) was obtained: mp 84−86 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.06 (s, 6 H, Si−CH_3), 0.95(s, 9 H, *t*-Bu), 7.36(d, J = 8.75 Hz, 4 H, Ar), 7.86-(d, J = 8.75 Hz, 4 H, Ar), 9.94(s, 2 H, −CHO); ^{13}C NMR($CDCl_3$, 67.8 MHz) δ −5.0, 18.0, 25.8, 120.1, 130.8, 132.6, 154.1, 190.8; FAB HRMS (m + 1)/z calcd for $C_{20}H_{26}NO_3Si$ 356.1682, found 356.1685.

***N*,*N*-Bis[*p*-(1,3-dihydroxy-4,4,5,5-tetramethylimidazolidin-2-yl)-phenyl]-*N*-(*tert*-butyldimethylsiloxy) amine (10).** **9** (3 g, 8.45 mmol) and 2,3-dimethyl-2,3-bis(hydroxyamino)butane[7] (5 g, 33.8 mmol) were dissolved in methanol (50 mL) and stirred for 3 days. Precipitates were collected by filtration and washed with a small amount of CH_2Cl_2. After drying, pentakis(hydroxyamino) derivative **10** (3.79 g, 6.2 mmol, 73%) was obtained: mp 136 °C; ^{1}H NMR (DMSO-d_6, 270 MHz) δ 0.05 (s, 6 H, Si−CH_3), 0.94 (s, 9 H, *t*-Bu), 1.02, 1.05(ss, 24 H, −CH_3), 4.46 (s, 2 H, −CH-), 7.14 (d, J = 8.25 Hz, 4 H, Ar), 7.40 (d, J = 8.57 Hz, 4 H, Ar), 7.72(s, 4 H, −OH); ^{13}C NMR (DMSO-d_6, 67.8 MHz) δ −4.9, 17.1, 17.8, 24.5, 26.0, 66.1, 119.9, 128.8, 138.1, 151.3; FAB HRMS (m + 1)/z calcd for $C_{32}H_{54}N_5O_5Si$ 616.3894, found 616.3876.

***N*,*N*-Bis[*p*-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)-phenyl]-*N*-(*tert*-butyldimethylsiloxy)amine (11).** To a solution of **10** (600 mg, 0.97 mmol) in CH_2Cl_2 (500 mL) was added an aqueous solution of $NaIO_4$ (430 mg, 2 mmol), and the mixture was stirred for

1 h under the open air. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel with hexane, CH_2Cl_2, and ethyl acetate. By evaporation of the solvent under reduced pressure, diradical **11** (430 mg, 0.71 mmol, 73%) was obtained: mp 195−196 °C; FAB HRMS (m + 1)/*z* calcd for $C_{32}H_{48}N_5O_5Si$ 610.3424, found 610.3431.

***N,N*-Bis[*p*-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)-phenyl] Nitroxide (3).** To a solution of **11** (430 mg, 0.71 mmol) in THF (30 mL) was added tetrabutylammonium fluoride trihydrate (2.2 g, 7.0 mmol) in THF (20 mL), and the mixture was stirred for 30 min. After aqueous workup followed by autoxidation as described in the synthesis of **2**, the residue was chromatographed on alumina gel with hexane, CH_2Cl_2, and ethyl acetate. By evaporation of the solvent under reduced pressure, **3** (218 mg, 0.44 mmol, 62%) was obtained as a purple microcrystalline solid: mp 258 °C; IR (KBr, cm^{-1}) 2988, 1584, 1482, 1431, 1420, 1393, 1370, 1296, 1258, 1215, 1167, 833; FAB HRMS (m + 1)/*z* calcd for $C_{26}H_{33}N_5O_5$ 495.2481, found 495.2492.

***p*-(1-Oxyl-4,4,5,5-tetramethylimidazolin-2-yl)-phenyl-*p*-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl Nitroxide (4).** To a solution of **3** (100 mg, 0.20 mmol) in CH_2Cl_2 (10 mL) was added *p*-toluenesulfonyl isocyanate (40 mL, 1.30 mmol), and the mixture was stirred for 2 h. The mixture was chromatographed on alumina with hexane, CH_2Cl_2, and ethyl acetate. By evaporation of the solvent under reduced pressure, **4** (37 mg, 0.08 mmol, 39%) was obtained as a brown-purple microcrystalline solid: mp 191−192 °C; IR (KBr, cm-1) 2982, 1586, 1483, 1435, 1422, 1412, 1395, 1368, 1296, 1262, 1215, 1169, 1136, 835; FAB HRMS (*m* + 3)/*z* calcd. for $C_{26}H_{35}N_5O_4$ 481.2481, found 481.2709.

Bis[*p*-(1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl)phenyl] Nitroxide (5). To a solution of **3** (100 mg, 0.20 mmol) in CH_2Cl_2 (20 mL) was added an aqueous solution of $NaNO_2$ (76 mg, 1.1 mmol) and 10 drops of acetic acid, and the mixture was stirred for 1 min under the open air. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was recrystallized from heptane/CH_2Cl_2, filtrated, washed with hexane, and dried in the air. **5** (68 mg, 0.147 mmol, 74%) was obtained as a dark orange microcrystalline solid: mp 163−165 °C; IR (KBr, cm^{-1}) 2978, 1591, 1545, 1483, 1458, 1439, 1418, 1408, 1389, 1377, 1368, 1308, 1264, 1287, 839; FAB HRMS (m + 1)/*z* calcd for $C_{26}H_{33}N_5O_3$ 463.2583, found 463.2559.

B. Crystallography. **4** was subjected to crystallographic studies. A single crystal of **4** was mounted on a glass fiber with epoxy resin. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo Kα radiation (λ = 0.710 70 Å). Indexing was performed from three oscillations which were exposed for 4.0 min. The crystal-to-detector distance was 110.00 mm with the detector at zero swing position. Readout was performed in the 0.100 mm pixel mode. The data were collected at a temperature of −150 ± 1 °C to a maximum 2θ value of 55.0°. A total of 215.00° oscillation images were collected, each being exposed for 30.0 min. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full matrix least-squares refinement was based on 2226 observed reflections ($I > 2.50\sigma(I)$) and 316 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.066$$

Neutral atom scattering factors were taken from Cromer and Waber.

$$R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w F_o{}^2\}^{1/2} = 0.096$$

Anomalous dispersion effects were included in F_{calc}; the values for $\Delta f'$ and $\Delta f''$were those of Creagh and McAuley. The values for the mass attenuation coefficients are those of Creagh and Hubbel. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.

C. Electrochemical Properties. The measurement of electrochemical properties of triradicals was performed with a BAS CV-50W electrochemical analyzer. The electrochemical behavior of triradicals was examined by means of cyclic voltammetry for oxidation. Measurements were carried out in acetonitrile solution containing tetra(*n*-butyl)ammonium perchlorate (TBAP, ca. 1×10^{-1} M) as the supporting electrolyte. A three-electrode assembly (BAS) was used which was equipped with a platinum working electrode, a platinum coil as the counter electrode, and a Ag/Ag^+ (TBAP/acetonitrile) electrode as the reference.

D. ESR Spectroscopy. A Bruker ESP 300E spectrometer was used to obtain X-band ESR spectra. Temperatures were controlled by an RMC CT-470-ESR cryogenic temperature controller. The ESR intensities for Curie plots in the temperature range at 20−70 K for **3** and 12−100 K for **4** were measured at appropriate power attenuation calibrated to exclude saturation effects.

E. SQUID Measurement. Magnetic susceptibilities of the powder samples of triradicals were measured by a Quantum Design MPMS-5S SQUID system. Diamagnetic corrections were made using Pascal's constants.

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Supporting Information Available: X-ray structural information on **4** (20 pages, print/PDF). An X-ray crystallographic file, in CIF format, is available through the Internet only. See any current masthead page for ordering information and Web access instructions.

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