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Synthesis and Magnetic Properties of (Pyrrolidin-1-oxyl)–(Nitronyl Nitroxide)/(Iminonitroxide)-Dyads

Haruki Tsujimoto,[a] Shuichi Suzuki,*[a,b] Masatoshi Kozaki,[a] Daisuke Shiomi,[a] Kazunobu Sato,[a] Takeji Takui,[a] and Keiji Okada*[a,c]

Dedication ((optional))

Abstract: Unlike extensively studied diradicals linked by π-conjugated systems, only a few studies have investigated weakly coupled diradicals linked by an sp^3 carbon atom. Herein, we prepared pyrrolidin-1-oxyl–(nitronyl nitroxide)-dyad **5** and pyrrolidin-1-oxyl–iminonitroxide-dyad **6.** From the observed temperature dependence of the magnetic susceptibility, **5** and **6** were determined to be in singlet ground states with $2J_{\mathrm{intra}}/k_B$ = –35.2 K and –13.6 K, respectively. From these results and theoretical calculations of related diradicals, the spin-polarization model counting the small spin density of the sp^3 carbon atom was shown to be used as a spin-prediction model.

Introduction

Preparations and investigation of new high-spin organic molecules are important for the research field of molecule-based magnets,[1] where the intramolecular exchange interactions play an important role in determining magnetic properties.[2] Diradical systems linked by π-frameworks have been extensively studied and their intramolecular spin-alignment can be predicted by parity-based models, the dynamic spin polarization model, and the disjoint and nondisjoint (coextensive) model.[3,4] In contrast, few studies have investigated diradicals linked by sp^3 carbon atoms (Figure 1).[5–7] For instance, Keana and coworkers reported that the spiro-dinitroxide diradical **1** had in a singlet ground state with weak exchange interaction ($2J/k_B$ ~ –12 K), although the *D* value is extremely large in dinitroxide diradical systems.[6] We previously reported on the dimethylmethylene-separated diradical **2**; the theoretical studies indicate that the signs of the intramolecular exchange interaction is conformation dependent: $2J/k_B$ = –178 K for **2**-conformer-I and $2J/k_B$ = +68 K for **2**-conformer-II.[7] Recently, Tretyakov and coworkers reported that intramolecular exchange interactions of hetero diradicals **3** and **4**, in which two radical sites are linked by sp^2- and sp^3-carbons, are most likely ferromagnetic based on theoretical calculations.[8] The first synthesis of diradical **4** was reported by Hideg and coworkers.[9] In addition to a small number studies of these sigma-linked diradicals, the prediction of the ground states of these diradicals, **1**–**4**, seems to be difficult. In order to obtain insight into the spin-prediction rule on these sigma-linked diradicals, we herein investigated simpler new hetero-diradical systems with rigid structures, where two standard open-shell π-conjugated systems are linked by one sp^3-carbon atom, (pyrrolidin-1-oxyl (PyrNO))–(nitronyl nitroxide (NN))-dyad **5** and PyrNO–(iminonitroxide (IN))-dyad **6** (Figure 1). The magnetic properties of **5** and **6** were experimentally and theoretically determined and a possible spin prediction model for these sp^3-carbon-separated diradicals is proposed.

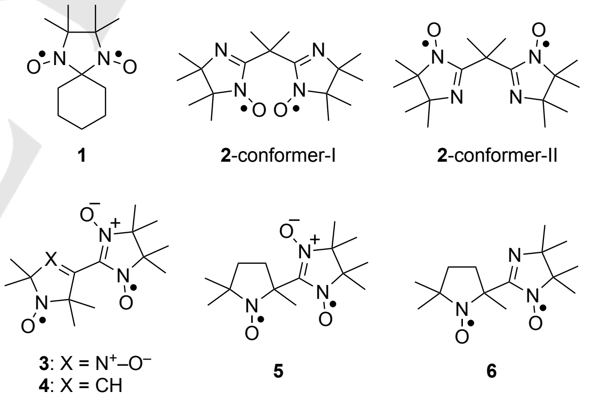
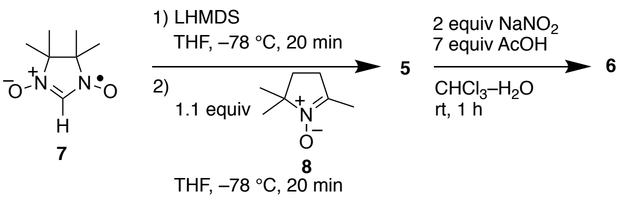


Figure 1. Chemical structures of **1**–**6**.



Scheme 1. Synthetic procedures of **5** and **6**.

Results and Discussion

Syntheses and stability of 5 and 6

The syntheses of **5** and **6** are shown in Scheme 1. Diradical **5** was synthesized from the reaction of radical **7** with lithium

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hexamethyldisilazane (LHMDS) at –78 °C in THF,[8,10] followed by addition of dihydropyrrol-1-oxide **8.**[11] Purification by silica gel column chromatography afforded the diradical **5** as a bluish purple solid. Single crystals of **5** suitable for X-ray crystal structure analysis were obtained by recrystallization from dichloromethane–hexane at –30 °C under an inert atmosphere. Diradical **6** was prepared from **5** by treatment with nitrous acid and obtained as a brown solid after purification by silica gel column chromatography. Single crystals of **6** were obtained by slow evaporation from hexane at ~4 °C. Diradicals **5** and **6** were quite stable in the solid state under aerated conditions, indicating that they are suitable for magnetic measurements in the solid state. UV/VIS spectra of **5** and **6** in dichloromethane were shown in Figure 2. The spectrum of **5** shows absorption bands at 325 and 550 nm, which are mainly attributed to the NN moiety because of the similarity of the spectrum of **7**.[12] The spectrum of **6** shows absorption bands at 265 and 380 nm. The spectrum is similar to that of **2**,[7] suggesting that the bands are mainly attributed to the IN moiety. In the solution state, diradical **6** was stable even under aerated and ambient light conditions while diradical **5** was unstable under the same conditions. It was observed that **5** was decomposed mainly into **6** and **8** under photochemical conditions (irradiated (> 300 nm) by a xenon lamp).

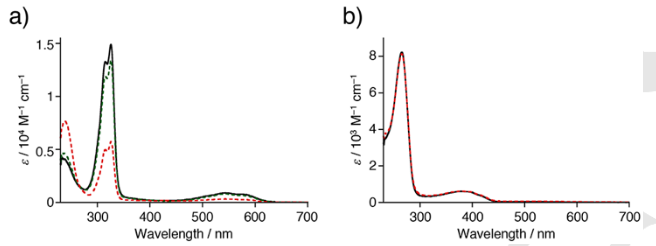

Figure 2. UV/VIS spectra of (a) **5** and (b) **6** in dichloromethane at room temperature (black solid (for **5**) or dotted (for **6**) line: just after sample preparation; red dotted: spectra of the solution samples left for 5 h under an ambient light; green dotted line for **5**: spectrum of the solution samples left for 5 h under a shading condition). The similar spectra changes were observed in the case of the acetonitrile solution.

Crystal structures of 5 and 6

The molecular structures of **5** and **6** were studied by X-ray crystal structure analyses[13,14] and the crystal structures are shown in Figure 3. The N–O bond lengths of **5** and **6** were typical of those in derivatives of pyrrolidin-1-oxyl, nitronyl nitroxide, and iminonitroxide. The averaged intramolecular distances between the spin units for **5** and **6** were found to be ~3.0 and ~3.1 Å, respectively. The dihedral angles for **5** and **6** between the C1–(N1–O1)–C3 and O2–N2–C2–N3–O3 (for **5**) or O2–N2–C2–N3 (for **6**) planes were ~78° and ~82°, respectively. Several intermolecular contacts were observed between the nitroxide oxygen atoms and the methyl groups on NN or IN in **5** and **6** (C_{sp3}–O ~ 3.46–3.49 Å, Figure 4), slightly longer than the sum of the van der Walls radii of C and O (3.3 Å). Therefore, intermolecular magnetic interactions are considered to be very small because the spin density distributions on the methyl groups are quite small (*See Supporting Information,* Table S1), which is experimentally convenient for analyzing the intramolecular exchange interactions.

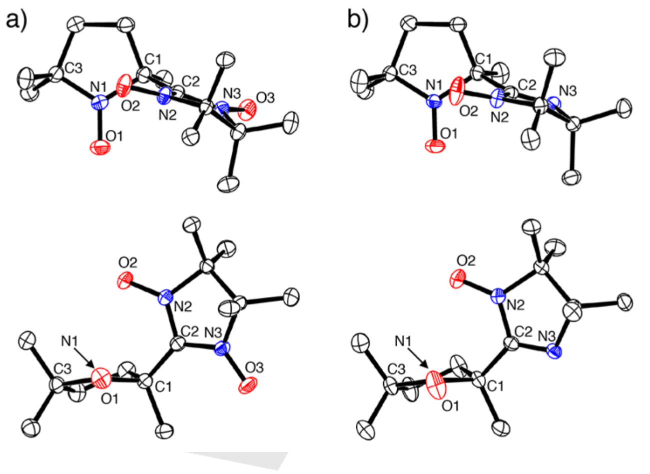

Figure 3. ORTEP views of (a) **5** and (b) **6** (50% probabilities): Top (top) and side (bottom) views. Hydrogen atoms were omitted for clarity.

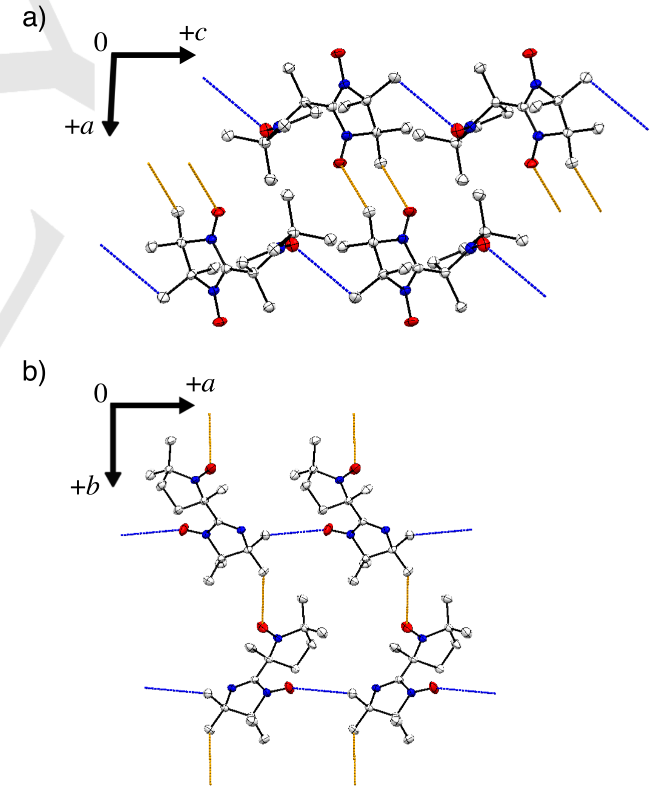

Figure 4. Perspective views of the packing diagrams for (a) **5** from the *b* axis and (b) **6** from the *c* axis. The orange and blue dashed lines denote contacts of C–O: (a) orange, 3.49 Å, blue, 3.46 Å; (b) orange, 3.48 Å, blue, 3.46 Å (sum of van der Waals radii of C–O: 3.3 Å).

ESR spectra of 5 and 6 in frozen matrix

To examine the spin-spin interactions of **5** and **6**, the ESR spectra were measured in a frozen 2-methyltetrahydrofuran (MTHF) matrix at 100 K (Figure 5). The ESR spectrum of **5** shows fine-structured signals with a quite small signal attributed to monoradical impurities at ~330 mT, indicating high sample purity (Figure 5a). The triplet nature of the compound is supported by the forbidden transition signal (ΔM_s = ±2) at ~165 mT. The spectrum at the spin-allowed transition signals was accurately simulated using the following zero-filed splitting parameters and g values for the S = 1 state: $|D/hc|$ = 0.0372 cm^{-1}, $|E/hc|$ = 0.0021 cm^{-1}, g_{xx} = 2.0060, g_{yy} = 2.0050, g_{zz} = 2.0040, and g_{ave} = 2.005. Applying the point-dipole approximation for the above D value, the distance between the two spin-centers was estimated to be approximately ~4.1 Å. This distance is comparable to that between the average centers of the PyrNO and NN moieties (~3.0 Å) in **5**, which was a little shorter than the estimated value.

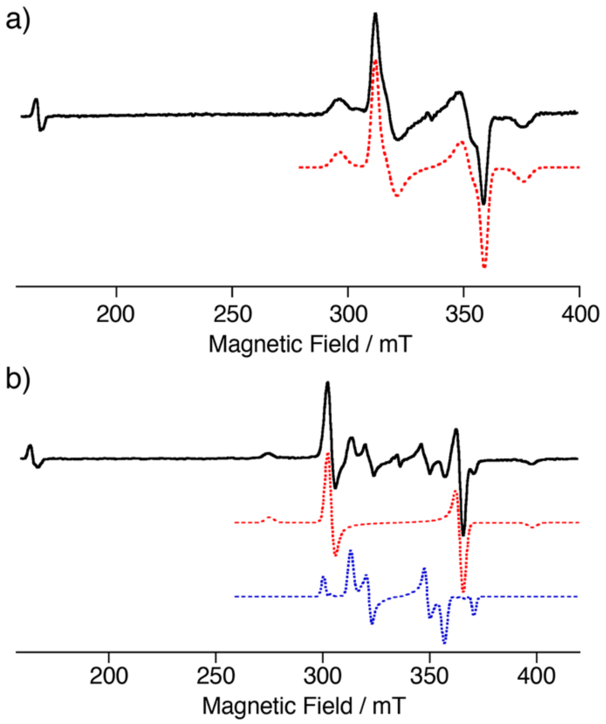

Figure 5. ESR spectra of (a) **5** (ν_0 = 9.425997 GHz) and (b) **6** (ν_0 = 9.424581 GHz) in frozen MTHF solution at 100 K. The dashed lines denote simulated spectra of the triplet species attributed to **5** (red, $|D/hc|$ = 0.0372 cm^{-1}, $|E/hc|$ = 0.0021 cm^{-1}, g_{xx} = 2.0060, g_{yy} = 2.0050, g_{zz} = 2.0040), and **6**-conformer-I (red, $|D/hc|$ = 0.0574 cm^{-1}, $|E/hc|$ ~ 0 cm^{-1}, g_{xx} = 2.0070, g_{yy} = 2.0070, g_{zz} = 2.0002) and **6**-conformer-II (blue, $|D/hc|$ = 0.0327cm^{-1}, $|E/hc|$ = 0.0026 cm^{-1}, g_{xx} = 2.0047, g_{yy} = 2.0075, g_{zz} = 2.0065).

The ESR spectrum of **6** in the spin-allowed region (270–400 mT) is somewhat complicated, but can be fitted using two sets of following parameters as conformers (Figure 5b): **6**-conformer-I; $|D/hc|$ = 0.0574 cm^{-1}, $|E/hc|$ ~ 0 cm^{-1}, g_{xx} = 2.0070, g_{yy} = 2.0070, g_{zz} = 2.0002, and g_{ave} = 2.005, and **6**-conformer-II; $|D/hc|$ = 0.0327cm^{-1}, $|E/hc|$ = 0.0026 cm^{-1}, g_{xx} = 2.0047, g_{yy} = 2.0075, g_{zz} = 2.0065, and g_{ave} = 2.006. The forbidden transition signal (ΔM_s = ±2) was clearly observed at ~165 mT). The estimated distances between the two spin-centers from the D values were calculated to be ~3.6 and ~4.3 Å for **6**-conformer-I and **6**-conformer-II, respectively, using the point-dipole approximation. The theoretical calculation by density functional theory (DFT, *Gaussian 09*, ub3lyp/6-31g*)[16] suggests the existences of two conformers, **6**-transoid and **6**-cisoid, in which the C1-methyl group and the nitroxide group in the IN moiety are oriented transoid and cisoid, respectively: The dihedral angles defined by Me–C1–N2–O2 were –179.8° for **6**-transoid and +57.7° for **6**-cisoid, respectively (Figure 6). **6**-transoid is more stable than **6**-cisoid by ~2.5 kcal/mol. In these conformers, the distances between the two NO-(spin-centers) were estimated to be ~3.1 and ~4.3 Å, indicating that **6**-conformer-I and **6**-conformer-II are **6**-transoid and **6**-cisoid isomers, respectively. In the crystalline state, **6** has a transoid conformation (dihedral angle of Me–C1–N2–O2: –172.0°) and the distance between the averaged NO-(spin-centers) in the PyrNO and IN moieties (~3.1 Å), which is in good agreement with the calculated **6**-transoid geometry.

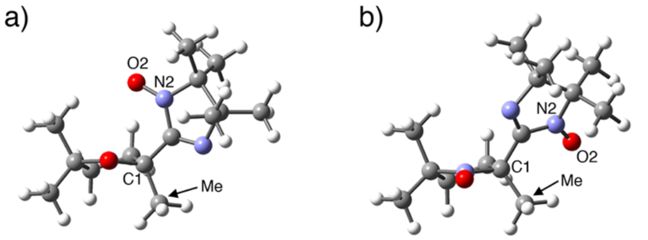

Figure 6. Optimized structures of (a) **6**-transoid and (b) **6**-cisoid (*Gaussian 09*, ub3lyp/6-31g*): Top (top) and side (bottom) views. The dihedral angles defined by Me–C1–N2–O2 were –179.8° for **6**-transoid and +57.7° for **6**-cisoid, respectively. The distances between the two spins for **6**-transoid and **6**-cisoid were estimated to be ~3.2 Å and ~4.3 Å, respectively.

Magnetic Properties of 5 and 6 in the polycrystalline samples

The bulk magnetic properties of the polycrystalline samples of **5** and **6** were examined by superconducting quantum interference device (SQUID) measurements. The temperature dependences of $\chi_{\mathrm{p}}T$ values are shown in Figure 7. The $\chi_{\mathrm{p}}T$ value for **5** at room temperature was found to be 0.734 emu K mol^{-1}, which is similar to that of the expected value for a magnetically independent two S = 1/2 spins (0.754 emu K mol^{-1} for g = 2.005). The $\chi_{\mathrm{p}}T$ value gradually decreased upon lowering the temperature and rapidly decreased below 60 K. The $\chi_{\mathrm{p}}T$–T curve was analyzed by using a modified Bleany–Bowers model (Eq. 1), which suggested an antiferromagnetic interaction, $2J/k_{\mathrm{B}}$ = –35.2 K, as intramolecular interaction in addition to an unspecified antiferromagnetic interaction, θ = –1.3 K ($H = 2J\boldsymbol{S}_{1/2}\bullet\boldsymbol{S}_{1/2}$). This result indicated that diradical **5** is found as a singlet in the ground state.

$$\chi_{\mathrm{p}}T = \frac{2N_{\mathrm{A}}g^2\mu_{\mathrm{B}}^2T}{k_{\mathrm{B}}(T-\theta)[3+\exp(-2J/k_{\mathrm{B}}T)]} \qquad \text{(Eq. 1)}$$

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Diradical **6** showed $\chi_p T$ = 0.752 emu K mol^{-1} at room temperature, which is similar to the expected value for magnetically independent two S = 1/2 spins (0.754 emu K mol^{-1} for g = 2.005). The $\chi_p T$ value decreased slowly upon lowering the temperature to approximately 50 K and then rapidly decreased below 30 K. Analysis of the $\chi_p T$–T curve by using Eq. (1) gave a good fit with an antiferromagnetic interaction, $2J/k_B$ = –13.6 K, with θ = 0 K ($H = 2J\boldsymbol{S}_{1/2}\bullet\boldsymbol{S}_{1/2}$), indicating that diradical **6** is also found to be in a singlet ground state.

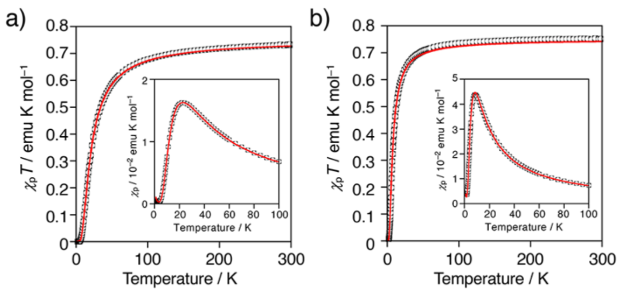

Figure 7. Temperature dependence of $\chi_p T$ and χ_p values for (a) **5** and (b) **6**. The red solid lines were simulated based on a modified Bleany–Bowers model using (a) $2J/k_B$ = –35.2 K with θ = –1.3 K (g = 2.006, doublet impurity: 0.0028) and (b) (a) $2J/k_B$ = –13.6 K with θ = 0 K (g = 2.006, doublet impurity: 0.01).

Table 1. Calculated total energies of triplet and singlet states, and the intramolecular exchange interactions (($2J_{\text{intra\_calc}}/k_B$) / K).[a]

Compd.	E / au (Spin state)	$<S^2>$	Exchange interaction ($2J_{\text{intra\_calc}}/k_B$) / K
5 [b]	–938.0165914 (S = 1)	2.053686	–62.5
	–938.0166900 (S = 0)	1.057275	
6 [b]	–862.8093470 (S = 1)	2.016573	–7.4
	–862.8093587 (S = 0)	1.017295	

[a] The total energies were calculated by *Gaussian 09* using density functional theory at ub3lyp/6-31G* level of theory.[16] In order to estimate the exchange interaction, a compensation equation, $2J_{\text{intra\_calc}} = 2(^{LS}E - {}^{HS}E)/(<^{HS}S^2> - <^{LS}S^2>)$, was used.[17] [b] Geometries were extracted from X-ray structures.

Theoretical calculations and prediction of intramolecular exchange interactions in sp^3-separated weakly coupled diradicals

To explore the intramolecular exchange interactions in detail, we performed DFT calculations with *Gaussian 09* (ub3lyp/6-31g*, Table 1).[16] The exchange interactions of the optimized structures calculated using an equation proposed by Yamaguchi and co-worker were determined to be $2J_{\text{intra\_calc}}/k_B$ = –62.5 K and –7.4 K for **5** and **6**, respectively.[17] The values are similar to the values estimated from the $\chi_p T$–T plot fitting, demonstrating that both diradical are in singlet ground states.

To gain further insight into the spin structure, we calculated the spin densities of the ground states of these sp^3-carbon linked diradicals (triplet state for **3** and **4**, and singlet state for **5** and **6**, Figure 8). There are two paths connecting the two nitroxides groups for these diradicals. Interestingly, the positive (red) and negative (green) spin densities aligned alternately in the shortest connecting path through the small spin density on the sp^3-carbon atom.[4] Consequently, the ground states of these diradicals can be explained by the spin polarization model for both series of diradicals (triplet diradicals **3** and **4**; singlet diradicals **5** and **6**). It should be noted that compound **5** exhibited a more negative spin density on the sp^3-carbon atom with a more negative $2J/k_B$ value than that of **6** (–0.04 for **5** and –0.03 for **6**).[4]

It should be noted that diradical **1** and diradical **2**-conformer-I cannot be described by this spin polarization model. These diradicals have two nitroxides in very close positions. Therefore, these diradicals receive two competing exchange interactions, i.e.; antiferromagnetic through-space interaction and ferromagnetic through-bond interaction, the latter of which is compatible with the proposed spin polarization model.

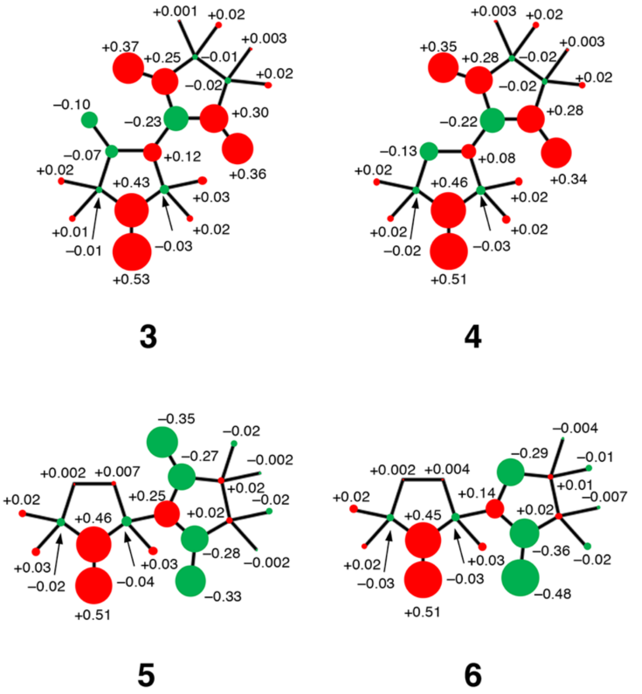

Figure 8. Schematic presentations of calculated spin density distributions of optimized structures (ub3lyp/6-31G*) for **3** and **4** in the triplet states, and **5** and **6** (**6**-transoid) in the broken-symmetry singlet states.

Conclusions

In contrast to strongly coupled diradicals linked by π-conjugated systems, few studies have been investigated the weakly coupled diradical linked by a sigma-frame. We prepared a novel hetero-diradical system, **5** and **6**, with rigid structures where two radicals were linked by a single sp^3-carbon. From the temperature dependences of χ_pT values in the SQUID measurements, **5** and **6** were found to be in the singlet ground states with $2J_{intra}/k_B$ = –35.2 K and –13.6 K, respectively. Diradicals **3** and **4** were previously investigated by Hideg and coworkers[9] and Tretyakov and coworkers[8]; the latter group calculated in detail and propose the triplet ground states. We have calculated the spin densities for the diradical **3**–**6** in their ground states: broken symmetry singlet states for **3** and **4**, and triplet states for **5** and **6**. The signs of the small spin densities on the sp^3 carbon atoms should be highlighted. For these diradicals **3**–**6**, the ground states could be explained by the spin polarization model (Figure 8). The singlet states for diradical **1** and **2**-conformer-I could be explained by the two competing opposite exchange interactions, antiferromagnetic through-space interaction and ferromagnetic through-bond interaction.

Experimental Section

General methods: ESR spectra were recorded on a Bruker ELEXSYS E500 spectrometer. ^{1}H NMR spectra were recorded on JEOL JNM-LA400, JNM-LA300, and Bruker AVANCE-III. EI-MS, FAB-MS, and APCI-MS spectra were recorded on SHIMADZU GCMS-QP2010 Plus, JEOL JMS-700T, and Bruker micrOTOF II-OCU. Infrared spectra were measured using a SHIMADZU FTIR-8700 spectrometer. UV/VIS spectra were measured using SHIMADZU UV-2550. Melting points were measured using a Yanaco MP-J3 apparatus and were not corrected. X-ray data were collected by a Rigaku Saturn CCD system with graphite monochromated MoKα radiation. Magnetic susceptibility measurements were performed using a Quantum Design SQUID magnetometer MPMS-XL. Silica gel 60 (100–200 mesh) and aluminium oxide 90 (70–230 mesh, neutral) were used for column chromatography. The progress of reactions was monitored using thin-layer chromatography (TLC silica gel 60 F_{254} or TLC aluminium oxide 60 F_{254} neutral, if not otherwise specified). All commercially available compounds were reagent grade and used without further purification. Tetrahydrofuran (THF) was dried and distilled over sodium–(benzophenone ketyl) under nitrogen. Dichloromethane (CH_2Cl_2) and *n*-hexane were dried and distilled over calcium hydride. 4,4,5,5-Tetramethylimidazoline-3-oxide-1-oxyl (**7**) [10a] and 3,4-Dihydro-2,2,5-trimethyl-2*H*-pyrrole-1-oxide (**8**) [11] were prepared according to the reported procedure.

Synthesis of 2-(4',4',5',5'-tetramethylimidazoline-3'-oxide-1'-oxyl-2'-yl)-2,5,5-trimethylpyrrolidin-1-oxyl (5): 4,4,5,5-Tetramethylimidazoline-3-oxide-1-oxyl (**7**, 602 mg, 3.83 mmol, 1.0 eq.) was dissolved in dry THF (8 mL) under nitrogen. After this solution was cooled at –78 °C, lithium bis(trimethylsilyl)amide (LHMDS, 1.6 M THF solution, 2.4 mL, 3.84 mmol, 1.0 eq.) was added dropwise. This solution was stirred for 20 min at –78 °C and a dry THF (3 mL) solution of compound **8** (543 mg, 4.27 mmol, 1.1 eq.) was added dropwise. This mixture was stirred for 20 min at –78 °C. To the cold reaction mixture, a saturated aqueous solution of $NaHCO_3$ (6 mL) was added, and the cold mixture was poured into water. The organic layer was separated, dried over anhydrous Na_2SO_4 and filtrated. The filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane–Et_2O (1:15 v/v) as eluent, to afford diradical **5** as a purple solid (296 mg, 30%). The diradical **5** was recrystallized from a CH_2Cl_2–hexane mixture at –30 °C. **5**: $C_{14}H_{25}N_3O_3$; MW 283.37; mp 135 °C (decomp.); TLC (silica) R_f 0.40 (1:15 hexane–Et_2O); MS (FAB$^+$) *m/z* 283 [M$^+$]; IR (KBr, cm^{-1}): 2984, 1456, 1404, 1373, 1167, 1142, 860, 542; UV-Vis λ_{max}/nm (ε/M^{-1} cm^{-1}) in CH_2Cl_2: 326 (14902), 543 (903); Anal. Calcd. For $C_{14}H_{25}N_3O_3$: C, 59.34; H, 8.89; N, 14.83. Found: C, 59.59; H, 8.89; N, 14.83; ESR (powder): *g* = 2.0067; χ_d/emu mol^{-1}: –165 × 10^{-6} (pascal).

Synthesis of 2-(4',4',5',5'-tetramethylimidazoline-1'-oxyl-2'-yl)-2,5,5-trimethylpyrrolidin-1-oxyl (6): An aqueous solution of $NaNO_2$ (158 mg, 2.29 mmol, 2.2 eq.) was added to a $CHCl_3$ solution of **5** (296 mg, 1.04 mmol, 1.0 eq.) with stirring at room temperature. Acetic acid (0.42 mL, 7.34 mmol, 7.0 eq.) was added dropwise to the solution. The mixture was stirred at room temperature for 1 h. A saturated aqueous solution of $NaHCO_3$ (12 mL) was added to this mixture. The organic layer was separated, and washed with water and a saturated aqueous solution of NaCl. This solution was dried over anhydrous Na_2SO_4 and filtrated. The filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using CH_2Cl_2–AcOEt (8:1 v/v) as eluent, to afford diradical **6** as a brown solid (230 mg, 82%). The diradical **6** was recrystallized from a hexane at 4 °C. **6**: $C_{14}H_{25}N_3O_2$; MW 267.37; mp 85 °C (decomp.); TLC (silica) R_f 0.28 (8:1 CH_2Cl_2–AcOEt); MS (FAB$^+$) *m/z* 267 [M$^+$]; IR (KBr, cm^{-1}): 2978, 2937, 1578, 1456, 1437, 1369, 1325, 1250, 1150, 872, 637, 540, 419; UV-Vis λ_{max}/nm (ε/M^{-1} cm^{-1}) in CH_2Cl_2: 265 (8228), 381 (609); Anal. Calcd. For $C_{14}H_{25}N_3O_2$: C, 62.89; H, 9.42; N, 15.72. Found: C, 62.78; H, 9.55; N, 15.66; ESR (powder): *g* = 2.0071; χ_d/emu mol^{-1}: –160 × 10^{-6} (pascal).

Decomposition reaction of 5: Diradical **5** (17 mg, 0.0616 mmol) was dissolved in dry CH_2Cl_2 under nitrogen. The solution was exposed to Xe light (>300 nm) for 20 min, and then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using CH_2Cl_2–AcOEt (2:1 v/v) and EtOH, to afford diradical **6** (8 mg, 0.0299 mmol, 49%) and brown oil (7 mg) involved in compound **8** which were identified by TLC and NMR.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: diradicals • nitroxides • electron spin resonance • magnetic property

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[13] Crystallographic data for **5**: monoclinic, space group $P2_1/n$ (#14), a = 10.803(9) Å, b = 9.104(7) Å, c = 15.527(12) Å, β = 92.315(10)°, V = 1526(2) Å^3, Z = 4, T = 120 K, ρ_{calcd} = 1.233 g cm^{-3}, R = 0.0453, Rw = 0.0637, GOF = 1.046 (CCDC: 1872881).

[14] Crystallographic data for **6**: monoclinic, space group $P2_1/n$ (#14), a = 7.4583(7) Å, b = 16.2410(18) Å, c = 12.3744(14) Å, β = 97.549(5)°, V = 1485.9(3) Å^3, Z = 4, T = 150 K, ρ_{calcd} = 1.195 g cm^{-3}, R = 0.0419, Rw = 0.0620, GOF = 1.331 (CCDC: 1872882).

[15] We also estimated the intermolecular spin-spin interactions for the close contacts shown in Figure 4. The calculated intermolecular interactions were quite smaller than those of the intramolecular ones. See, Table 1 and Table S1.

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Diradicals linked by sp^3-carbon atom were prepared, pyrrolidin-1-oxyl–(nitronyl nitroxide)-dyad **5** and pyrrolidin-1-oxyl–iminonitroxide-dyad **6.** From the temperature dependence of their magnetic susceptibility, **5** and **6** were found to be in the singlet ground states with $2J_{\mathrm{intra}}/k_B$ = –35.2 K and –13.6 K, respectively. From these results and theoretical calculations of related biradicals, the spin-polarization model counting the small spin density of the sp^3 carbon atom was successfully used as a spin-prediction model.

H. Tsujimoto, S. Suzuki, M. Kozaki, D. Shiomi, K. Sato, T. Takui, K. Okada**

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Synthesis and Magnetic Properties of (Pyrrolidin-1-oxyl)–(Nitronyl Nitroxide)/(Iminonitroxide)-Dyads