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Exchange Interaction of Bispyridinyl Diradicals Linked by σ-Frames

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Abstract : 1,1'-(Di-, tri-, tetramethylene, and *trans*-1,4-cyclohexanediyl)bis(2,4,6-triphenylpyridinyl) diradicals were prepared and their exchange interaction was studied. The exchange interaction was found to be considerably variable depending on the structure of the σ-framed linkers: a singlet ground state with $\Delta E_{S\text{-}T} >$ 1.7 kJ/mol for the dimethylene-, singlets with $\Delta E_{S\text{-}T} <$ 230 J/mol for the trimethylene- and tetramethylene-, and a triplet or a degenerate singlet with the triplet for *trans*-1,4-cyclohexandiyl-linked diradicals.

Keywords: electron spin resonance; pyridinium salts; radicals and radical reactions

1. Introduction

Organic high-spin molecules have recently attracted intense attention in relation to material science as well as basic understanding of spin alignment. In many of the reported studies, spin units are incorporated into π-type linkers, typically *m*-phenylene. However, there has been relatively little study of spin units linked by σ-frames. On the pyridinyl radicals, Kosower and Ikegami reported an ESR spectrum of a dimethylene-linked bispyridinyl diradical in 1967.[1] Later, Ikegami and co-workers generated dimethylene- and trimethylene-linked bispyridinyl diradicals from photolysis of their cyclomers.[2,3] These studies focussed on the identification of these diradicals, including the monomer-dimer equilibrium and the reactivity of the cyclomers. The exchange interaction of these diradicals has not been reported. However, it is expected that the exchange interaction is dependent on the σ-frame structure. In connection with our previous studies of pyridinyl radicals incorporated in π-frames [4-6], we have been interested in the exchange interaction in σ-framed diradicals. We report the structure-dependence of the exchange interaction in σ-framed pyridinyl diradicals using a spin source of 2,4,6-triphenylpyridinyl which is connected with σ-frames at the 1-positions of the pyridinyl radicals.

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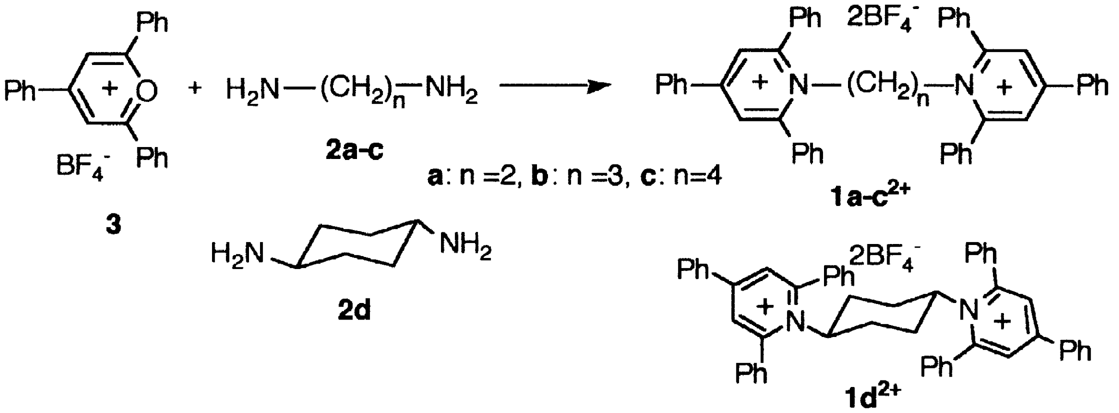
2. Results and Discussion

2-1. *Syntheses of the diradical precursors and diradical preparation*

The dimethylene and trimethylene-linked pyridinyl diradicals studied by Kosower et al. [1] and Ikegami et al. [2,3] undergo dimerization in solution. In order to avoid the dimerization pathway, we used the 2,4,6-triphenylpyridinyl radical which exists as a monomer in solution.[4] The syntheses of the precursory dipyridinium dications **1a-c**$^{2+}$ were achieved by the treatment of 2,4,6-triphenylpyrylium tetrafluoroborates (**3**; 2 equiv) with the diamines **2a-c** (1 equiv) in the presence of triethylamine (4 equiv) in refluxed acetonitrile.[1] This method is easily extended to the synthesis of **1d** with the *trans*-cyclohexane-1,4-diyl-linker.



The reduction potentials to the cation radical and the subsequent diradical [-0.88, -1.02 V for **1a**$^{2+}$, -1.02, -1.13 V for **1b**$^{2+}$, -1.10 V[2] for **1c**$^{2+}$, -1.11 V[2] for **1d**$^{2+}$] were all reversible. These results indicate that the diradicals **1a** - **1d** are stable in the CV time scale. The reduction of the dications **1a**$^{2+}$, **1b**$^{2+}$, and **1c**$^{2+}$ was achieved using 3% Na-Hg in acetonitrile under degassed conditions at room temperature. The colorless solution turned to reddish-purple (345, 576 nm for **1a**$^{2+}$, 352, 572 nm for **1b**$^{2+}$, and 352, 576 nm for **1c**$^{2+}$). This color is characteristic of the 1-methyl-2,4,6-triphenylpyridinyl radical (352, 580 nm).[4] The reduction was stopped when the intensity of the colored species was maximized. The produced diradicals **1a** - **1c** were stable for a few hours at room temperature. However, the diradical from **1d**$^{2+}$ was considerably unstable and the developed reddish-purple color disappeared in a few seconds at room temperature under similar reduction conditions, giving a pale yellow solution. The instability of the diradical **1d** suggests some fast chemical reactions other than the dimerization. From the pale yellow reduction mixture, 2,4,6-triphenylpyridine was isolated along with colorless polymeric materials. Similar reduction of **1d**$^{2+}$ in the presence of diphenyl diselenide (2 equiv) gave 2,4,6-triphenylpyridine (85%) and *trans*- and *cis*-1,4-di(phenylselenenyl)cyclohexane [7] (35% in 1 : 1.7 ratio). Finally and fortunately, the diradical **1d** (355, 553 nm) was found to be stable when the reduction was carried out at -30 °C and the resulting mixture was stored at -30 °C or lower temperature.

2-2. *Detection of the triplet state by ESR*

All the reddish-purple solutions above mentioned showed typical, randomly oriented triplet patterns in the mixed acetonitrile-MTHF (1:1 v/v) solvent at -150 °C. Figure 1 shows the spectra for the selected diradicals **1a** (upper) and **1d** (lower). The zero-field splitting parameters for **1a-d** are summarized in Table 1. The diradical **1a** has a non-zero value of E (1.1 mT), which suggests that **1a** has a conformation of low symmetry. This consideration may be supported by Ikegami's conformational analysis which suggests a conformation with the dihedral angle of N-C-C-N = ca. 90°.[2] Table 1 also shows averaged distances (r) between the two radical centers. The diradicals **1b** and **1c** have similar D-values (8.9 mT and 9.3 mT, respectively) and the value are considerably smaller than that of **1d** which has a zigzag conformation. The larger D-values for **1b** and **1c** suggest that the conformations of **1b** and **1c** are considerably different from the zigzag structure. A π-π interacting conformation (formula **A**) may explain the larger (compared to **1d**) and similar (between **1b** and **1c**) D-values. In such a case, we may expect an antiferromagnetic interaction for the diradical **1b** and **1c**.

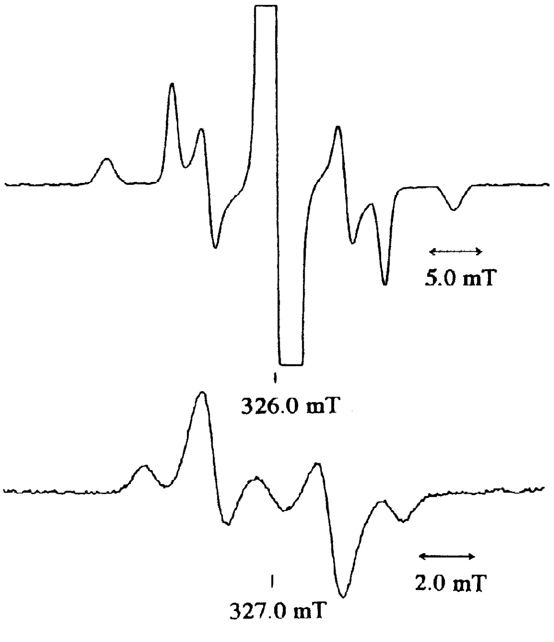
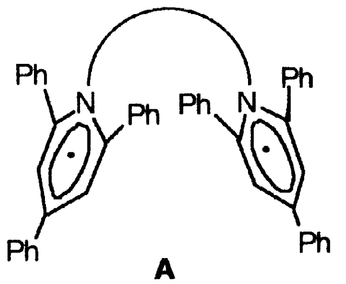


Figure 1. ESR spectra for the selected diradical **1a** (top) and **1d** (bottom) measured at -150 °C in CH_3CN-MTHF (1:1 v/v) matrix.

Table 1. Fine structure parameters of **1a-1d**

	1a	**1b**	**1c**	**1d**
D (mT)	16.0	8.9	9.3	4.8
E (mT)	1.1	0.0	0.0	0.0
r (Å)[a]	5.6[b]	6.8	6.7	8.3

[a] The averaged distances were obtained for **1b-d** by application of the point dipole approximation.
[b] The same method was applied for **1a** ($E \neq 0$).



A

2-3. *Temperature dependence of the ESR signals*

Temperature dependence of the ESR signals was studied using $\Delta m_S = \pm 2$ transition signals. The signal intensity of **1a** decreased as temperature decreased (120 - 77 K). Obviously, the ground state of **1a** is a singlet state. The $\Delta E_{S\text{-}T}$ value cannot precisely be determined. The monotonous decrease of the signal intensity in this temperature range places the lower limit of $\Delta E_{S\text{-}T}$ value as > 1.7 kJ/mol. Figure 2 (left) shows Curie plots for the diradical **1b**. The signal intensity increased as temperature decreased (59 - 20 K). However, curiously, the intensity becomes almost constant in the lower temperature range (20 - 5 K). This is not due to the saturated transition in ESR absorption, because the signal intensity proportionally increased to the square root of microwave power under the measurement conditions. The plateau region is probably ascribed to the presence of several conformational isomers whose triplet states have different temperature dependence. The observed curve is difficult to simulate using the theoretical S-T model. In such a case, the simulated curve [solid line in Figure 2 (left)] would provide $\Delta E_{S\text{-}T}$ = ca. 230 J/mol for a conformer which has the highest $\Delta E_{S\text{-}T}$ value. Quite similar temperature dependence was observed for **1c** ($\Delta E_{S\text{-}T}$ < ca. 230 J/mol). In contrast to these results, the signal intensity of **1d** increased linearly as temperature decreased (25 - 5 K) [Figure 2 (right)]. This indicates that the ground state of **1d** is a triplet state or a singlet state which is degenerate with the triplet state.

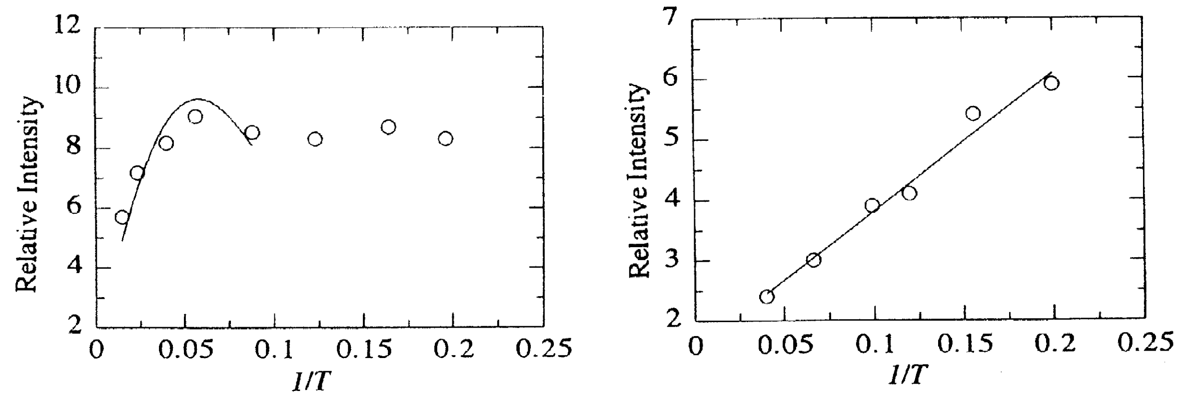


Figure 2. Temperature dependence of the signal intensity for the selected diradicals **1b** (left) and **1d** (right).

Further studies on the exchange interaction of σ-framed polypyridinyls and the related spin sources are in progress. This work was supported by a grant (No. 10146101) from Ministry of Education, Science and Culture, Japan.

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Footnotes:

1. Spectral and physical data; **1a**$^{2+}$: mp 179 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 4.73 (s, 4H), 7.13 (d, *J* = 7.6 Hz, 8H), 7.56 (t, *J* = 7.6 Hz, 8H), 7.62-7.74 (m, 10H), 8.01 (s, 4H), 8.04 (d, *J* = 7.1 Hz, 4H); HRMS (FAB) *m/z* Calcd for $C_{48}H_{38}N_2BF_4$ ([M-BF_4]$^+$): 729.3064. Found: 729.3072; **1b**$^{2+}$: mp 175 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 1.66-1.68 (m, 2H), 3.74-3.78 (m, 4H), 7.36-7.38 (m, 8H), 7.56-7.62 (m, 12H), 7.64-7.70 (m, 6H), 7.95 (dt, *J* = 7.1 Hz, 1.5 Hz, 4H), 8.06 (s, 4H); HRMS *m/z* Calcd for $C_{49}H_{40}N_2BF_4$ ([M-BF_4]$^+$): 743.3221. Found: 743.3229; **1c**$^{2+}$: mp >300 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 0.84-0.86 (m, 4H), 3.72-3.74 (m, 4H), 7.46-7.49 (m, 8H), 7.59-7.65 (m, 14H), 7.73 (t, *J* = 7.2 Hz, 4H), 7.95 (dt, *J* = 7.2 Hz, 1.5 Hz, 4H), 8.09 (s, 4H); HRMS (FAB) *m/z* Calcd for $C_{50}H_{42}N_2BF_4$ ([M-BF_4]$^+$): 757.3377. Found: 757.3386; **1d**$^{2+}$: mp >300 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 0.97-1.02 (m, 4H), 1.85-1.87 (m, 4H), 3.92-3.96 (m, 2H), 7.40-7.42 (m, 8H), 7.54-7.58 (m, 12H), 7.60-7.64 (m, 2H), 7.74 (br s, 4H), 7.90 (dt, *J* = 7.1 Hz, 1.4 Hz, 4H), 8.02 (br s, 4H); HRMS (FAB) *m/z* Calcd for $C_{52}H_{44}N_2BF_4$ ([M-BF_4]$^+$):: 783.3534. Found: 783.3543.
2. Two-electron reduction judging from a single wave in the region of -0.8 ~ -1.2 V where N-methyl-2,4,6-triphenylpyridinium cation is known to be reduced [4].