Preparations and Spin-spin Interactions of 4,4'-(Triptycene-1,8-diyl)bis(1-methyl-2,6-diphenylpyridinyl) Diradical and Its 1,5-Diyl Isomer

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4,4'-(Triptycene-1,8-diyl)bis(1-methyl-2,6-diphenylpyridinyl) diradical was prepared by 3%-Na-Hg reduction of the corresponding dication and the ground state was estimated to be triplet or singlet with small S-T energy gap (< 20 J mol^{-1}). No triplet signal was observed under the similar conditions for the corresponding 1,5-diyl derivative.

We have recently reported spin-spin interactions of pyridinyl radicals incorporated in non-Kekulé type aromatic spacers (*m*-phenylene and anthracene-1,8-diyl) and found that the most stable spin state is subtly dependent on the structure of spacers: 4,4'-(*m*-phenylene)bis(1-methyl-2,6-diphenylpyridinyl) diradical (**1**) is triplet, whereas 4,4'-(anthracene-1,8-diyl)bis(1-methyl-2,6-diphenylpyridinyl) diradical (**2**) is singlet in the ground state; the triplet is a little (52.3 J mol^{-1}) above the singlet.[1] In this context, triptycene-1,8-diyl seems to be an interesting spacer because two pyridinyls may interact either by through-space or through-bond manner.[2] We report the preparation and spin-spin interaction of 4,4'-(triptycene-1,8-diyl)bis(1-methyl-2,6-triphenylpyridinyl) diradical (**3**). The related 1,5-diyl isomer (**4**) is also reported.

The radical precursor, 4,4'-(triptycene-1,8-diyl)bis(1-methyl-2,6-diphenylpyridinum) bis(tetrafluoroborate) ($\mathbf{3}^{2+}$) was synthesized from 1,8-diformyltriptycene. 1,8-Diformyltriptycene[3] was converted to 1,8-bis(2-benzoylethenyl)-triptycene (**5**) in 90% yield by Wittig reaction. Acetophenone condensation of **5** gave the diketone, 1,8-bis[2-benzoyl-1-(benzoylmethyl)ethyl]triptycene (**6**) in 88% yield. The diketone **6** was converted to the bispyrylium salt ($\mathbf{7}^{2+}$) in 54% yield by heating (110 °C for 3 h) in excess amount (13 equiv.) of BF_3•etherate. Treatment of $\mathbf{7}^{2+}$ with methylamine in ethanol gave the dication $\mathbf{3}^{2+}$ in 68% yield as colorless powder {$\mathbf{3}^{2+}$: mp 257 °C, MS (FAB) *m/z* 829 $[M-BF_4]^+$, ^{1}H-NMR (270 MHz, CD_3CN) δ = 3.85 (s, 6H), 5.88 (s, 1H), 6.12 (s, 1H), 6.94 (td, 1H, J = 7.3, 1.3 Hz), 7.07 (td, 1H, J = 7.3, 1.3 Hz), 7.13 (d, 1H, J = 7.9 Hz), 7.15 (dd, 2H, J = 7.9, 1.3 Hz), 7.26 (t, 2H, J = 7.6 Hz), 7.55 (d, 1H, J = 7.3 Hz), 7.60-7.73 (m, 22H), 7.77 (s, 4H); ^{13}C-NMR (67.8 MHz, CD_3CN) δ = 46.7, 48.4, 54.9, 123.8, 125.9, 127.1, 127.2, 127.3, 127.7, 128.7, 129.6, 130.3, 130.4, 132.5, 133.3, 133.8, 143.0, 143.8, 146.3, 148.2, 157.0, 158.2. UV-vis (CH_3CN) λ_{max}/nm (log ε): 303 (4.63)}.

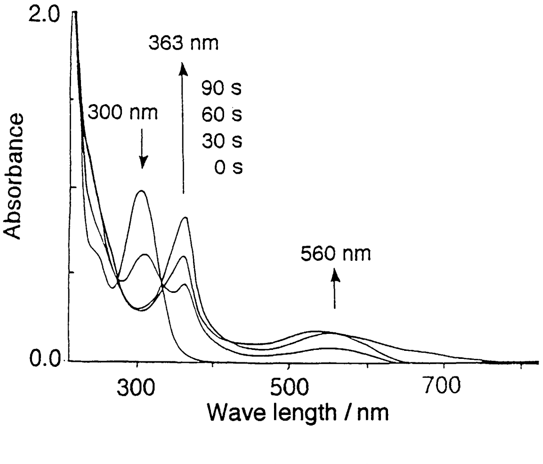
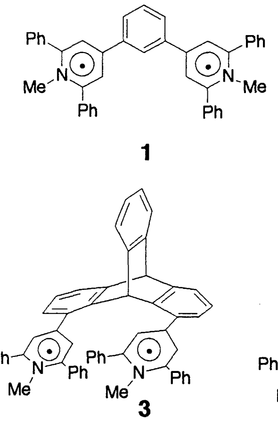


Figure 1. Electronic spectral change in the reduction of $\mathbf{3}^{2+}$ with 3%-Na-Hg in CH_3CN-MTHF (1:1) at room temperature; each spectrum is recorded as a function of contact time (30 s) with 3%-Na-Hg.

The compound $\mathbf{3}^{2+}$ showed a reversible reduction wave at -1.20 V vs. S. C. E. in CH_3CN. The related dications $\mathbf{1}^{2+}$ has nearly overlapped two waves (-1.10, -1.23 V) in this region.[2] The observed single wave for $\mathbf{3}^{2+}$ would be due to two electron reduction processes corresponding to the dication to diradical. The reduction of $\mathbf{3}^{2+}$ with 3%-Na-Hg in CH_3CN-MTHF (2-methyltetrahydrofuran) (1:1 v/v) was followed by measurement of the UV-vis spectra as a function of contact time (30 s each). A colorless solution (λ_{max} = 300 nm in CH_3CN-MTHF) turns to purple (363 and 560 nm) as the reduction proceeds (Figure 1). After 90 s, the decrease of 300 nm absorption almost stopped and at this point the absorptions were assigned to diradical **3**. The absorptions are similar to those of diradicals, **1** and **2**. The ESR spectrum of this species at 13 K showed typical triplet pattern with zero-field splitting parameters of D = 9.8 mT and $E \approx 0$ mT (Figure 2). Assuming the point-dipole approximation, the averaged distance between the radical centers is calculated to be 6.6 Å. The calculated distance is larger than the distance between C-1 and C-8 of triptycene (4.5 Å). The difference would be probably attributed to poor approximation of the point-dipole method and also partly to steric repulsion between the



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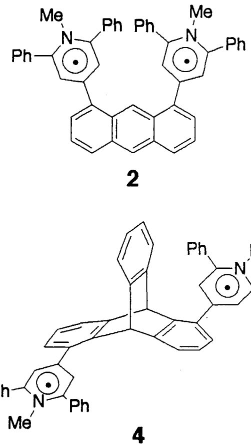

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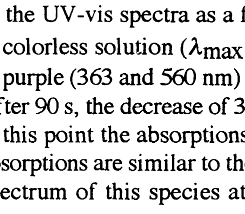

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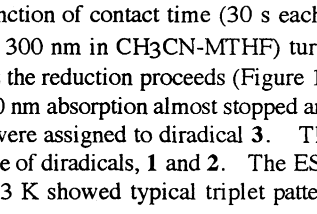

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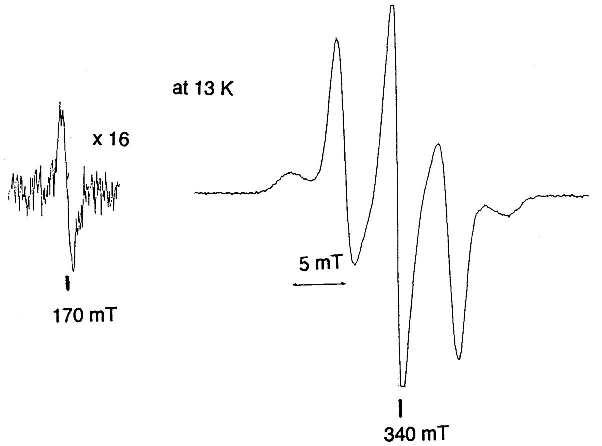

Figure 2. ESR spectrum of the diradical **3** recorded at 13 K in CH_3CN-MTHF (1:1) matrix; $\Delta m_S = \pm 1$ region (right), $\Delta m_S = \pm 2$ region (left).

pyridinyl rings. In addition to these $\Delta m_S = \pm 1$ transition signals, a weak signal due to $\Delta m_S = \pm 2$ transition was observed in the half magnetic field region (also shown in Figure 2). The Curie plot (18 - 4.3 K) using the intensity of this signal can be simulated by a straight line (r = 0.995) or by a curvature based on a S-T model [S-T gap = 15 J mol^{-1}, r = 0.998 (Figure 3)]. Therefore the observed triplet is the ground state or the thermally excited state with small S-T energy gap (< 20 J mol^{-1}).

In this particular diradical **3**, several antiferromagnetic exchange-interaction may be thought. For instance, triptycene framework may act as an antiferromagnetic spacer. Recently Tukada reported that a bis(carbene) spaced by triptycene-2,6-diyl shows ferromagnetic exchange interaction in the temperature range between 40 and 10 K.[4] According to the proposed spin polarization model, the through-bond exchange interaction of the triptycene framework would be antiferromagnetic. Furthermore, the diradcal **3** has a ratively large tortional angle (ca. 65°)[5] between the pyridinyl ring and the adjacent benzene ring of triptycene spacer. Under such circumstances, the direct through-space antiferromagnetic interaction between local pyridynyl rings may not be neglected. The present result indicates that theses antiferromagnetic exchange interactions are in total smaller than 20 J mol^{-1}, if any.

It is interesting to expect that the ground state may be altered by changing substitution pattern in the triptycene framework. Thus, the preparation of triptycene-1,5-diylbis(1-methyl-2,6-diphenylpyridinyl) diradical (**4**) was examined. Synthesis of dication $\mathbf{4}^{2+}$ and its reduction were similarly achieved. The electronic spectral change in the reduction of $\mathbf{4}^{2+}$ was also quite similar with $\mathbf{3}^{2+}$. However, under the similar conditions, only monoradical absorption was observed and the expected zero-field splitting was not observed. No observation of the triplet state of **4** may be explicable by one of the following two reasons; 1) the ground state of **4** is singlet with relatively large singlet-triplet energy gap (> ca. 2000 J mol^{-1}), 2) the triplet state of **4** may have a small *D*-value and the signals are hidden in the the monoradical absorption which is rather broad (ca.7 mT) at the bottom parts. The distance between the two radical centers, which may be roughly assumed to be the distance between the two centers of pyridinyl rings is estimated to be ca. 10 Å which corresponds to 2*D* = ca. 5.6 mT. The diradicals with such small interaction may be approximated to be two monoradicals (two doublets). Differentiation of these explanations is difficult at present. Further clarification on the exchange interaction through triptycene spacer would be required.

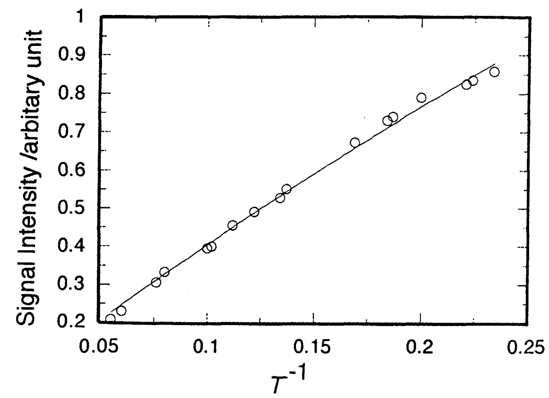

Figure 3. Curie plots of the triplet signals ($\Delta m_S = \pm 2$ transition).

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References and Notes

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5 The tortional angle was estimated by molecular mechanics calculation using 1,8-diphenyltriptycene as a model compound.