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PREPARATIONS AND SPIN-SPIN INTERACTIONS OF 4,4'-(m-PHENYLENE)BIS(1-METHYL-2,6-DIPHENYLPYRIDINYL) AND ITS ANALOGUE

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Abstract: 4.4'-(m-Phenylene)bis(1-methyl-2,4.6-triphenylpyridinium) (1^2^+) and 4.4'.4"-(benzene-1.3,5-triyl)tris(1-methyl-2,4,6-triphenylpyridinium) (2^3^+) were synthesized and their metal reductions were studied; 1^2^+ gave the triplet diradical (1) in the ground state, and 2^3^+ produced also a triplet diradical and the expected quartet species was not observed.

Since Kosower and Poziomek isolated 1-ethyl-4-methoxycarbonylpyridinyl in 1963,² pyridinyl radical has attracted attention as a stable free radical. Hitherto, several pyridinyl radicals have been studied by means of esr spectroscopy and the monomer-dimer equilibrium has been established. The stability of pyridinyl radical is strongly dependent on the substituents and substitution patterns;³ for instance, 1-methyl-4-phenylpyridinyl radical has an equilibrium constant of $10^5 (dm)^3 mol^{-1}$ in much favor of the dimer. Although it is expected that stable pyridinyl radicals would be good probes for studies of spin-spin interaction of radical centers, such studies have been reported a little.^{4,5} Ikegami and co-workers reported that photolysis of a dimer of pyridinyl radicals has not been reported except for bispyridinyls linked by alkyl chain at N,N'-positions.⁵ Use of rigid aromatic spacers in place of alkyl chains may simplify the conformational factors and give topological insights in spin-spin interaction. We report here the preparations of new triplet diradicals by the metal-reduction of 4,4'-(*m*-phenylene)bis(1-methyl-2,4,6-triphenylpyridinium) bistetrafluoroborates (1²+) and 4,4',4*-(benznene-1,3,5-triyl)tris(1-methyl-2,4,6-triphenylpyridinium) tristetrafluoroborates (2³+) where *m*-phenylene or benzene-1,3,5-triyl are used as rigid spacers.





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Scheme 1. Reaction conditons: a) Ph3P=CHCOPh in DMSO, 80 °C for 4 hs, 75% yield; b) tert-BuOK in THF-tert-BuOH (3 : 2) rt for 3 hs, 42%; c) BF3•OEt2 (13 equiv.) in the presence of 2 equiv. of chalcone, 110 °C for 3 hs, 76%; d) MeNH2 (2 equiv.) in EtOH, rt overnight, 72%.

Table 1. Uv-vis absorption maxima and reduction potentials^a of pyridinium cations

Compds	Solvents	E1 ^{1/2}	$E_2^{1/2}$	E3 ^{1/2}	$\lambda max/nm(\varepsilon \times 10^{-4})$
12+	CH3CN	-1.10	-1.23	-	298 (5.94)
2 ³⁺	CH ₃ CN	-1.02	-1.12	-1.27 ^b	296 (8.14)
3+	CH3CN	-1.20	-	-	302 (3.16)

^a: supporting electrolyte; 0.1 M tetrabutylammonium tetrafluoroborate, working electrode; glassy carbon, reference electrode; S.C.E., sweep rate; 100mV/s. ^b: irreversible peak potential.



Figure 2. Electronic spectral change in the reduction of 1^2 + with 3%-Na-Hg in CH₃CN at room temperature; each spectrum is recorded as a function of contact time with 3%-Na-Hg.

At first the metal reduction of 1-methyl-2,4,6-triphenylpyridinium (3^+) was studied.⁶ When a degassed acetonitrile solution of 3^+ is treated with 3% Na-Hg alloy, the blue radical $(3, \lambda max = 352, 580 \text{ nm})$ is cleanly formed (Figure 1). Learning from the known absorptions of 1-methyl-4-phenylpyridinyl and its dimer,⁴ it is probable that the both absorptions at 352 and 580 nm are due to the monomer 3, because the dimer would have absorptions in the range 400-500 nm. If one assume that the dimer absorption overlaps with the absorption at 352 nm, then the intensity ratio of absorptions at 352 and 580 nm should be concentration-dependent. However, the ratio is almost constant at any conversion of the reduction, indicating small concentration of the dimer if any. The clear isosbestic points observed during the reduction also supports this conclusion.

Synthesis of 1^{2+} was achieved by starting from 1,3-diformyl benzene via the corresponding pyrylium salt as outlined in Scheme 1. The conversion of the tetraone 4 to the pyrylium salt 5^{2+} required a little severe conditions (treatment with a large excess of BF3 .OEt2 in the presence of two equivalents of chalcone at 110 °C without solvent). Treatment of the pyrylium salt 5^{2+} with two equivalents of methylamine in ethanol gave the expected bispyridinium salt 1²⁺ as pale yellow powder in 72% yield {mp 289 °C, MS (FAB) m/z 653 [M- BF_{4}]+, 1 H-NMR (270 MHz, CD₃CN) δ = 8.51 (t, 1H, J = 1.7Hz), 8.34 (s, 4H), 8.26 (dd, 2H, J = 7.9, 1.7) Hz), 7.84 (t, 1H, J = 7.9 Hz), 7.75-7.66 (m, 20H), 3.78 (s, 6H)}. Synthesis of 2^3 + was similarly achieved from 1,3,5-triformylbenzene in an overall yield of ca. 10%. The compound 2^{3+} was also obtained as pale yellow powder {mp ca. 220 °C (decomp.), MS (FAB) m/z 985 [M-BF4]⁺, ¹H-NMR (270 MHz, CD₃CN) δ = 8.69 (s, 3H), 8.43 (s, 6H), 7.72-7.64 (m, 30H), 3.80 (s, 9H)}. Uv-vis absorption maximum and electrochemical data of theses cations as well as 1-methyl-2,4,6-triphenylpyridinium cation (3+) are shown in Table 1. It is reasonable that the absorption maximum wavelengths of theses cations are nearly the same and the molecular absorption coefficient increases in the order of $3^+ \rightarrow 1^{2+} \rightarrow 2^{3+}$, reflecting *m*-substituted relationship of these cationic chromophores. The compound 1^{2+} showed two reversible reduction waves corresponding to the formation of cation radical (-1.10 V vs S.C.E) and diradical (-1.23 V).⁷ The compound 23+ showed three reduction waves; however, the third wave was irreversible, suggesting some instability of the triradical 2.

Figure 2 shows electronic spectral change in the reduction of 1^{2+} by 3%-Na-Hg in CH₃CN. Each spectrum is recorded as a function of contact time with Na-Hg. After contact time of 200 s, 12+ is almost completely converted to the diradical species and the spectrum is quite similar to that of 1-methyl-2,4,6triphenylpyridinyl radical (3) except for 1.6 times larger molecular absorption coefficient (obtained by assuming clean conversion) at 588 nm. At this stage, the concentration of the conceivable cation radical may be small, since this m-substituted cation radical would show both the cation and radical absorptions. When the degassed uv-vis cell is opened and exposed to air, the diradical absorptions (358 and 588 nm) quickly disappear and the absorption of the starting dication 1^{2+} is regenerated probably via electron transfer to oxygen. The recovery of 1^{2+} reaches about 80% of the original intensity, indicating high concentration of diradical 1. The similar electronic-spectral change was also obtained in the mixed solvent of CH3CN-MTHF (MTHF: 2-methyltetrahydrofuran, 1:1 v/v). Figure 3 shows esr spectrum of the diradical 1 at 77 K in CH3CN-MTHF. The spectrum can be assigned to triplet signals with zero field splitting parameters of D = 0.0037 cm⁻¹. The parameter E cannot be determined because the central monoradical absorptions cover the triplet absorptions of x and y components.⁸ Assuming point dipole approximation, the averaged distance between the radical centers is calculated to be about 9 Å. The calculated distance suggests that the unpaired electrons are located closer to the distance between the nitrogen atoms rather than to the carbon atoms at 4- or

4'-positions in the pyridinyl rings.⁹ In addition to the $\Delta Ms = \pm 1$ transition signals, we observed a weak ΔMs $= \pm 2$ transition in the half magnetic field region. The signal intensity of $\Delta Ms = \pm 2$ transition increases with decrease of the temperature and the Curie plot gives a straight line (Figure 4), indicating that the observed triplet is the ground state or the degenerated state with the singlet.

Similar reduction of 2^{3+} gave similar spectral change in electronic spectra [363, 591 (sh) and 676 nm] in overall. Esr spectrum at 77 K in CH₃CN-MTHF showed a similar triplet pattern ($D = 0.0037 \text{ cm}^{-1}$) and esr signals assignable to the quartet species 2 have not been observed. We at present assume ionic triradical A for the triplet species that is to be studied further.



Figure 3. Esr spectrum of the diradical 1 recorded at 77 K in CH3CN-MTHF (1:1) matrix.



Figure 4. Curie plots of the triplet signals $(\Delta Ms = \pm 2 \text{ transition}).$

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Signal Intensity (arbitrary unit)

References and Notes

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- 7. The reversible reduction potentials corresponding to the radical to the anion were also observed for 3+
- (1.65 V) and 1²⁺ (-1.66 V and -1.77 V vs S.C.E. in acetonitrile).
 8. The possibility that the observed shoulders may be due to x or y components and the small z-component signals will be located outsides of the observed shoulders is unlikely, because such weak signals were not observed at lower temperature.
- 9. A referee suggested a possibility of dimeric diradical. The calculated distance (9Å) is shorter than the distance between the nitrogens (10Å) of diradical 2, while the conceivable dimeric diradical may have a larger distance between the radical centers. The assignment is compatible with the electronic spectrum.

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