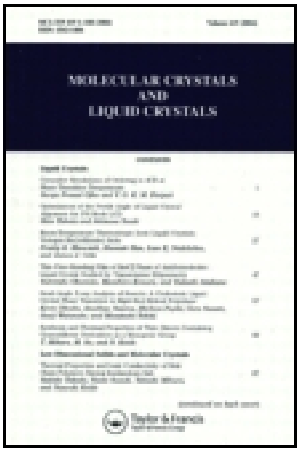

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Preparation and Property of 2-(3′,5′-Di-Tert-Butylphenyl-4′-Oxyl)-4,4,5,5-Tetramethyl-4,5,-Dihydro-1h-Imidazole-3-Oxide-1-Oxyl

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PREPARATION AND PROPERTY OF 2-(3',5'-DI-TERT-BUTYLPHENYL-4'-OXYL)-4,4,5,5-TETRAMETHYL-4,5,-DIHYDRO-*1H*-IMIDAZOLE-3-OXIDE-1-OXYL

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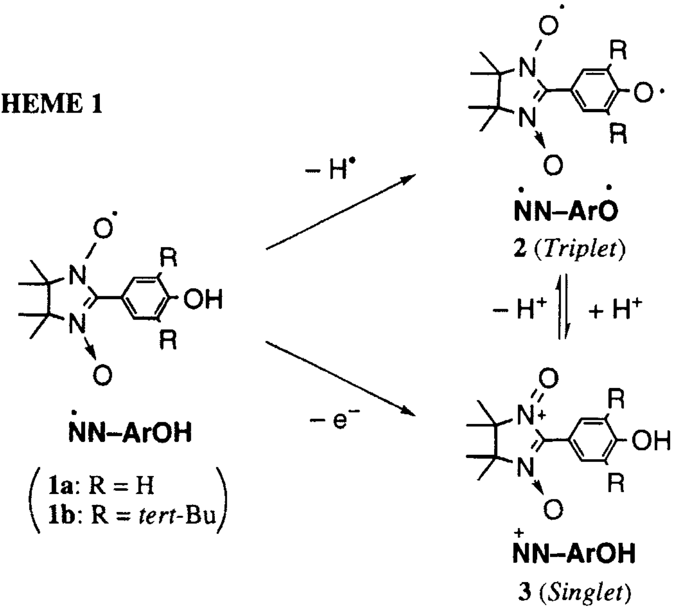
Abstract Title compound, a cross-conjugated biradical with phenoxyl-nitronyl nitroxide structure, was prepared by the lead dioxide oxidation of a *p*-hydroxyphenyl nitronyl nitroxide, 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4,4,5,5-tetramethyl-4,5,-dihydro-*1H*-imidazole-3-oxide-1-oxyl (**1b**), and was characterized by ESR spectroscopy. On the other hand, the γ-radiolysis in a freon matrix and the anodic or chemical oxidation of **1b** did not generate **2b** but lead to the formation of a phenol-substituted nitronyl nitroxide cation **3b**. Thus, a stable acid/base pair with different spin multiplicities, **2b** and **3b**, could be prepared independently.

INTRODUCTION

Spin-crossover, which means the switching between two phases with different magnetic properties in transition metal complexes, has been focussed much attention in terms of potential applications in information storage technology.[1] Molecular-based spin-crossover is an attracting target in organic chemistry and may be useful for novel functional organic ferromagnets.[2] A simple model for such molecules is a cross-conjugated unsymmetrical biradical with donor and acceptor characters ($D^{\bullet}$–$A^{\bullet}$), in which spin-crossover may be induced when the triplet diradical state is energetically close to the singlet zwitterionic state (D^+–A^-). Since a large difference is expected in dipole moments or acid-base properties between $D^{\bullet}$–$A^{\bullet}$ and D^+–A^-, the transition may bring about specific intermolecular interactions which affect the relative stabilities of low- and high-spin states; e.g., the closed-shell zwitterion may be stabilized in acidic media by forming D^+–AH species.

Previously, we reported that the one-electron oxidation of a *p*-hydroxyphenyl nitronyl nitroxide (**1a**) by γ-radiolysis or by electrolysis lead to the generation of a closed-shell cation (**3a**) rather than the corresponding biradical (**2a**).[3] However, both triplet biradical

SCHEME 1



2a and singlet cation **3a** were not stable enough to demonstrate such a spin crossover induced by pH change. Thus, our study was extended to a similar nitronyl nitroxide with bulky *tert*-butyl substituents (**1b**), which allowed the isolation of the corresponding biradical **2b** and the spectroscopic observation of cation **3b**.

RESULTS AND DISCUSSION

Synthesis and Characterization of 2-(3',5'-di-*tert*-butyl-4-hydroxyphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-*1H*-imidazole-3-oxide-1-oxyl (2b)

A phenol-substituted nitronyl nitroxide radical, 2-(3',5'-di-*tert*-butyl-4-hydroxyphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-*1H*-imidazole-3-oxide-1-oxyl (**1b**) as the precursor for biradical **2b**, was obtained by the *m*-chloroperbenzoic acid (*m*CPBA) oxidation of the corresponding bis-hydoxylamine prepared from 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, as shown in Scheme 2, and was purified by column chromatography. The ESR spectrum of **1b** in toluene (Figure 1) showed a five-line splitting pattern with the hyperfine coupling constant (a_N) of 7.4 G (2N) as observed for common 2-aryl substituted nitronyl nitroxides.

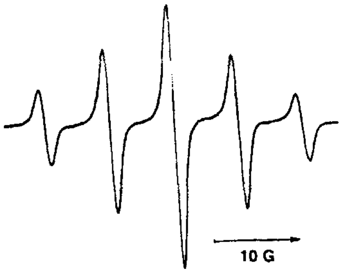
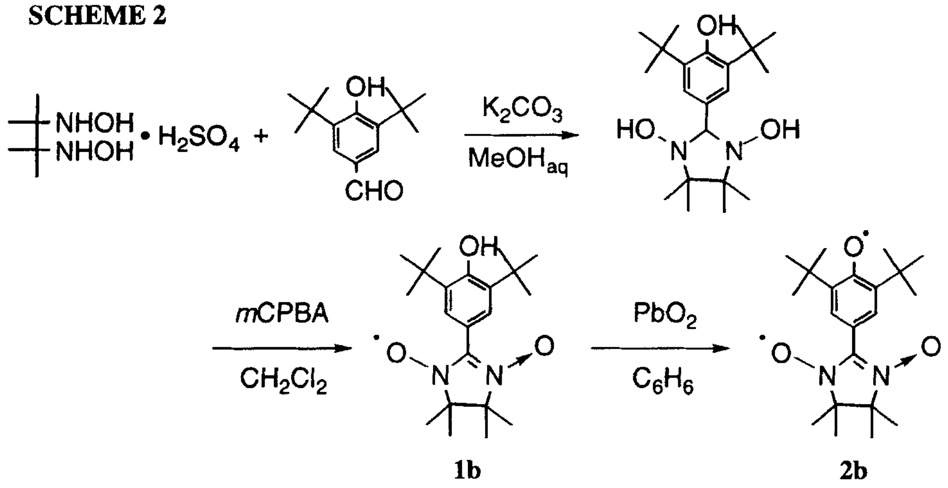


FIGURE 1 ESR spectrum of **1b** in toluene at room temperature.

SCHEME 2



When **1b** was oxidized with lead dioxide in benzene or toluene, the ESR spectrum changed to a five-line spectrum (Figure 2a). The observed coupling constant of $a_N \approx 3.7$ G (2N), a half of a_N in **1b**, is consistent to that of biradical **2b**, since a rapid oscillation of each unpaired electron makes the relevant spin densities on the atoms to be halved.[4] The line-width became broader owing to the electron-electron dipolar interaction. When the solution was frozen at 77 K, an ESR spectrum characteristic for triplet biradical species ($S = 1$) was observed (Figure 2c) with the zero field splitting parameters of $|D/hc| = 0.107$ cm^{-1} and $|E/hc| = 0$. In addition, a weak $\Delta M_s = \pm 2$

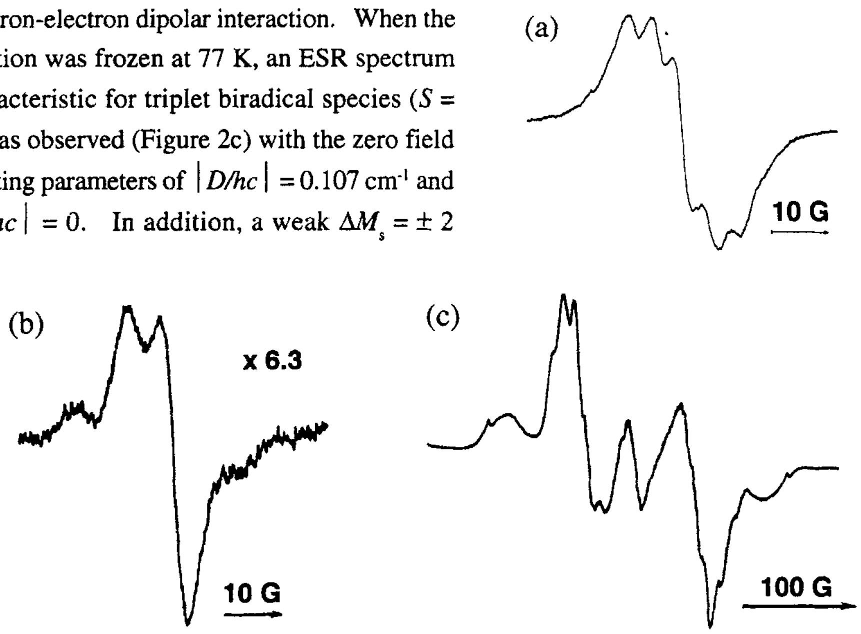


FIGURE 2 ESR spectra of **2b** observed (a) in toluene solution at room temperature and (b) $\Delta M_s = \pm 2$ and (c) $\Delta M_s = \pm 1$ lines at 77 K in toluene.

transition was observed (Figure 2b). Thus, the ESR spectra indicated the triplet biradical structure of **2b** as expected from its cross-conjugated π-system similar to trimethylenemethane.

The diradical **2b** was stable over several days in solution at ambient temperature. By removing the solvent carefully under vacuum at low temperature, **2b** could be isolated as deep blue powder. The purity of **2b** as estimated from anodic peak current on the cyclic voltammetry was more than 90%, indicating that **1b** was converted to **2b** by the PbO_2 oxidation almost quantitatively. The absorption spectrum of **1b** in acetonitrile (cf. Figure 4) showed maximum absorption bands at 283, 322, 365, and 615 nm, while those of **2b** were observed at 318, 359, and 604 nm.

Generation of Closed-Shell Cation 3b by the One-Electron Oxidation of 1b

The diradical **2b** might be also prepared by the one-electron oxidation of **1b** followed by its deprotonation (cf. Scheme 1). The oxidation of **1b** by γ-radiolysis in $CFCl_3$ matrix at 77 K, however, resulted in decrease of ESR intensity of **1b**, showing no additional signals. This result seems to indicate the generation of a singlet cation **3b** by removal of unpaired electron from nitronyl nitroxide moiety of **1b**, without elimination of proton, under the matrix-isolated conditions.

In order to characterize species generated by the one-electron oxidation, anodic

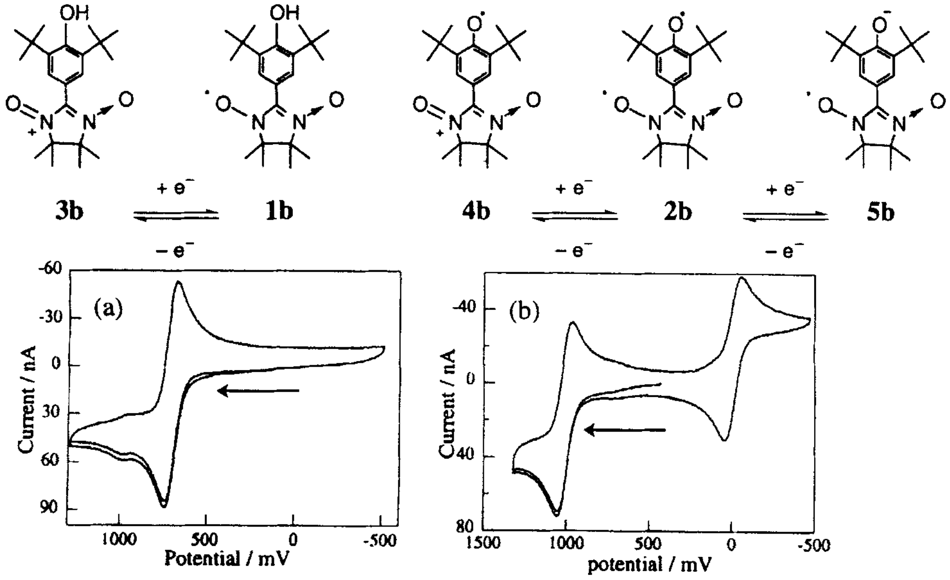
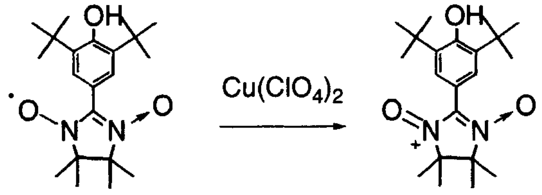


FIGURE 3 Cyclic voltammograms of 1.0 mM (a) **1b** and (b) **2b** in acetonitrile containing 0.1 M n-Bu_4NBF_4 at sweep rate = 1 V/s.

oxidation of **1b** was investigated by cyclic voltammetry. The voltammogram of **1b** in acetonitrile containing 0.1 M n-Bu$_4$NBF$_4$ as a supporting electrolyte showed a reversible couple at +0.71 V vs SCE (Figure 3a), which corresponds to the redox of **1b/3b**. Under the similar conditions, the reversible oxidation of **2b** occurred at +1.00 V vs SCE (Figure 3b). In addition, a cathodic reversible couple was observed at –0.05 V vs SCE. These results indicate that singlet cation **3b**, cation radical **4b**, and anion radical **5b** are stable during the voltammetric analyses.

The controlled potential electrolysis (+0.9 V vs SCE, ~1 F/mol) of **1b** in acetonitrile containing 0.1 M *n*-Bu$_4$NBF$_4$ resulted in almost complete conversion of the nitronyl nitroxide, but no radical or diradical species were detected by ESR spectroscopy. Instead, an alternative product showing the maximum absorption at 334 nm was formed, which was assigned as the cation **3b** according to the reversibility of **1b/3b** on the cyclic voltammetry. The assignment was supported by the fact that almost identical spectrum (Figure 4) was obtained by the chemical oxidation of **1b** employing Cu(ClO$_4$)$_2$ (E_{red} = +1.0 V vs SCE)[5] or NO$^+$BF$_4^-$ (E_{red} = +1.3 V vs SCE).[6] Spectral changes associated with



1b **3b**

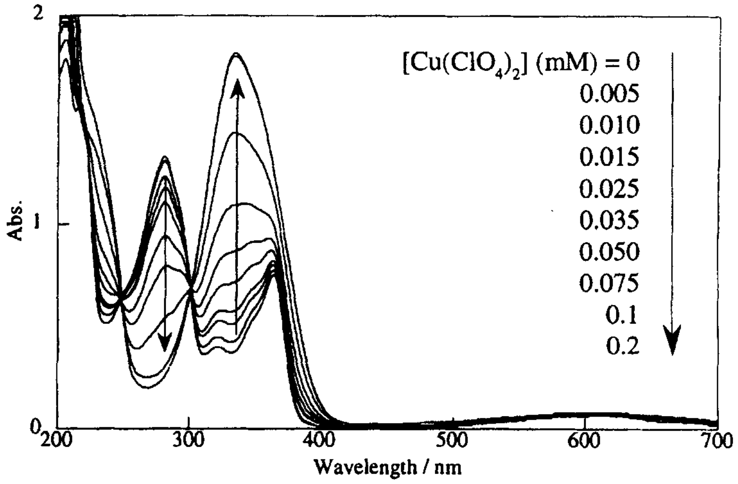


FIGURE 4 UV-vis spectral changes upon the addition of Cu(ClO$_4$)$_2$ to an acetonitrile solution of 0.05 mM **1b**.

the reaction of 0.05 mM **1b** and 0–0.2 mM $Cu(ClO_4)_2$ in acetonitrile is illustrated in Figure 4. The qualitative nature of the transformation (**1b** → **3b**) was established by the presence of clear isosbestic points at 248 and 303 nm.

A solution containing only the BF_4^- salt of **3b** was prepared by the reaction of **1b** with equimolar of $NO^+BF_4^-$, since $NO^\cdot$ formed could be removed by introducing inert gas into the solution. However, the isolation of the salt was unsuccessful because the cation **3b** decomposed slowly in acetonitrile.

CONCLUSION

An acid/base pair with different spin multiplicities,, **2b** and **3b**, could be generated independently. The PbO_2 oxidation of **1b** in solvents with low polarity resulted in the formation of biradical **2b**, while a closed-shell cation **3b** was generated by the one-electron oxidation of **1b** in acetonitrile. The deprotonation of **3b** leading to **2b** did not proceed in solution, indicating the relatively low acidity of **3b**. Thus, the present molecule is expected to be a good component for pH-induced spin crossover. The redox and acid-base properties of these species are currently under investigation.

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