

Communications to the Editor

Remarkable Heteroatom Dependence of the Spin Multiplicity in the Ground State of 9,9'-(*m*-Phenylene)dixanthyl and -dithioxanthyl Diradicals

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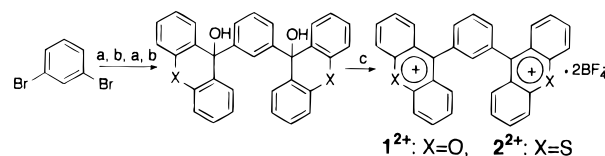
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High-spin organic compounds have recently received intense attention with implications for material science and basic research on the spin alignment.^{1,2} To achieve ferromagnetic interaction of two radicals, a *m*-phenylene spacer is frequently used. This methodology is based on several theories² and many experiments demonstrating non-Kekulé hydrocarbon high-spin compounds.^{1a–c} However, it has been recently reported that some diradicals (bisnitroxides^{1d–g} and bisphenothiazine dication³) with a *m*-phenylene spacer⁴ give the singlet ground states. These diradicals have a large torsion angle between the nodal plane of the spin source and the spacer plane. Recently, Borden and his co-workers reported that the reason for the singlet states of the bisnitroxides can be attributable to the large torsion angle which induces orbital interaction through the σ -bond of the spacer.^{1g} This rationalization does not take into consideration whether the spin sources have heteroatoms or not. However, it is also true that the above singlet species with a *m*-phenylene spacer have heteroatoms in their spin carriers. We report remarkable heteroatom dependence of the spin multiplicity in the ground state of the titled diradicals.

The diradical precursors, dications **1**²⁺ and **2**²⁺, were prepared in 24 and 20% overall yields using sequential lithiation method as outlined in Scheme 1. When these dications (373 nm for **1**²⁺ and 383 nm for **2**²⁺) are treated with granular zinc in a mixed solvent acetonitrile–MTHF (2-methyltetrahydrofuran) (2:3 v/v) at room temperature under degassed conditions, new absorptions assignable mainly to the diradicals (at 346 nm for **1** and 361 nm for **2**) appear with a clear isosbestic point (352 nm for **1** and 371 nm for **2**).⁵ However, when the temperature of the diradical solution is lowered, the diradical absorptions

Scheme 1^a



^a Reagent and conditions: (a) *n*-BuLi (1 equiv), -78 °C/ether, (b) 9-xanthone or 9-thioxanthone (1 equiv), and (c) aqueous HBF₄ (42%).

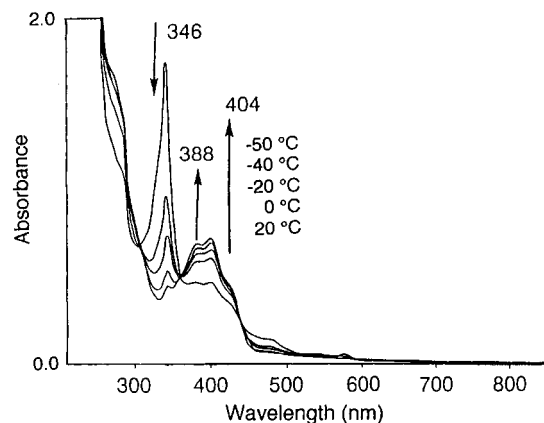


Figure 1. Temperature dependent electronic spectrum of the species derived from the zinc reduction of **1**²⁺.

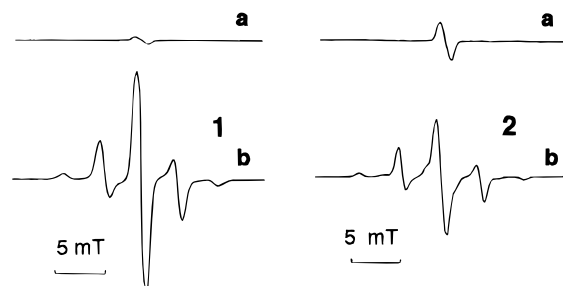


Figure 2. Photolysis (>310 nm) of the frozen matrices (acetonitrile–MTHF, 2:3) after the zinc reduction of **1**²⁺ (left) and of **2**²⁺ (right), (a) before irradiation, (b) after 30 s irradiation for **2**, or during irradiation (60–300 s) for **1**.

are reversibly converted to new absorptions showing their maxima at the longer wavelength region (Figure 1 for **1**) with decrease of ESR signal intensities in solution.⁶ These observations suggest the formation of a diamagnetic σ - or π -dimer in equilibrium with the diradical.⁷ Photolytic bond cleavage of the dimer may revert the expected diradical, provided that the media is soft enough to allow the relaxation of steric repulsion between the generated diradicals. Thus, photolysis (>310 nm) of the frozen soft matrix (freezing point ca. -140 °) in an ESR probe at -150 °C cleanly produced a randomly oriented triplet pattern (Figure 2).⁸ The conversion to the triplet pattern is extremely slow at 77 K or lower temperatures. The photolysis at -150 °C of the diamagnetic dimer derived from 9-phenylxanthyl or -thioxanthyl monoradical only increases the central signal, thus confirming that the triplet signal is due to the expected intramolecular diradical. The zero-field splitting parameters D were determined to be 83.5 G for **1** and 92.5 G for **2**.⁹ The $\Delta m_s = \pm 2$ transition signals were also observed in the half-magnetic field region for the both cases.

Figure 3 shows Curie plots using the $\Delta m_s = \pm 2$ signals. The

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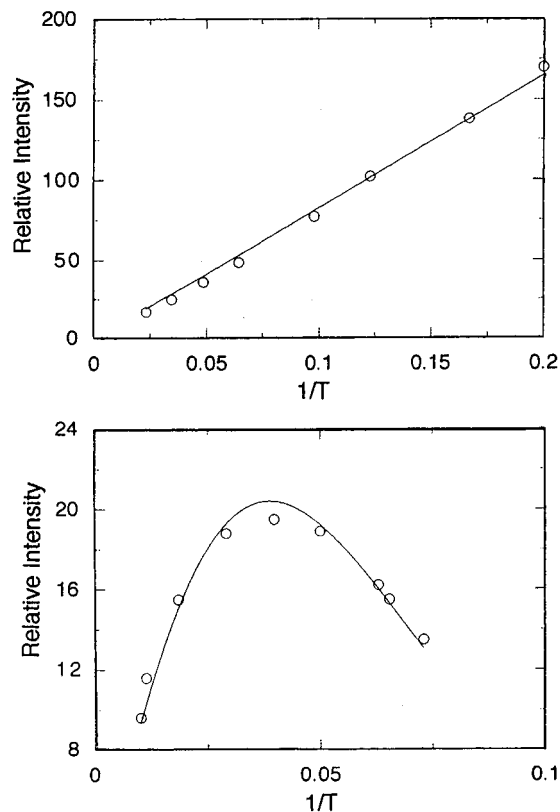


Figure 3. Curie plots of the signal intensity for **1** (upper) and for **2** (lower) in the mixed solvent acetonitrile–MTHF (2:3).

plots for **1** gave a straight line in the temperature range between 5 and 43 K, indicating that **1** is a triplet in the ground state. However, similar plots for **2** surprisingly afforded a convex curve which indicates a singlet ground state. The energy gap between the singlet and the thermally excited triplet for **2** is determined to be about 82 cal/mol.

Geometrical insight was successfully obtained by semiempirical level MO calculations: full optimizations by AM1-UHF with a keyword "PRECISE". The xanthyl and thioxanthyl rings are confirmed to be almost planar. Their triplet states are found

(5) A similar spectral change was observed for the reduction to 9-phenylxanthyl or -thioxanthyl radical whose molar absorptivity is roughly half of that of the diradical.

(6) The photolysis of the reduced species in solution at $-50\text{ }^{\circ}\text{C}$ slightly enhances the ESR signal intensity without a clear change in the ESR pattern. The contamination of monoradical impurity disturbed the analysis of the ESR spectra in solution.

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(8) The triplet species is stable for **2**, but a little unstable and slowly converted to the central signal at $-150\text{ }^{\circ}\text{C}$ for **1**. At lower temperature, these species are perfectly stable. The very weak but same ESR absorptions (xy component) were detected by the shock freezing method.

(9) The difference in D -values between **1** and **2** indicates the conformational difference: the diradical **1** is in the triplet conformation, whereas **2** is likely to be in the singlet conformation. Conformational dependence of the D -value has been documented: Veciana, J.; Rovira, C.; Ventosa, N.; Isabel, M.; Crespo, I.; Palacio, F. *J. Am. Chem. Soc.* **1993**, *115*, 57–64.

to be in almost C_2 geometry with the torsion angles $56 \pm 1^{\circ}$ for **1** and $67 \pm 1^{\circ}$ for **2**. However, the singlet states have two distinct torsion angles: ca. 58 and 88° for **1** and ca. 69 and 89° for **2**. Calculation of heat of formation with electron correlations [OPEN(2,2), CI = 6 at the UHF geometries] indicates the following: (1) **1** is triplet in the ground state with the singlet–triplet energy gap [$\Delta E(S-T) = +0.50$ kcal/mol] and (2) **2** is singlet with $\Delta E(S-T) = -0.06$ kcal/mol. These results are compatible with the experiments.

Since the triplet state of **2** has a slightly larger torsion angle than that of **1**, the results of Curie plots may be explicable by the torsion angle effect. However, interestingly enough, the high-spin for **1** and low-spin ground state for **2** are also predicted at the same torsion angle (two 60° for the triplet states, 60 and 90° for singlet states), [$\Delta E(S-T) = +0.46$ kcal/mol for **1**, -0.31 kcal/mol for **2**], suggesting the importance of the electronic effect in addition to the torsion angle effect.

In general, xanthyl radicals have a large spin density at the C9 carbon (LCAO coefficient of SOMO of the unsubstituted xanthyl radical by Hückel MO, 0.63)¹⁰ and the oxygen atom has a only small spin density (0.11), whereas thioxanthyl radicals have a large spin density not only at the C9 carbon (0.58) but also at the sulfur atom (0.32). As a consequence, the spin density at the C9 carbon is larger in xanthyl radicals. The diradicals **1** and **2** with singlet configuration have α and β spins at the C9 and C9' carbons and would experience electronic repulsion between β spin (C9') and β spin (spacer carbon attached to C9') which is induced by the α spin on the C9 carbon through the dynamic spin polarization.¹² Such electronic repulsion must be released in the perpendicular (to the spacer) geometry at one of the xanthyl or thioxanthyl rings. On the other hand, both diradicals with triplet configuration are stabilized by the dynamic spin polarization. The stabilization energy is smaller in the thioxanthyl diradical **2** since the spin density at C9 (C9') is diffused by the sulfur atom. Furthermore, the singlet thioxanthyl diradical will receive the stabilization by the mixing of several resonance structures including ionic states.

In short, we have shown clear experimental evidence for heteroatom dependence on the spin multiplicity. Although the mechanism of this heteroatom dependence has not yet been conclusively clarified, the reason seems to be related to the delocalization of the lone-pair electrons of heteroatoms.

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(10) Hückel MO calculation ($\alpha_x = \alpha_c + h_x \beta_{c-c}$, $\beta_{c-x} = k_{c-x} \beta_{c-c}$; $h_o = 2.0$, $h_s = 1.0$, $k_{c-o} = 0.34$, $k_{c-s} = 0.68$)¹¹ indicates that the two SOMOs are not degenerated: $\Delta E_{\text{SOMOs}} = 0.0027\beta$ for **1** and 0.0163β for **2**. Increasing the k_{c-x} in the resonance integral and decreasing h_x in the Coulombic integral increases the energy gap, indicating the importance of the delocalization effect of the lone-pair electrons on heteroatoms.

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