Pergamon

Tetrahedron Letters, Vol. 38, No. 34, pp. 6007-6010, 1997

PII: S0040-4039(97)01335-X
0040-4039/97 $17.00 + 0.00

1,1'-(*p*- OR *m*-PHENYLENE)BIS(2,4,6-TRIPHENYLPYRIDINYL) DIRADICALS: GROUND STATE IN A HETEROATOM-CONTAINING SYSTEM IN RELATION TO THE TOPOLOGY RULE

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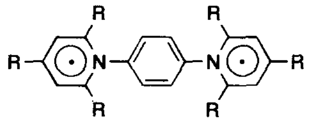
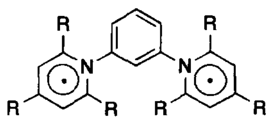
Abstract: 1,1'-(*p*- or *m*-Phenylene)bis(2,4,6-triphenylpyridinyl) diradical were prepared by the reduction of the corresponding dications. The plots of the ESR signal intensity vs. 1/T show that both the *p*- and *m*-diradicals are singlet in the ground state with a singlet-triplet energy gap of 51 cal/mol for the *p*-isomer and 44 cal/mol for the *m*-isomer. © 1997 Elsevier Science Ltd.

It is well known as a topology rule in hydrocarbon high-spin compounds that *m*-xylylene type hydrocarbons are a triplet species, whereas *p*-xylylenes are in quinoid form with a singlet ground state. This rule has been well supported theoretically[1] and experimentally[2] during past decades. However, it has recently been found that some diradicals with *m*-topology give singlet ground states.[3] Furthermore, we have more recently found that 10,10'-(*p*-phenylene)diphenothiazine dication is in a triplet or a pseudo-triplet ground state.[4]

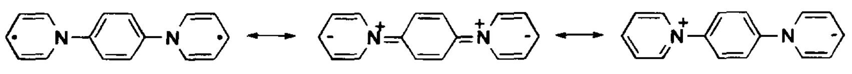
In the course of our study of pyridinyl radicals,[5] we have also been interested in the compounds with phenylene linkages at the nitrogen positions of pyridinyl radicals. The unique features of these compounds can be envisioned for the unknown 1,1'-(*p*-phenylene)dipyridinyl diradical (**1**). Formula **A** presents a typical canonical structure of **1**. Quinoid-type non-ionic resonance structures are difficult to draw. Instead, intramolecular electron transfer type ionic structures **B** (bis-ylide type) or **C** can be drawn. However, such ionic structures may have higher energy than the structure **A**.



1 (R = H), **3** (R = Ph)



2 (R = H), **4** (R = Ph)



A **B** **C**

In accordance with this qualitative consideration, the orbital energy gap (ΔE by Hückel MO with the heteroatom parameter of 0.89[6] for the resonance integral and 1.37[6] for the coulombic integral) between the two SOMOs is calculated to be small; **1** ($\Delta E = 0.16\beta$) compared to *p*-xylylene ($\Delta E = 0.62\beta$) and Thiele's hydrocarbon ($\Delta E = 0.31\beta$). This value 0.16β is comparable to the above-mentioned 10,10'-(*p*-phenylene)dithiazine dication ($\Delta E = 0.14\beta$).[4] The non-planar geometry with a large torsion angle between the pyridinyl radicals and the spacer would further decrease the energy gap. The *m*-isomer 1,1'-(*m*-phenylene)dipyridinyl diradical (**2**) has also non-degenerated SOMOs, but the energy gap is considerably smaller ($\Delta E = 0.03\beta$). We report herein the preparation and determination of the ground states of the substituted analogues 1,1'-(*p*-phenylene)bis(2,4,6-triphenylpyridinyl) diradical (**3**) and the corresponding *m*-isomer (**4**).

The radical precursors, 1,1'-(*p*-phenylene)bis(2,4,6-triphenylpyridinium) bis(tetrafluoroborate) ($\mathbf{3}^{2+}$) and the corresponding *m*-isomer ($\mathbf{4}^{2+}$) were synthesized by the condensation of *p*- or *m*-phenylenediamine with 2,4,6-triphenylpyrylium terafluoroborate in 54% and 35% yields according to the Katritzky procedure.[7] Both compounds showed four reversible reduction waves corresponding to stepwise reduction of the dications to dianions; -0.95, -1.08, -1.19, and -1.38 V vs. S.C.E. for $\mathbf{3}^{2+}$, -0.95, -1.11, -1.26, and -1.47 V for $\mathbf{4}^{2+}$.[8] The reduction was performed with 3%-Na-Hg in CH_3CN-MTHF (1 : 1 v/v) under degassed conditions. The colorless solutions (λ_{max} = 317 nm for $\mathbf{3}^{2+}$, λ_{max} = 318 nm for $\mathbf{4}^{2+}$) turned purple (λ_{max} = 354, 549 nm for **3**; λ_{max} = 351, 546 nm for **4**) during the reductions.[9] Clear isosbestic points were observed. When the cation absorption was totally replaced to the new absorptions, the species is assignable to the expected diradical. The assignment is reasonable in comparison with the reported pyridinyl radicals.[5] Similarity in absorption spectra between **3** and **4** indicates that **3** is best represented by the formula **A** rather than **B** or **C**.

ESR spectrum of **3** at 77 K showed a randomly oriented triplet pattern (Figure 1, left). The zero-field splitting parameters are determined to be D = 5.5 mT and E = 0.3 mT. Averaged distance between the two radical centers can be calculated as 7.9 Å by the point-dipole approximation. The calculated distance is close to the distance between the two centers of the pyridinyl rings: [r(N1-N1') ≈ 5.7 Å, r(C4-C4') ≈ 11.3 Å]. The signal due to $\Delta m_S = \pm 2$ transition was observed at lower temperature (ca. 5 K) as a very weak signal. These results establish the triplet nature of **3**. The *m*-isomer **4** also showed a triplet pattern with a little larger zero-field splitting parameters (D ≈ 6.7 mT, E ≈ 0.0 mT, Figure 1, right). The calculated distance (7.5 Å) is again reasonable with the structure of **4** [r(N1-N1') ≈ 5.0 Å, r(C4-C4') ≈ 9.9 Å].[8]

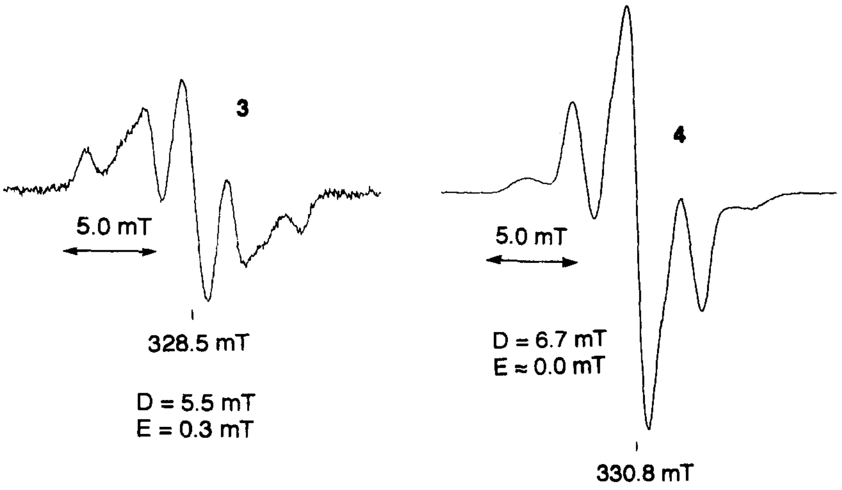


Figure 1. ESR spectra of the diradicals **3** (left) and **4** (right) measured at 77 K in CH_3CN-MTHF (1 : 1 v/v).

Temperature dependence of the ESR signal intensity for **3** and **4** was investigated using the axial z-components (Figure 2, left and right, respectively). The plots for **3** gave a convex curve indicating that the observed triplet is a thermally excited state. The energy gap between the singlet and triplet is estimated as 51 cal/mol. The Curie plots for **4** also gave a convex curve, again indicating the observed triplet is slightly above (44 cal/mol) the singlet state.

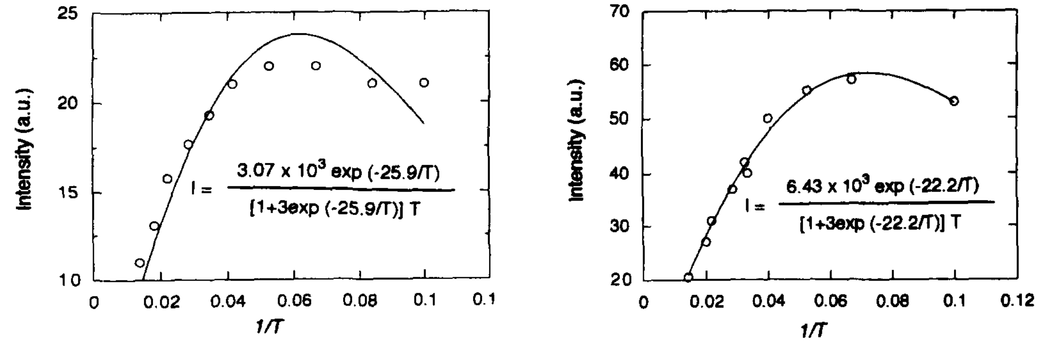


Figure 2. Curie plots of the triplet signals for the diradicals **3** (left) and **4** (right).

In general, pyridinyl radicals have large spin densities at C4 (SOMO coefficient of the unsubstituted pyridinyl radical by Hückel MO[7], 0.56), at C2 (0.48), and at N1(0.43). Since the spin density on the nitrogen atom (N1) is smaller than that on C4, the π-facial dynamic spin polarization may not be an exclusive factor to control the exchange interaction in this heterocyclic spin system. Under such conditions, the exchange interaction may also be affected by the orbital interaction via a through-space or σ-bond of the linker[3c]. Obviously, the planar geometry favors the orbital interaction through the π-bond of the linker, whereas the perpendicular geometry favors the interaction through-space or σ-bond[3c] of the linker. In both cases, the orbital splitting favors the low-spin states. Molecular models of these diradicals **3** and **4** suggest that the dihedral angle between the pyridinyl ring and the phenylene linker is relative large but not as large as perpendicular, because the edge of the phenyl group at the 2- or 6-position on one of the pyridinyl rings experiences a severe steric repulsion with that on the opposite pyridinyl ring at the perpendicular geometry: Semiempirical calculation of the 1,2,4,6-tetraphenylpyridinyl monoradical suggests that the pyridinyl ring is almost coplanar and the dihedral angle between the pyridinyl plane and the phenyl plane attached to the nitrogen atom is about 72°. The steric repulsion between the phenyl edges in the phenylene-bridged diradicals certainly reduces the dihedral angles: two 59° for the singlet state **3**, 55° and 70° for the triplet state **3**, 58° and 69° for the singlet state **4**, two 55° for the triplet state **4** (AM1-UHF).[10,11,12] These intermediate dihedral angles allow the several modes of the orbital interaction.

The low-spin state for the *m*-isomer **4** may be rationalized by the orbital splitting *via* a through-space or σ-bond[3c] manner. The orbital interaction through the π-bond in **4** will not lead to the orbital splitting because of its *meta* topology. The *p*-phenylene linked diradical **3** also has a similar dihedral angle to that of **4**. The orbital interaction through-space or σ-bond in **3** is likely to be weaker than that in **4**, simply because of the longer distance between the spin carriers.[4] However, the orbital interaction through the π-bond in **3** would lead to the orbital splitting, giving the low-spin ground state of **3**. In this context, it should be noted that the similarly spin diffused 10,10'-(*p*-phenylene)bisphenothiazine dication [a (pseudo) high-spin ground state molecule] has a perpendicular geometry which prohibits the π-facial orbital interaction. Further studies on this aspect and the related systems are in progress.

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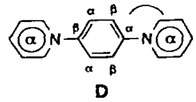
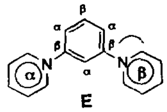
7. Katritky, A. R.; Eweiss, N. F.; Nie, P-N. *J. Chem. Soc., Perkin I*, **1979**, 433-435.
8. The weak signal due to $\Delta m_S = \pm 2$ transition was also detected in **4**.
9. The diradical **3** and **4** is unstable under aerated conditions but stable under inert atmosphere for long time at room temperature.
10. Geometries for both of the singlet and triplet states were calculated by UHF method which is known to permit some electron correlation but afford spin contaminated wave functions (S^2 = ca. 3.8 for the singlet states, ca. 4.8 for the triplet states); Greenberg, M. M.; Blackstock, S. C.; Stone, K. J.; Berson, J. A. *J. Am. Chem. Soc.*, **1989**, *111*, 3671-3679.
11. The pyramidarization of nitrogen atoms was observed. The distances between the nitrogen atom and the plane defined by the three sp^2-carbons linked to the nitrogen atom are in the range between 0.13-0.24 Å.
12. Interestingly, the triplet state of the *para* diradical **3** and the singlet state of the *meta* diradical **4** have two distinct dihedral angles, whereas the singlet state of **3** and the triplet state of **4** have nearly equal dihedral angles. Since the triplet (singlet) state has an α spin in one pyridinyl ring and an α (β) spin in the opposite ring, the triplet state of **3** (the singlet state of **4**) would receive the electronic repulsion between the α (β) spin on the N1 atom and the α (β) spin on the N1-attached phenylene carbon, where the spin is induced by the α spin on the N1' atom through the dynamic spin polarization as shown in **D** (*p*-phenylene triplet) and **E** (*m*-phenylene singlet). Such electronic repulsion must be released by increasing the dihedral angle in one of the pyridinyl rings.



D



E

An electronic repulsion is marked by ⌒ .

(*Received in Japan* 30 *May* 1997; *revised* 20 *June* 1997; *accepted* 27 *June* 1997)