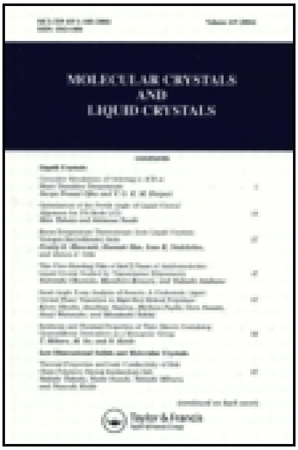

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Preparation and Exchange Interaction of DPPH-Derived Polyradicals

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To cite this article: Masatoshi Kozaki, Shogo Nakamura, Kazunobu Sato, Takeji Takui & Keiji Okada (1999): Preparation and Exchange Interaction of DPPH-Derived Polyradicals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 334:1, 131-138

To link to this article: http://dx.doi.org/10.1080/10587259908023310

*Mol. Cryst. and Liq. Cryst.*, 1999, Vol. 334, pp. 131-138
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# Preparation and Exchange Interaction of DPPH-Derived Polyradicals

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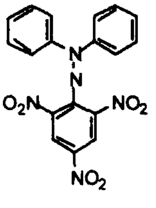
A series of 1,1'-(benzene-1,3-diyl)bis(1-phenyl-2-picrylhydrazine) derivatives was prepared and oxidized to generate the corresponding bis-**DPPH** diradicals. No triplet species was observed for the parent compound in the ESR. Incorporation of substituents in both the central benzene ring and the N-phenyl groups resulted in the detection of triplet diradicals. Especially, the diradical with Me and *t*-Bu groups on the central benzene and the N-phenyl rings, respectively, was successfully purified and isolated at 0 °C as a purple solid. Temperature-dependence of the intensity of the ESR signal showed that the isolated radical had a triplet ground state.

*Keywords:* exchange interaction; DPPH; esr; triplet; diradicals

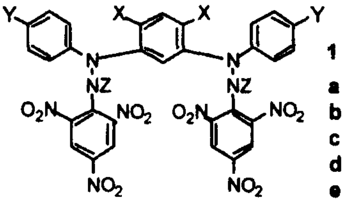
## INTRODUCTION

**Recently, stable organic high-spin molecules have attracted considerable interest not only from the viewpoint of basic science but also for their potential applicability to molecular ferromagnets[1]. In the latter approaches, nitroxide radicals have frequently been used as organic spin sources because of their high stability and easy accessibility[2]. To**

achieve further development in this field, access to a wide variety of stable high-spin species is highly desired. However, it seems that there is a fundamental problem related to the stability of high-spin species. The stability of the high-spin species that is constructed by stable radicals with suitable ferromagnetic couplers may not be guaranteed by the stability of the monoradicals. For instance, diphenylpicrylhydrazyl (**DPPH**) is a well-known stable radical[3]. However, the bis-**DPPH** analogue with 2,4,6-trinitrobenzene-1,3-diyl as a coupler was reported as a very unstable species by Heidberg and Weil[4]. The generated species was ESR silent and assumed to be a diamagnetic spin-paired species. In the course of our study of the spin-spin interaction of heteroatomic multi-spin systems[5-7], we have designed a series of new *m*-phenylene coupled bis-**DPPH** diradicals, 1,1'-(benzene-1,3-diyl)bis(1-phenyl-2-picryl-hydrazyl) diradicals (**1a**-**e**). The preparation, detection (for **1c**-**e**), isolation (for **1e** at 0 °C), and the determination of the spin multiplicity of the ground states are reported.



**DPPH**

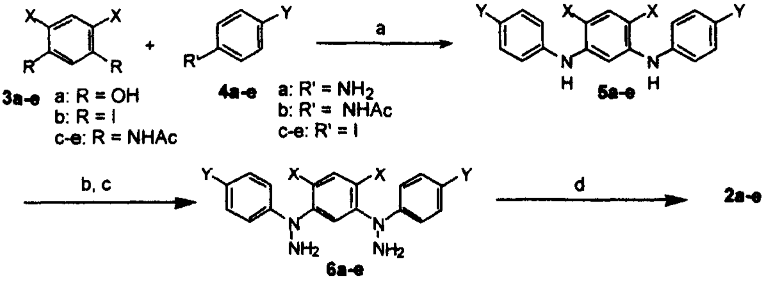


**1** : Z = •  **2** : Z = H
**a** : X = H, Y = H
**b** : X = H, Y = OMe
**c** : X = Me, Y = OMe
**d** : X = Me, Y = Ph
**e** : X = Me, Y = *t*-Bu

## Results and Discussion

Synthesis of the radical precursor **2a** is outlined in Scheme 1. N,N'-Diphenyl-*m*-phenylenediamine (**5a**) was prepared by the condensation of resorcinol (**3a**) with aniline (**4a**) in 17% yield according to the reported procedure[8]. The compound **5a** was lithiated by *n*-butyllithium, nitrosated by isoamyl nitrite in THF, followed by reduction with a large excess of zinc powder in acetic acid to give the expected bishydrazine **6a** in 78% yields. The bishydrazine **6a** was treated by picryl chloride in the presence of potassium carbonate in dichloromethane to give the diradical precursors **2a** as an orange powder in 55% yield. When a toluene solution of the precursors **2a** was oxidized with a large excess of lead dioxide or silver oxide at -30 °C under nitrogen atmosphere, the brownish color turned to purple ($\lambda_{max}$: 516 nm). The oxidation was monitored by measuring the ESR spectra in frozen toluene at -150 °C [Fig. 1(a)]. No triplet signal was detected, but a monoradical pattern split into five lines (with apparent splitting of ca. 21 G in frozen toluene at -150°C) by the two nitrogen nuclei was observed. TLC analysis of the reaction mixture showed many decomposition products. These results suggest that the non-detection of the monoradical is due not to the poor reactivity for the oxidation of **2a**, but to the instability of the diradical **1a**.

SCHEME 1



*Reagents;* a) $I_2$ (for **a**); Cu, $K_2CO_3$, then HCl (for **b-e**); b) *n*-BuLi, *i*-AmONO; c) Zn; d) Picryl choride, $K_2CO_3$

After the unsuccessful trial to generate the diradical **1a**, chemical modification was considered to stabilize the diradical. Molecular orbital calculations suggest that the 2,4-positions in the central benzene ring and the 4-position of the N-phenyl group are the reactive centers. Blocking these positions with appropriate substituents would stabilize the diradical.

For this purpose, the radical precursors **2b-e** were prepared according to Scheme 1. Phenylenediamines **5b-e** were prepared in 46-70% yields via Ullmann coupling reactions (190 °C for 2-3 days) of **3b-e** with **4b-e** followed by acidic hydrolysis of the amides. The radical precursors **2b-e** were obtained from **5b-e** in ~50% yields by the same procedure as described for **2a**.

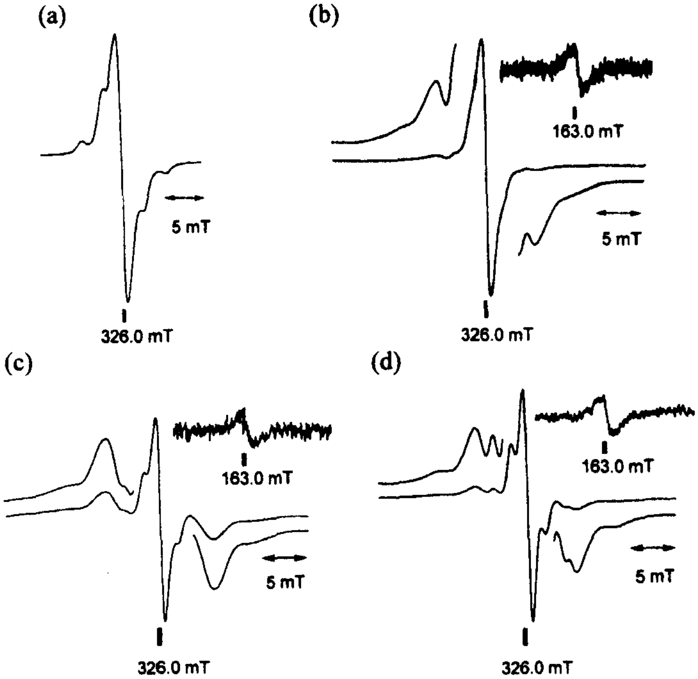


FIGURE 1 ESR spectra for the oxidation of (a) **2b**, (b) **2c**, (c) **2d**, and (e) **2e**. The spectra were measured at -150 °C in frozen toluene. The insertions are signals due to the forbidden $\Delta m_S = 2$ transition.

The oxidation of the precursors **2b-e** using the same procedure for **2** gave purple solutions ($\lambda_{max}$: 530-556 nm). The precursor **2b** gave the same results as for **2a**; namely, only the monoradical was observed by

ESR. In contrast to **2a** and **2b**, the oxidation of **2c** afforded a weak, randomly oriented triplet pattern ($D$ = 10.4 mT, $E$ = 0.0 mT) besides the strong monoradical signal [Fig. 1(b)]. Interestingly, the oxidation of **2d** and **2e** resulted in an increase of the intensity of the triplet signals [$D$ = 10.4 mT, $E$ = 0.0 mT for **2d**, Fig. 1(c); $D$ = 10.0 mT, E = 0.0 mT for **2e**, Fig. 1(d)]. These $D$-values correspond to ca. 6.5 Å as the averaged distance between the two radical centers by the point dipole approximation. According to a molecular model, the distance between the two nitrogen atoms attached to *m*-phenylene is about 4.9 Å. The distance between the two nitrogen atoms attached to the picryl group is about 5.0 Å for the syn-conformation, about 7.5 Å for the anti-conformation. The calculated distance from the $D$-values is close to the averaged value. The forbidden $\Delta m_S = \pm 2$ transition signals were also observed in the half-magnetic field region in both cases (Fig. 1).

The oxidation of **2d,e** could be monitored by rapid development of TLC (silica gel) which showed that the spots of the monoradical and the diradical are very close and hardly separable for **2d** but fortunately separable for **2e**. The oxidation of **2e** was carried out using silver oxide at 0 °C in toluene and the solution was analyzed with ESR [Fig. 2(a)]. The spectrum showed dominant generation of the triplet diradical over the monoradical. The reaction mixture was then rapidly separated at 0 °C by column chromatography on silica gel using hexane-ether (8 : 2) as a developing solvent. The eluents were also cooled at 0 °C. Evaporation of the fractions of the diradical at 0 °C gave the almost pure **1e** as a purple solid. Fig. 2(b) shows the ESR spectrum of the isolated **1e** in frozen toluene at −150 °C. This triplet spectrum contains only a small amount of the monoradical. The diradical **1e** is stable at low temperature (< 0 °C) but unstable at room temperature in both solution and the solid state. After standing at room temperature for 15 min, the diradical signals were converted into monoradical signals [Fig. 2(c)]. The instability of this diradical is not due to reactions with molecular oxygen since 1) **1e** was isolated under aerated column chromatography conditions and 2) the ESR spectrum could be observed even under aerated conditions. The instability seems to be related to the thermal reactivity of the bishydrazyl diradical, which may undergo hydrogen abstraction or dimerization. The hydrogen abstraction may occur via direct hydrogen abstraction from the solvent or via intramolecular hydrogen abstraction from the methyl groups on the central benzene ring.

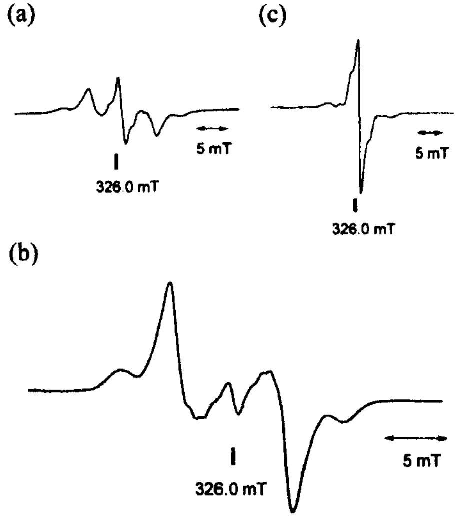


FIGURE 2 ESR spectra of **1e** observed in toluene at -150 °C (a) just after oxidation of **2e**, (b) after separation, and (c) after standing at room temperature for 15 min.

Temperature dependences of the signal intensity of the diradical **1d** and the purified **1e** were studied using weak $\Delta m_S = 2$ signals. Linear relationship of the signal intensity vs. reciprocal temperature shows that both **1d** and **1e** have triplet ground states. These results are interesting when compared to the related bisnitroxide radical **7** or **8**, both of which have singlet ground states[9-11]. According to Borden and coworkers, the low-spin ground state for **7** and **8** is ascribable to the large dihedral angle between the nitroxide plane and the plane of the central benzene ring[11]. In the present bis-DPPH diradicals, the dihedral angle between the plane of the central benzene ring and the nodal plane of the hydrazyl radical may be smaller than that of 7 or 8, since steric repulsion can be released by the rotation of both the N-phenyl rings and the picryl groups (**1eA**).

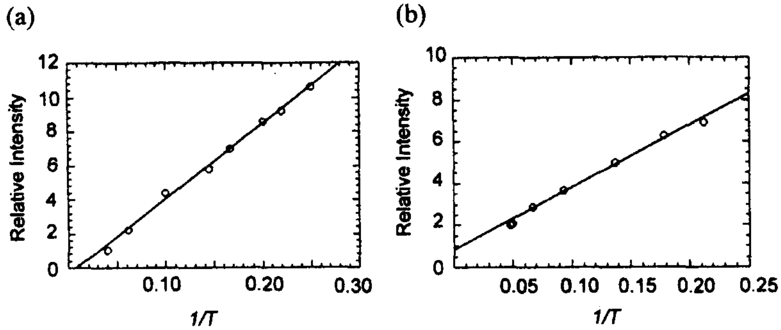
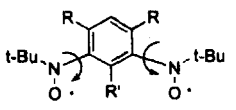
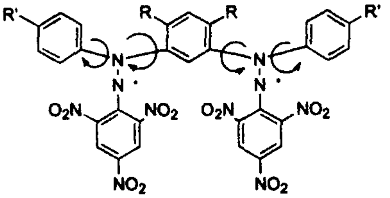


FIGURE 3 Temperature dependence of the signal intensities for $\Delta m_s = 2$ transitions of (a) **1d** and (b) the pure diradical **1e**.



**7** : R = R' = Me (singlet)
**8** : R = OMe, R' = H (singlet)



**1eA** (triplet)

Work on isolation at room temperature and clarification of the magnetic properties is under way.

## Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) (No. 10146102) from the Ministry of Education, Science, Sports and Culture, Japan.

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