Pergamon

Tetrahedron Letters 39 (1998) 5979–5982

TETRAHEDRON
LETTERS

Preparation and Characterization of Novel **DPPH**-based Diradicals

Masatoshi Kozaki, Shogo Nakamura, Kazunobu Sato,
Takeji Takui, Takeaki Kamatani,† Masaji Oda,†
Katsumi Tokumaru,†† and Keiji Okada*

Department of Chemistry, Graduate School of Science, Osaka City University, Sugimoto, Sumiyoshi, Osaka 558-8585, Japan
† *Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*
†† *Department of Chemistry, University of Tsukuba, 1-1-1 Tennodai, Tsukuba,,Ibaraki, 305-8571, Japan*

Received 6 May 1998; revised 8 June 1998; accepted 12 June 1998

Abstract: A series of 1,1'-(2,4-di-X-benzene-1,3-diyl)bis[1-(4-Y-phenyl)-2-picrylhydrazine]s were prepared and oxidized to generate the corresponding bis-**DPPH** diradicals. No triplet species was observed for the compounds with X = H in the ESR measurement. Modification of the central benzene ring (X = Me) and N-phenyl group (Y = OMe, Ph, *t*-Bu) allowed the detection of their triplet diradicals. Especially, the diradical with X = Me, Y = *t*-Bu was successfully purified, isolated at 0 °C as a purple solid, and was shown to be in a triplet ground state.

Keywords: molecular design; radicals and radical reactions; electron spin resonance

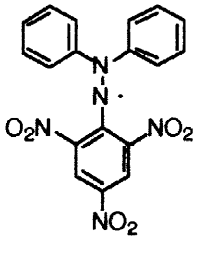
1.Introduction

Stable high-spin molecules have attracted much attention because of their potential applicability to molecular ferromagnets [1]. It has been desired for this purpose to develop a wide variety of stable high-spin species. However, only a limited number of stable spin units, typically as nitroxide radicals, has been employed. The reason is due to the stability of the radicals. Frequently, stable monoradicals do not ensure the stability of polyradicals. For instance, diphenylpicrylhydrazyl (**DPPH**) is a well-known stable radical [2]. However, the diradicals derived from it by suitable chemical modifications may not be stable. In fact, Heideberg and Weil prepared a very unstable bis-**DPPH** analogue using 2,4,6-trinitrobenzene-1,3-diyl as a coupler. Unfortunately, the generated species was ESR silent and assumed to be a diamagnetic spin-paired species [3]. In the course of our study of the spin-spin interaction of heteroatomic multi-spin systems [4-6], we have designed new *m*-phenylene coupled bis-**DPPH** diradicals, 1,1'-(2,4-di-X-benzene-1,3-diyl)bis[1-(4-Y-phenyl)-2-picryl-hydrazyl] diradicals (**1a-e**). The preparation, detection [for **1c-e** (X = Me and Y = OMe, Ph, and *t*-Bu, respectively), isolation (for **1e** at 0 °C), and the determination of the spin multiplicity of the ground state (triplet for **1d,e**) are reported.

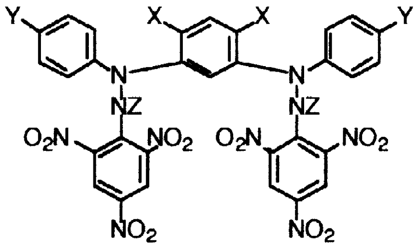
PII: S0040-4039(98)01227-1

2 Results and Discussion

As shown below, after unsuccessful trials to generate the diradical **1a** from the precursor **2a**, chemical modification was achieved to stabilize the diradical. The strategy of the modification used in this study is based on the blocking the reactive center (the 2,4-positions in the central benzene ring and the 4-position of the N-phenyl group) by appropriate substituents. For this purpose, the radical precursors **2b-e** were prepared. Scheme 1 illustrates their syntheses. 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 [7]. Other 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 deprotection of the amines. The compounds **5** were lithiated by *n*-butyllithium, nitrosated by isoamyl nitrite in THF, and followed by reduction with a large excess of zinc powder in acetic acid to give the expected bishydrazine **6** in 33-78% yields. The bishydrazine **6** was treated by picryl chloride in the presence of potassium carbonate in dichloromethane to give the diradical precursors **2** in 22-69% yields.[1]



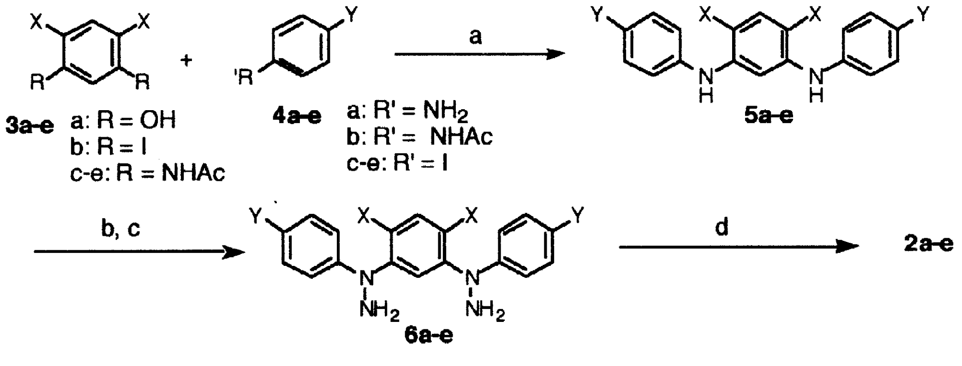
DPPH



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

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) PicCl, K_2CO_3

When a toluene solution of the precursors **1a-e** was oxidized with a large excess of lead dioxide or silver oxide at low temperature (-20 ~ 0 °C) under nitrogen atmosphere, the brownish color turned to purple (λmax: 516-556 nm). The oxidation was monitored by measuring the ESR spectra in frozen toluene at -150 °C. No triplet signal was detected for the unprotected *m*-phenylene-coupled compound **2a**. Similar results were observed for **2b**.

These compounds only showed the monoradical pattern split into five lines (with apparent splitting of ca 21 G in frozen toluene at -150°C) by the two nitrogen nuclei. The monoradical formation is not due to the poor reactivity for the oxidation of **2a,b**, but due to the instability of the diradical **1a,b**.[2] This consideration is supported by the TLC analysis which showed many decomposition products. In contrast to **1a** and **1b**, the oxidation of **2c** afforded a weak, randomly oriented triplet pattern (D = 10.4 mT, E = 0.0 mT) beside strong monoradical signals. Interestingly, the oxidation of **2d** and **2e** dramatically increased the intensity of the triplet signals (D = 10.4 mT, E = 0.0 mT for **2d**; D = 10.0 mT, E = 0.0 mT for **2e**). These D-values correspond to ca. 6.5 Å as an averaged distance between the two radical centers by the point dipole approximation. The calculated value is compatible with the model of a *m*-phenylene-linked bishydrazyl diradical.[3] The forbidden $\Delta m_S = \pm 2$ transition signals were also observed in the half-magnetic field region for both cases.

Rapid monitoring (TLC on silica gel) of the oxidation products from **2d,e** showed that the monoradical and the diradical are separable for **2e**, but their spots are very close and hardly separable for **2d**. The mixture from the oxidation of **2e** with silver oxide was then rapidly separated at 0 °C by column chromatography on silica gel using hexane-ether (8 : 2) as a developing solvent. The almost pure diradical **1e** was obtained as a purple solid. Figure 1 shows the ESR spectrum of the isolated **1e** in frozen toluene at -150 °C. This spectrum contains only a small amount of the monoradical. The diradical **1e** is stable at low temperature (< 0 °C) even under aerated conditions but unstable both in solution[4] and in solid state[5] at room temperature. The diradical signals were converted into monoradical signals after standing at room temperature for 15 min in solution. Apparently, the instability of this diradical is not due to the reactivity toward oxygen, but is related to the thermal instability of the second hydrazyl radical, which may undergo hydrogen abstraction or dimerization.[6]

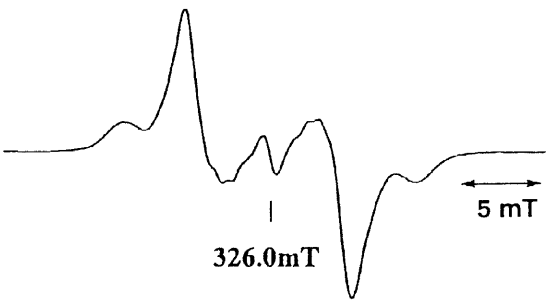


Figure 1. ESR spectrum of the purified **1e** in frozen toluene at -150 °C.

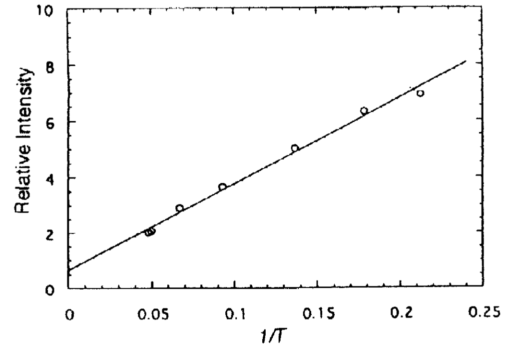
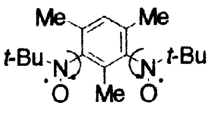


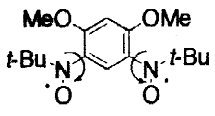
Figure 2. Curie plots for the signal intensity for **1e** in frozen toluene.

Temperature dependence of the signal intensity of this purified diradical **1e** was monitored using the weak $\Delta m_S = 2$ signal (Figure 2). The signal intensity linearly increases to the reciprocal temperature, showing that this diradical has a triplet ground state. The same results were obtained for **1d**.

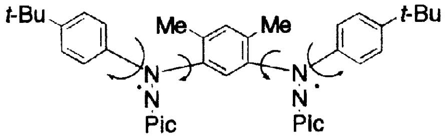
These results are interesting when compared to the related bisnitroxide radical **7** or **8**, both of which have singlet ground states [8-10]. According to Borden's interpretation, the low-spin ground state for **7** and **8** is ascribable to the large dihedral angle between the nitroxide plane and the plane of the central benzene ring [10]. 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 those of **7** and **8**, since steric repulsion would be released by the rotation of the N-phenyl rings or the picryl groups (**1eA**).



7: singlet



8: singlet



1eA: triplet

Isolation at room temperature and clarification of magnetic properties are under way.

This work was supported by a grant (No. 10146101) from Ministry of Education, Science and Culture, Japan.

References

[1] For instance, Turnbull, MM, Sugimoto T, Thompson LK. Ed. Molecular-Based Magnetic Materials, Theory, Techniques, and Applications. American Chemical Society:ACS Symposium Series 644, 1996:1-328.
[2] Goldschmidt S, Renn K. Chem. Ber. 1922;55:628-643.
[3] Heidberg J, Weil JA. J. Am. Chem. Soc. 1964; 86:5173-5174.
[4] Okada K, Imakura T, Oda M, Kajiwara A, Kamachi M, Yamaguchi M. J. Am. Chem. Soc. 1997;119:5740-5741.
[5] Okada K, Imakura T, Oda M. Murai H. J. Am. Chem. Soc. 1996;118:3047-3048.
[6] Okada K, Matsumoto K, Oda M, Akiyama K, Ikegami Y. Tetrahedron Lett. 1997;34:6007-6010.
[7] Buu-Hoï NP. J. Chem. Soc. 1952:4346-4349.
[8] Dvolaitky M, Chiarelli R, Rassat A. Angew. Chem. Int. Ed. Engl. 1992; 31: 180-181.
[9] Kanno F, Inoue K, Koga N, Iwamura H. J. Am. Chem. Soc. 1993;115: 847-850.
[10] Fang S, Lee M-S, Hrovat DA, Borden WT. J. Am. Chem. Soc. 1995;117:6727--6731.

Footnotes

1. In ^{1}H NMR spectrum of **1a**, two unequivalent aromatic protons (δ = 8.00 and 8.55 ppm in bromobenzene-d_5) on the picryl group were observed at 30 °C. These two signals coalesce at 50 °C and become a sharp singlet (δ = 8.35 ppm) at 100 °C. This spectral change indicates that the rotation of the picryl group is rather slow because of the double bond character of C(picryl)-N(hydrazine) bond. Similar results were observed for other derivatives.
2. Since there is no particular reason why the second oxidation of **2a,b** is slow, it is reasonable to assume that the diradicals **1a,b** is generated as an intermediate to produce decomposition products. The cleaner oxidation reaction for the relatively stable diradicals **2d,e** which gave almost no low Rf component (TLC) in contrast to that of **2a,b** also supports this hypothesis. Although the origin for the instability of **1a,b** is not clear at present, the dimerization or the oxygenation reaction at the 2-position of the central benzene ring or the 4-position in the N-phenyl ring is probable.
3. According to the molecular model, the distance between the two nitrogens attached to *m*-phenylene is about 4.9 Å. The distance between the two nitrogens attached to the picryl group is about 5.0 Å in syn-conformation, about 7.5 Å in anti-conformation. The calculated distance from the *D*-values is close to the averaged value.
4. The ESR signal intensity (measured at -150 °C) under degassed condition drops almost to the 1/9 of the original intensity with appearance of the strong monoradical signal after standing the ESR tube for 15 min at room temperature.
5. When the isolated **1e** was stood for 30 min at room temperature under argon atmosphere, the color of the crystals was considerably darken and the diradical spot (TLC) almost disappeared.
6. The instability of **1e** is not due to the reactivity toward oxygen. This is confirmed by several experiments: 1) **1e** was isolated under aerated column chromatography conditions. 2) The ESR signal intensity (-160 °C in frozen toluene) in degassed ESR tube quickly decreased by warming up to room temperature but did not change by opening to air. The hydrogen abstraction may occur via direct hydrogen abstraction from the solvent or via intramolecular hydrogen abstraction from the methyl group on the central benzene ring.