ELSEVIER

Synthetic Metals 82 (1996) 211–213

SYNTHETIC METALS

Magnetic properties of isomeric *N*,*N*′-di-(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl)xylyl imine

Mong-Jong Tien, Gene-Shiang Lee, Yu Wang, Tong-Ing Ho *

Department of Chemistry, National Taiwan University, Roosevelt Road, Section 4, Taipei, Taiwan, ROC

Received 2 June 1996; accepted 3 July 1996

Abstract

Three novel isomeric *N*,*N*′-di-(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl)xylyl imine (compounds **1**, **2** and **3**) were prepared and their structures were determined by X-ray single-crystal diffraction (except compound **1**). ESR spectra were measured at room temperature. Temperature dependences of magnetic susceptibility down to 5 K for the organic biradicals **2** and **3** are described. The Weiss constants for compounds **2** and **3** are 0.2 and −0.03 K, respectively. The small differences in the magnetic properties of compounds **2** and **3** might arise from the isomeric difference in the molecular structure.

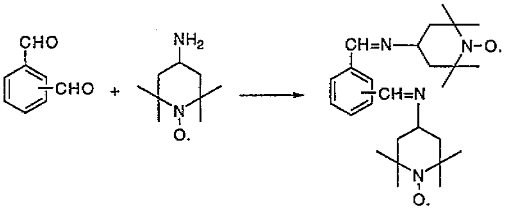
Keywords: Nitroxyl biradicals; Electron spin resonance; Magnetic susceptibility; X-ray crystal

1. Introduction

The search for a nonpolymeric organic radical with ferromagnetic properties has been of current interest for the past few years [1–4]. For example, the X-ray structure studies and magnetic properties of pure organic ferromagnetic *p*-nitrophenyl nitronyl nitroxide have been published [5–7]. The spin–spin interaction, whether it is intramolecular or intermolecular, can be related to the three-dimensional alignment of the spin and the interaction in the molecular structure. There are few reports on the magnetic properties of stable biradicals. The magnetic properties for biradicals are seldom discussed on a three-dimensional structural basis [8,9]. We present the preparation, X-ray structure and magnetic properties for isomeric *N*,*N*′-di(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl)xylyl imine.

2. Experimental

The syntheses for compounds **1**, **2** and **3** followed a known procedure [10]. The reaction of *o*- (*m*- and *p*-) benzenedialdehyde with 4-amino-2,2,6,6-tetramethyl-piperidin-1-oxyl affords imines **1**, **2** and **3** [1].



1: o- ; 2: m- ; 3: p-

The magnetic susceptibility was measured on a SQUID magnetometer with a magnetic field of 1 T and the temperature between 5 and 300 K. Pascal's constant was included in the calculation of diamagnetic susceptibility. X-ray diffraction data of **2** [2] and **3** [3] were collected on a Nonius CAD4 (four-circle diffractometer) with monochromic Cu K_α radiation.

3. Results and discussion

Compound **1** is liquid so no single crystal is obtained. The crystal structure of *m*-(**2**) and *p*-(**3**) isomers are shown in Figs. 1 and 2, respectively. The hydrogen atom is included to show the radical center. The imino group and the phenyl

---

* Corresponding author.

[1] Imine **1** is obtained as a purple liquid; imine **2** as a solid, m.p. 196–198 °C; imine **3** as a solid, m.p. 202–204 °C.

[2] Monoclinic *C*2/*c*, $a=20.711(6)$, $b=11.809(4)$, $c=11.229(4)$ Å, $V=2551.3(15)$ Å^3, $Z=4$, $R_f=0.078$, $R_w=0.086$.

[3] Monoclinic *C*2/*c*, $a=19.995(6)$, $b=11.751(4)$, $c=11.149(3)$ Å, $V=2567.9(13)$ Å^3, $Z=4$, $R_f=0.046$, $R_w=0.044$.

PII S0379-6779(96)03791-5

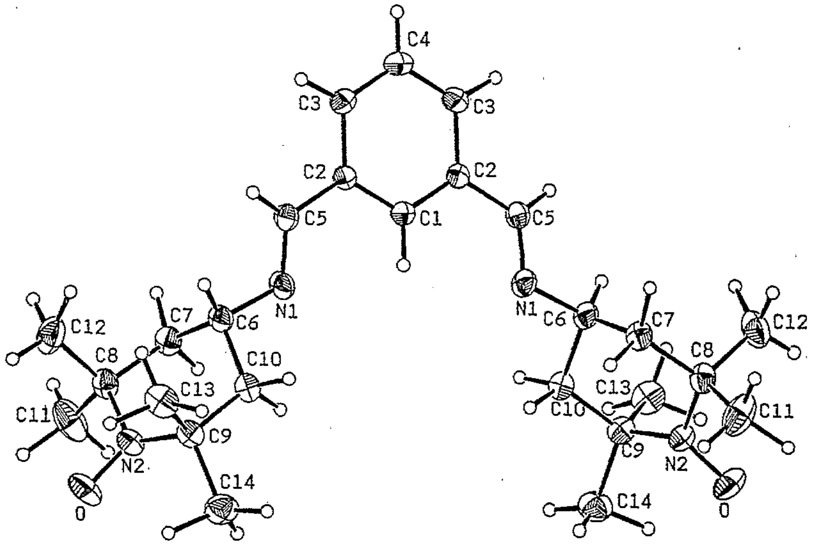


Fig. 1. Crystal structure of 1,3-*N*,*N*′-di(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl)xylyl imine (**2**).

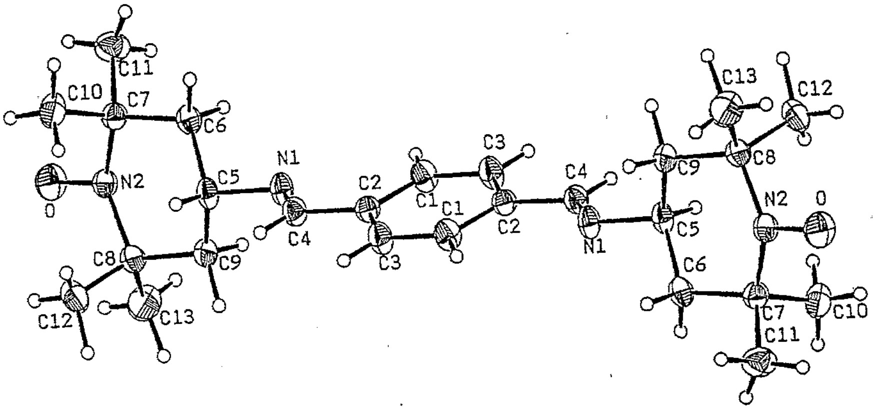


Fig. 2. Crystal structure of 1,4-*N*,*N*′-di(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl)xylyl imine (**3**).

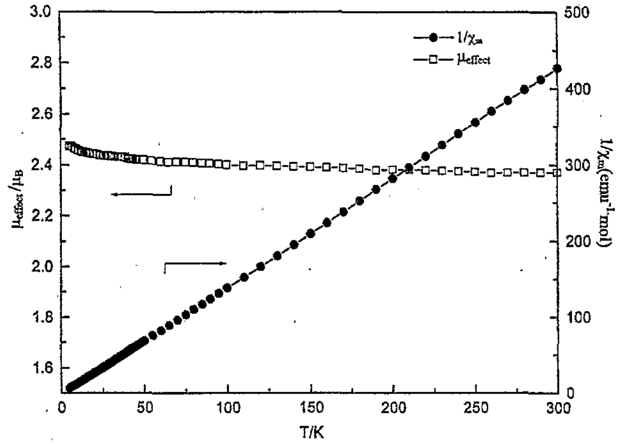


Fig. 3. Temperature dependence of the reciprocal molar magnetic susceptibility ($1/\chi_m$, ●) and the effective moment (μ_{eff}, □) of **2**.

group are almost coplanar. The dihedral angles (between phenyl and piperidine) for compounds **2** and **3** are 113.9 and 106.5° respectively. The averaged piperidine plane is defined by the carbon atoms at the 7,8,9,10-positions for **2** (6,7,8,9-positions for **3**). The intermolecular O···O distance between adjacent NO groups is 5.6852(22) Å for compound **2** (5.629(2) Å for **3**). The bond lengths for N–O are 1.274(4) Å (for **2**) and 1.2828(23) Å (for **3**), respectively. The electron spin resonance (ESR) spectra for compounds **1**, **2** and **3** in benzene solution at room temperature all indicate three simple lines due to the hyperfine splitting constants (hfsc) from the interaction with nitrogen (hfsc are 15.5 G for **1** ($g=2.0062$); 15.4 G for **2** ($g=2.0062$); 15.4 G for **3** ($g=2.0062$)). The ESR spectra show that there is no intramolecular interaction between two radical centers for compounds **1–3**.

The temperature dependence (5–300 K) of the magnetic susceptibility of a microcrystalline sample of **2** was measured at 1 T, and the data are expressed by the reciprocal molar magnetic susceptibility (χ_{mol}^{-1}) and the effective moment (μ_{eff}) versus temperature, as plotted in Fig. 3. As the temperature decreases, the μ_{eff} of the *m*-isomer increases to a maximum of about 2.47 μ_B at 5 K. Compound **2** gave a positive Weiss constant 0.2 K at temperatures between 5 and 20 K. This behavior indicates a stronger ferromagnetic interaction at lower temperature. The experimental plot matches the theoretical curve of $S=2\frac{1}{2}$ with $g=2$.

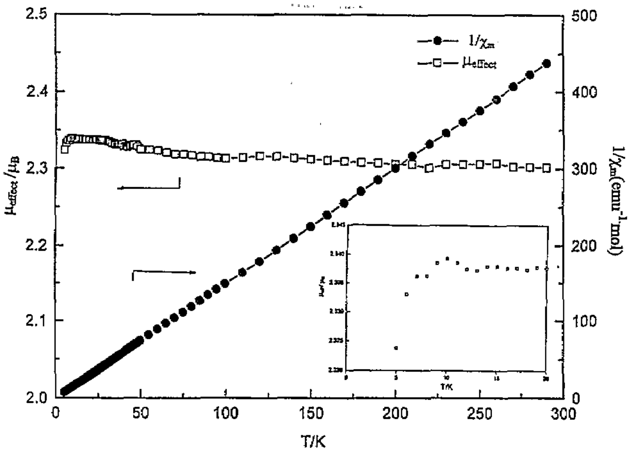


Fig. 4. Temperature dependence of the reciprocal molar magnetic susceptibility ($1/\chi_m$, ●) and the effective moment (μ_{eff}, □) of 3.

The plots of the reciprocal molar magnetic susceptibility (χ_{mol}^{-1}) and the effective moment (μ_{eff}) of compound **3** are shown in Fig. 4. The effective moment increases slowly to extend to about 2.34 μ_B at 10 K, then decreases below 10 K. Compound **3** gives a negative Weiss constant (-0.03 K). This behavior indicates a weak antiferromagnetic interaction. It matches the theoretical curve of $S=2\frac{1}{2}$ with $g=2$.

The slight difference in the magnetic properties, leading to different Weiss constants, might be ascribed to the isomeric difference in the molecular structure for compounds **2** and **3**.

Acknowledgements

Financial support from the National Science Council (ROC) of Taiwan (NSC85-2113-M-002-014) is greatly acknowledged.

References

[1] J.S. Miller, A.J. Epstein and W.M. Reiff, *Chem. Rev.*, *88* (1988) 201.
[2] J.S. Miller and A.J. Epstein, *Angew. Chem., Int. Ed. Engl.*, *33* (1994) 385.
[3] H. Iwamura and J.S. Miller, *Mol. Cryst. Liq. Cryst.*, *232* (1993) 1.
[4] A. Rajca, *Chem. Rev.*, *94* (1994) 871.
[5] M. Kinoshita, P. Turek, M. Tamura, K. Nozawa, D. Shiomi, Y. Nakazawa, M. Ishikawa, M. Takahashi, K. Awaga, T. Inabe and Y. Maruyama, *Chem. Lett.*, (1991) 1225.
[6] M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi and M. Kinoshita, *Chem. Phys. Lett.*, *186* (1991) 401.
[7] K. Awaga, T. Inabe and Y. Maruyama, *Chem. Phys. Lett.*, *190* (1992) 349.
[8] D. Shiomi, M. Tamura, H. Sawa, R. Kato and M. Kinoshita, *Synth. Met.*, *55–57* (1993) 3279.
[9] T. Sugano, M. Tamura and M. Kinoshita, *Synth. Met.*, *55–57* (1993) 3305.
[10] T. Ishida, H. Tsuboi, T. Nogami, H. Yoshikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda and M. Ishikawa, *Chem. Lett.*, (1994) 919.