

Nitroxide-Substituted Nitronyl Nitroxide and Iminonitroxide

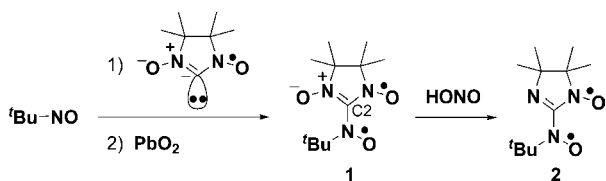
Shuichi Suzuki, Takanori Furui, Masato Kuratsu, Masatoshi Kozaki, Daisuke Shiomi, Kazunobu Sato, Takeji Takui, and Keiji Okada*

Department of Chemistry, Graduate School of Science, Osaka City University, Sugimoto Sumiyoshi-ku, Osaka 558-8585, Japan

Received August 29, 2010; E-mail: okadak@sci.osaka-cu.ac.jp

Abstract: We report on the highly compact nitroxide-substituted nitronyl nitroxide **1** and iminonitroxide **2**; they have isoelectronic structures with trimethylenemethane. These diradicals are stable under aerated conditions at room temperature and have large positive exchange interactions: $J/k_B = +390$ K ($H = -2JS_{1/2} \cdot S_{1/2}$) for **1** and $J/k_B \approx +550$ K for **2**.

Studies of stable open-shell molecules have recently attracted considerable attention because of their unique properties based on electron spins; several approaches including stable high-spin molecules,¹ singlet diradicaloids,^{2,3} and stable radicals containing various main group elements³ have emerged. Of these, trimethylenemethane (TMM) is the simplest species that shows a large positive exchange interaction,⁴ although it undergoes a facile ring closure at above 123 K to yield methylenecyclopropane through a thermally accessible singlet diradical state.⁵ Thus far, several high-spin molecules have been designed and synthesized using typically *m*-phenylene or alkylidene bridged nitroxide, nitronyl nitroxides (NN), and iminonitroxides (IN). However, very few stable diradicals with large exchange interactions, $J/k_B > +300$ K, $H = -2JS_1 \cdot S_2$, have been reported.⁶ We report on highly compact TMM-analogues, **1** and **2**, with large positive exchange interactions.



Diradical **1** was prepared by the nucleophilic addition of 2-lithio(nitronyl nitroxide)⁷ to 2-methyl-2-nitrosopropane followed by oxidation with lead(IV) dioxide. **1** was stable in spite of the close proximity of the two radical sites: It could be readily purified using conventional silica gel column chromatography and subsequently recrystallized from a benzene–hexane mixture to produce air-stable red prisms.⁸ **1** was converted to **2** by treatment with nitrous acid.⁸

Figure 1 shows the molecular and packing structures of **1**.⁹ The N–O bond lengths (i, iv, vi in Figure 1I) showed typical values in NN and *tert*-butyl nitroxide frameworks.¹⁰ The C–N bond length (v) was similar to that in 2-dimethylamino-NN (1.377 Å).¹¹ The dihedral angle between the O–N=C2–N–O and C2–(N–O)–C(sp³) planes was $\sim 73^\circ$. The molecules formed a hexagonal structure in a crystalline state with short intermolecular contacts between the oxygen atoms and the carbon atoms (H₃C groups), forming a hydrophobic hole of an internal diameter of ~ 5 Å. The recrystallization solvents (benzene–hexane) were incorporated as disorder between the holes.

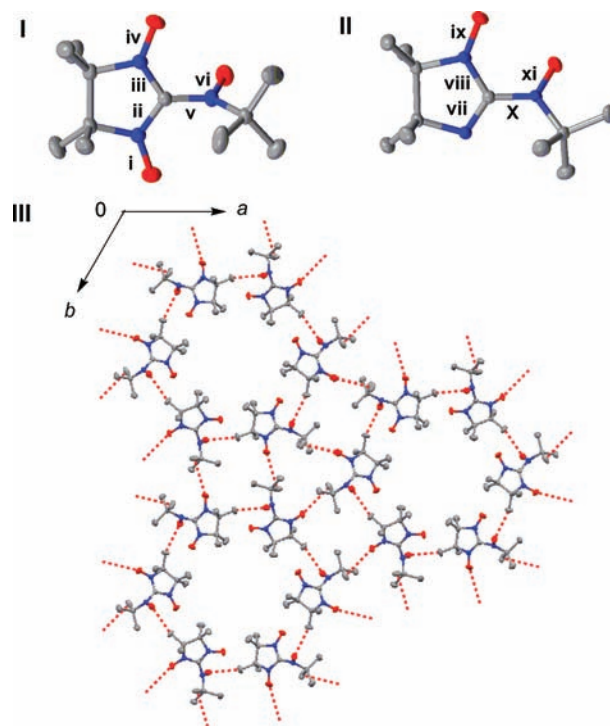


Figure 1. Molecular structure of **1** (I): bond length (Å) i: 1.273, ii: 1.338, iii: 1.346, iv: 1.276, v: 1.391, vi: 1.282. Molecular structure of **2** (II): bond length (Å) vii: 1.277, viii: 1.392, ix: 1.275, x: 1.403, xi: 1.281. Packing structure of **1** (III): The red dotted lines denote intermolecular contacts between the nitroxide oxygen atoms and the sp³ carbon atoms (intermolecular contacts of 3.028 Å within a hexagon and 3.380 Å between the nearest hexagons). Incorporated solvents, benzene and hexane ($\sim 1:1$ by NMR), are not shown. Hydrogen atoms are omitted for clarity.

Diradical **2** had a smaller dihedral angle between the N=C2–N–O and C2–(N–O)–C(sp³) planes ($\sim 40^\circ$). Two nitroxides were found to be in a cisoid conformation. Several intermolecular contacts were observed between the sp³ carbon atoms and the nitroxide oxygen atoms (3.468–3.596 Å, Figure S1).

In order to obtain insight into the spin–spin interaction between the two spin centers, the EPR spectra of these diradicals were measured: The close proximity of the two spin centers may provide a singlet ground state. Alternatively, the TMM type cross-conjugation of the spin centers may give a triplet ground state. The EPR spectrum of **1** in frozen diethylphthalate clearly exhibited a randomly oriented triplet pattern ($|D/hc| = 0.0250$ cm⁻¹, $|E/hc| = 0.0016$ cm⁻¹) with a small amount of doublet impurity (Figure 2). A half field signal due to $|\Delta m_s| = 2$ transition was clearly observed. The plots of $|\Delta m_s| = 2$ signal intensity (*I*) vs reciprocal temperature ($1/T$) gave a straight line, indicating

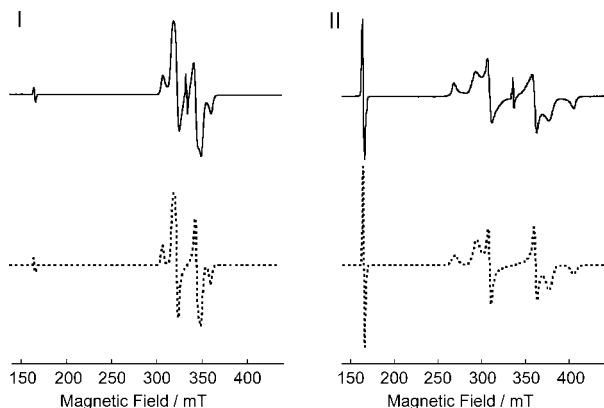


Figure 2. EPR spectrum of **1** (I) and of **2** (II) measured in frozen diethylphthalate matrix at 200 K with $\nu_0 = 9.416402$ GHz (for **1**) and $\nu_0 = 9.425181$ GHz (for **2**). The dotted lines indicate simulation spectra. **1**: $|D/hc| = 0.0250$ cm $^{-1}$, $|E/hc| = 0.0016$ cm $^{-1}$, $g_{xx} = 2.0070$, $g_{yy} = 2.0023$, $g_{zz} = 2.0041$, and $g_{av} = 2.0045$. **2**: $|D/hc| = 0.0639$ cm $^{-1}$, $|E/hc| = 0.0050$ cm $^{-1}$, $g_{xx} = 2.0032$, $g_{yy} = 2.0048$, $g_{zz} = 2.0032$, and $g_{av} = 2.0037$. The simulation was carried out using the software package of *EasySpin*.¹²

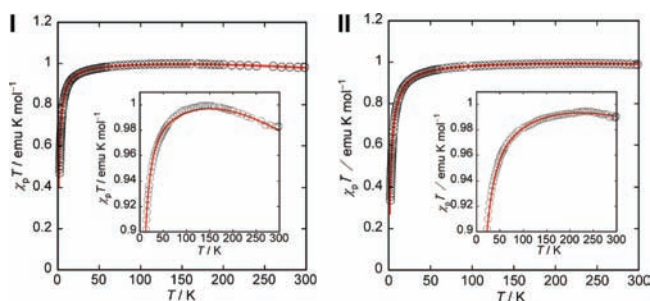


Figure 3. Temperature dependence of $\chi_p T$ for **1** (I) and for **2** (II). The red solid lines show simulation lines based on a modified Bleaney–Bowers model (**1**: $J/k_B = +390$ K ($H = -2J\mathbf{S}_{1/2} \cdot \mathbf{S}_{1/2}$) and $\theta = -1.5$ K using $g = 2.0045$; **2**: $J/k_B = +550$ K and $\theta = -2.7$ K using $g = 2.0037$). Insets: expanded (y-axis) plots.

a triplet ground state. A triplet pattern was also observed for **2** ($|D/hc| = 0.0639$ cm $^{-1}$, $|E/hc| = 0.0050$ cm $^{-1}$). Interestingly, **2** has a considerably larger $|D/hc|$ value and hence stronger $|\Delta m_s| = 2$ signal intensity than **1**. The larger $|D/hc|$ value in **2** can be qualitatively explained by the closer distance between the nitroxide spin centers in the cisoid form (atomic spin densities and their maps in Figure S2).

Bulk magnetic properties of these diradicals were investigated by measuring the temperature dependence of molar paramagnetic susceptibility (χ_p) (Figure 3). The $\chi_p T$ value of **1** was found to be 0.983 emu K mol $^{-1}$ (effective magnetic moment $\mu_{\text{eff}} = 2.804 \mu_B$) at room temperature. As the temperature was lowered to ~ 150 K, the $\chi_p T$ value gradually increased to show a broad maximum ($\chi_p T = 1.000$ emu K mol $^{-1}$, $\mu_{\text{eff}} = 2.828 \mu_B$); the value then slowly decreased when the temperature was further lowered from 150 to 30 K and rapidly decreased below 30 K. The increase in $\chi_p T$ (300 \rightarrow 150 K) indicates a sizable ferromagnetic interaction. The observed $\chi_p T - T$ curve was simulated using a modified Bleaney–Bowers model (eq 1),¹³ giving a large ferromagnetic interaction of $J/k_B = +390$ K ($H = -2J\mathbf{S}_{1/2} \cdot \mathbf{S}_{1/2}$) and a weak antiferromagnetic interaction of $\theta = -1.5$ K. The large J/k_B value can be assigned to the intramolecular ferromagnetic interaction between the two spin centers. The weak antiferromagnetic interaction can be assigned as the intermolecular antiferromagnetic interaction between the C(sp 3)–ON contacts observed in the crystal structure analysis. Theoretical calculations of the exchange interactions (ub3lyp/6-

31G(d)) using models based on the intermolecular contacts provided comparable results (Table S1).^{14,15}

$$\chi_p T = \frac{2N_A \mu_B^2 g^2 T}{k_B(T - \theta)[3 + \exp(-2J/k_B T)]} \quad (1)$$

Diradical **2** showed a larger $\chi_p T$ value (0.990 emu K mol $^{-1}$) ($\mu_{\text{eff}} = 2.814 \mu_B$) at room temperature. The $\chi_p T$ value was almost constant between 300 and 100 K and decreased below 100 K. In the 300–100 K region, a very broad maximum ($\chi_p T = 0.995$ emu K mol $^{-1}$, $\mu_{\text{eff}} = 2.821 \mu_B$) was observed at ~ 230 K, which indicates a larger intramolecular magnetic interaction between the two spin centers. The simulation of the $\chi_p T - T$ curve gave a large ferromagnetic interaction of $J/k_B \approx +550$ K and a weak antiferromagnetic interaction of $\theta = -2.7$ K. **2** has a larger J value than **1**, which is attributed to the smaller dihedral angle between the nodal planes of the spin centers.

The energy gap (E_{ST} gap) between the triplet ground state and the singlet diradical state is thus estimated as E_{ST} gap = $2J/k_B = +780$ K (1.56 kcal/mol) for **1** and +1100 K (2.20 kcal/mol) for **2**. Although the singlet diradical states are readily accessible at room temperature, we have observed no tendency of the transformation to the ring-closed forms by the formation of the O–O bond in contrast to the chemical behavior of TMM. The ring-closed structures should have significantly higher energy levels because of the electronic repulsion between six pairs of lone pair electrons in the five-membered –C2–N–O–O–N– ring in accord with theoretical calculations (Table S2).¹⁴ The unstable nature of the ring closed forms eventually contributes to the chemical stability of these diradicals.

In summary, we demonstrated the high stability of new TMM-type triplet diradicals whose triplet occupancies are nearly 100% at room temperature. From a structural perspective, these diradicals can be utilized as magnetic metal ligands. Furthermore, these species are easily sublimed under reduced pressure (~ 70 °C/20 mmHg for **1**, ~ 55 °C/20 mmHg for **2**) without decomposition. Owing to these features, these diradicals have various potential applications in spintronics. Such studies are in progress.

Acknowledgment. K.O. thanks JSPS for financial support (22350066).

Supporting Information Available: The synthetic procedures of **1** and **2**; Tables S1, S2; Figures S1, S2; and complete Gaussian citation for ref 14. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) For example: (a) Rajca, A.; Wongsriratanakul, J.; Rajca, S. *Science* **2001**, *294*, 1503–1505. (b) Inoue, K.; Hayamizu, T.; Iwamura, H.; Hashizume, D.; Ohashi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 1803–1804. (c) Masuda, Y.; Kurtasu, M.; Suzuki, S.; Kozaki, M.; Shiomi, D.; Sato, K.; Takui, T.; Hosokoshi, Y.; Lan, X.-Z.; Miyazaki, Y.; Inaba, A.; Okada, K. *J. Am. Chem. Soc.* **2009**, *131*, 4670–4673.
- (2) For example: (a) Abe, M.; Kubo, E.; Nozaki, K.; Matsuo, T.; Hayashi, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 7828–7831. (b) Konishi, A.; Hirao, Y.; Nakano, M.; Shimizu, A.; Botek, E.; Champagne, B.; Shiomi, D.; Sato, K.; Takui, T.; Matsumoto, K.; Kurata, H.; Kubo, T. *J. Am. Chem. Soc.* **2010**, *132*, 11021–11023. (c) Koide, T.; Furukawa, K.; Shinokubo, H.; Shin, J.-Y.; Kim, K. S.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2010**, *132*, 7246–7247. (d) Iwasaki, A.; Hu, L.; Suizu, R.; Nomura, K.; Yoshikawa, H.; Awaga, K.; Noda, Y.; Kanai, K.; Ouchi, Y.; Seki, K.; Ito, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 4022–4024.
- (3) For example: (a) *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds*; Hicks, R., Ed.; John Wiley & Sons: West Sussex, 2010. (b) Power, P. P. *Chem. Rev.* **2003**, *103*, 789–809. (c) Breher, F. *Coord. Chem. Rev.* **2007**, *251*, 1007–1043. (d) Rodriguez, A.; Präsang, C.; Gandon, V.; Bourg, J.-B.; Bertrand, G. In *Modern Aspects of Main Group Chemistry*; Lattman, M.; Kemp, R. A., Eds.; ACS Symposium Series 917; American Chemical Society: Washington, DC, 2005; Chapter 6, pp 81–93. (e) Ito, S.; Miura, J.; Morita, N.; Yoshifuji, M.; Arduengo, A. J.,

- III. *Angew. Chem., Int. Ed.* **2008**, *47*, 6418–6421. (f) Chiu, C.-W.; Gabbai, F. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 1723–1725.
- (4) (a) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; John Wiley & Sons: New York, 1982; pp 1–72. (b) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 475–476.
- (5) Dowd, P.; Chow, M. *J. Am. Chem. Soc.* **1977**, *99*, 6438–6440.
- (6) (a) Mukai, K.; Ishizu, K.; Deguchi, Y. *J. Phys. Soc. Jpn.* **1969**, *27*, 783. (b) Iwamura, H.; Inoue, K. In *Magnetism: Molecules to Materials II*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: New York, 2001; pp 61–108. (c) Shultz, D. A. In *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcell Dekker: New York, 1999; pp 103–146. (d) Hiraoka, S.; Okamoto, T.; Kozaki, M.; Shiomi, D.; Sato, K.; Takui, T.; Okada, K. *J. Am. Chem. Soc.* **2004**, *126*, 58–59. (e) Rajca, A.; Shiraishi, K.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.* **2007**, *129*, 7232–7233. (f) Rajca, A.; Shiraishi, K.; Rajca, S. *Chem. Commun.* **2009**, 4372–4374.
- (7) (a) Boocock, D. G. B.; Darcy, R.; Ullman, E. F. *J. Am. Chem. Soc.* **1968**, *90*, 5945–5946. (b) Chupakhin, O. N.; Utepova, I. A.; Varaksin, M. V.; Tretyakov, E. V.; Romanenko, G. V.; Stass, D. V.; Ovcharenko, V. I. *J. Org. Chem.* **2009**, *74*, 2870–2872.
- (8) **1**: mp 106 °C (decomp.); MS (FAB⁺) *m/z* 244 [(M + H)⁺]; IR (KBr, cm⁻¹) 2980, 2937, 1456, 1420, 1373, 1335, 1202, 1175, 1138, 870, 748; EPR (powder): *g* = 2.0090; UV–vis λ_{max} /nm (ϵ) in *n*-hexane: 310 (14668), 521 (914). **2**: mp 81 °C (decomp.); MS (FAB⁺) *m/z* 228 [(M + H)⁺]; IR (KBr, cm⁻¹) 2980, 2937, 1533, 1448, 1362, 1306, 1261, 1220, 1144, 937, 880, 775; EPR (powder): *g* = 2.0079; UV–vis λ_{max} /nm (ϵ) in *n*-hexane: 205 (9910), 359 (918).
- (9) Crystallographic data for **1**: trigonal, space group: $R\bar{3}$ (#148), *a* = *b* = 34.674(2) Å, *c* = 6.0958(4) Å, $\alpha = \beta = 90.0^\circ$, $\gamma = 120.0^\circ$, *V* = 6347.2(7) Å³, *Z* = 18, $\rho_{\text{calcd}} = 1.146 \text{ g cm}^{-3}$, *T* = 170(2) K, *R* = 0.0756, *R_w* = 0.1840, GOF = 1.172 (CCDC#:783983). Crystallographic data for **2**: monoclinic, space group *P2₁/c* (#14), *a* = 6.118(2) Å, *b* = 17.652(6) Å, *c* = 12.494(4) Å, $\alpha = \gamma = 90^\circ$, $\beta = 109.434(6)^\circ$, *V* = 1272.4(7) Å³, *Z* = 4, $\rho_{\text{calcd}} = 1.187 \text{ g cm}^{-3}$, *T* = 150(2) K, *R* = 0.0793, *R_w* = 0.1235, GOF = 1.153 (CCDC#: 783982).
- (10) Hosokoshi, Y.; Katoh, K.; Nakazawa, Y.; Nakano, H.; Inoue, K. *J. Am. Chem. Soc.* **2001**, *123*, 7921–7922.
- (11) Sakurai, H.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **2000**, *122*, 9723–9734.
- (12) Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 42–55. The software *EasySpin* (ver. 3.1.4) is available at <http://www.easyspin.org/>.
- (13) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451–465.
- (14) *Gaussian 09, Revision A.02*, Frisch, M. J. et al. Gaussian, Inc., Wallingford CT, 2009.
- (15) Yamaguchi, K.; Kawakami, T.; Takano, Y.; Kitagawa, Y.; Yamashita, Y.; Fujita, H. *Int. J. Quantum Chem.* **2002**, *90*, 370–385.

JA107769Z