

A Stable Radical-Substituted Radical Cation with Strongly Ferromagnetic Interaction: Nitronyl Nitroxide-Substituted 5,10-Diphenyl-5,10-dihydrophenazine Radical Cation

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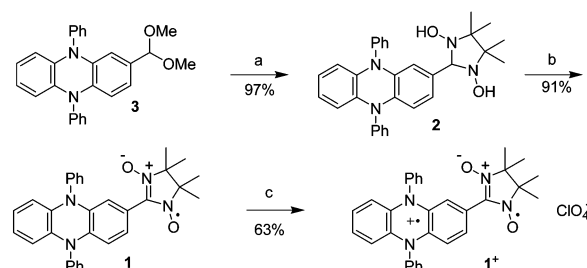
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Recently, the magnetic properties of organic compounds have attracted a great deal of attention. Various approaches toward organic magnetic materials have been taken, both theoretically and experimentally.¹ Of these, an approach with a radical-substituted radical ion as a spin building block is particularly interesting. Yamaguchi and co-workers theoretically explored organic ferro- and ferrimagnets with various patterns of radical-substituted donor-acceptor charge transfer (CT) complexes.² Although the related experimental studies have been examined using aniline-,³ ferrocene-,⁴ and TTF-frameworks^{5,6} as basic structures of CT-complexes, paramagnetic behavior has been observed in most cases and the expected ferro- or ferrimagnetic properties have not been observed. In general, spins on donors and acceptors in usual CT-complexes have large intermolecular antiferromagnetic interactions ranging between -100 and -1000 K.⁷ To realize the expected properties, a comparably large intramolecular J (half the singlet-triplet energy gap ΔE_{ST}) between the radical and radical ion moieties^{3a} should therefore be essential. In this context, the thianthrene-based radical cations recently reported by Sugawara and co-workers seem to be attractive, although the J values of these spectroscopically detected species have not been determined because of their instability.⁸ The development of a molecular system with isolable stability and a large J is extremely important in the construction of molecular magnets. Dihydrophenazines are superior electron donors,⁹ giving highly stable radical cations that have large spin densities on the nitrogen and the C2 carbon atoms.¹⁰ We report the synthesis, structure, and magnetic properties of a nitronyl nitroxide-substituted 5,10-diphenyl-5,10-dihydrophenazine radical cation (1^+).

The synthesis of 1^+ is outlined in Scheme 1. Cyclic bis-(hydroxylamine) **2** was synthesized by the condensation of dimethyl acetal **3** with 2,3-bis(hydroxylamino)-2,3-dimethylbutane in the presence of a catalytic amount of pyridinium tosylate in dry methanol. The treatment of **2** with silver(I) oxide in methylene chloride gave the neutral radical **1**. The oxidation of **1** to 1^+ was achieved using tris(4-bromophenyl)ammonium perchlorate in dry acetonitrile in a glovebox. Concentration of the solvent and the addition of dry ether gave fine precipitates of the salt of $1^+\cdot\text{ClO}_4^-$. Recrystallization of the crude salt from the methylene chloride-toluene mixture gave dark-red crystals of $1^+\cdot\text{ClO}_4^- \cdot \text{CH}_2\text{Cl}_2$. The salt was stable under aerated conditions at room temperature.

X-ray crystal structure analyses were achieved for the neutral **1**¹¹ and the 1^+ salt.¹¹ Figure 1-I shows the molecular structure of **1**⁺. The phenyl groups at 5 and 10 positions had large dihedral angles to the dihydrophenazine plane in both **1** and 1^+ (A/C and C/E in Figure 1-I). The dihedral angle D/F was a little smaller in cation 1^+ . The bond lengths, **a**, **a'**, **c**, **c'** were shortened for 1^+ , whereas those of **b**, **b'** were elongated. These changes in bond lengths are in qualitative accord with the expectations from the

Scheme 1^a



^a Reaction conditions: (a) 2,3-bis(dihydroxylamino)-2,3-dimethylbutane (1.6 equiv) in the presence of pyridinium tosylate (0.3 equiv) in dry methanol; (b) silver(I) oxide (5 equiv) in methylene chloride; (c) tri(4-bromophenyl)ammonium perchlorate (1 equiv) in dry acetonitrile.

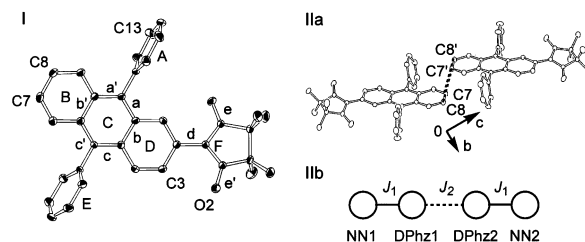


Figure 1. Molecular structure (I), a dimer structure in the crystal packing (IIa), and a schematic diagram of magnetic interaction (IIb) for 1^+ . (I) Drawn at 50% ellipsoids level; hydrogen atoms, the counteranion, and the solvent are eliminated for clarity. Selected bond lengths (Å) and dihedral angles (deg) for $1^+\cdot\text{ClO}_4^- \cdot \text{CH}_2\text{Cl}_2$: **a**, **a'**: 1.386(2), 1.380(2), **b**, **b'**: 1.414(3), 1.411(3), **c**, **c'**: 1.374(2), 1.383(2), **d**: 1.450(3), **e**, **e'**: 1.280(2), 1.279(2), A/C, C/E: 88.70, 102.26, D/F (F:-N=C-N- plane): 20.83. Selected bond lengths (Å) and dihedral angles (deg) for the neutral **1**: **a**, **a'**: 1.407(4), 1.409(4), **b**, **b'**: 1.408(5), 1.403(5), **c**, **c'**: 1.395(4), 1.410(4), **d**: 1.456(4), **e**, **e'**: 1.286(3), 1.279(3), A/C, C/E: 84.65, 85.52, D/F: 25.34. (IIa) The distance of C7-C8' contact: 3.566(3) Å. (IIb) The circles represent $S = 1/2$ spins, NN: nitronyl nitroxide; DPhz: dihydrophenazine.

shape of the HOMO of the neutral dihydrophenazine structure; the elongated (shortened) bonds in 1^+ have a bonding (antibonding) relation in the HOMO of 5,10-dihydrophenazine. The N-O bond length (**e**, **e'**) of 1^+ is similar to that of neutral **1** and longer than that of a nitrosonium nitroxide (1.23 Å).¹²

A short intermolecular contact was observed between the C7 atom and the C8' atom in adjacent 1^+ , both of which had large spin densities, forming a dimer structure (Figure 1-IIa).¹³ The distance of the contact (3.57 Å) is close to the van der Waals contact (3.54 Å).¹⁴ A schematic model of the magnetic interaction is expressed in Figure 1-IIb.

Figure 2-Ia, Ib shows the EPR spectrum for 1^+ in butyronitrile at 123 K and its simulation spectrum. The weak forbidden $|\Delta m_s| = 2$ signal was observed at low temperatures. The intensity of the $|\Delta m_s| = 2$ signal linearly increased to the reciprocal temperature

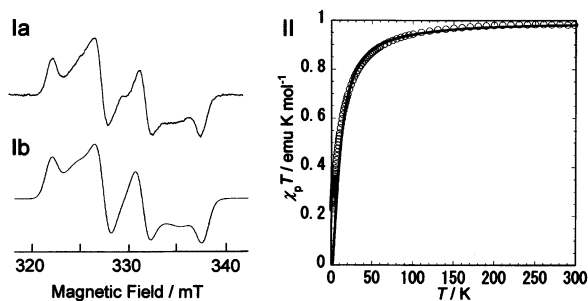


Figure 2. EPR spectra (Ia,b) and temperature dependence of $\chi_p T$ of $1^+\cdot\text{ClO}_4^-\cdot\text{CH}_2\text{Cl}_2$ (II). (Ia) Measured at 123 K in a frozen butyronitrile matrix with $\nu_0 = 9.251147$ GHz. (Ib) The simulation spectrum with parameters $|D/hc| = 0.00725$ cm^{-1} , $|E/hc| = 0.0011$ cm^{-1} , $g_{xx} = 2.0065$, $g_{yy} = 2.0020$, $g_{zz} = 2.0040$, $g_{av} = [(g_{xx}^2 + g_{yy}^2 + g_{zz}^2)/3]^{1/2} = 2.004$, (II) Measured for a powder sample under $B = 0.1$ T. The solid line represents the simulation curve with $J_1/k_B = 700$ K and $J_2/k_B = -18$ K.

(6–50 K). The linearity indicates either the quasi-degeneracy of singlet and triplet states, $\Delta E_{ST}/k_B \ll 6$ K, or a triplet ground state with a large S–T gap, $\Delta E_{ST}/k_B \gg 50$ K.

A much clearer insight was obtained by measuring the magnetic susceptibility of 1^+ (Figure 2-II). The $\chi_p T$ value at room temperature was 0.98 emu K mol^{-1} , which is close to that expected for $S = 1$ state ($g_{av} = 2.004$). The value decreased with lowering temperature, which is ascribable to intermolecular magnetic interactions. The temperature dependence of $\chi_p T$ clearly demonstrates a large S–T gap of $\Delta E_{ST}/k_B \gg 300$ K. The spin Hamiltonian, $H = -2J_1(\mathbf{S}_{\text{NN}2} \cdot \mathbf{S}_{\text{DPHz1}} + \mathbf{S}_{\text{NN}2} \cdot \mathbf{S}_{\text{DPHz2}}) - 2J_2\mathbf{S}_{\text{DPHz1}} \cdot \mathbf{S}_{\text{DPHz2}}$, was used to analyze the $\chi_p T$ value on the basis of the molecular packing in the crystal (Figure 1-IIb). The $\chi_p T$ values were reproduced using parameters of $J_1/k_B \geq +700$ K and $J_2/k_B = -18 \pm 0.6$ K (solid line in Figure 2-II).¹⁵ The large J_1 is qualitatively understandable with the spin polarization mechanism via a large positive spin density of the C2-carbon of dihydrophenazine radical cation.^{10,16} The intramolecular ferromagnetic interaction J_1 falls within the same range as those of general CT-type intermolecular magnetic interactions.⁷

To obtain theoretical insights into the exchange interaction in this system, DFT calculations were performed using the Gaussian 98 program (UB3LYP/6-31G*).¹⁷ The geometry of the radical cation was taken from X-ray structure analysis. For the calculation of low-spin singlet state, the trial UHF wave function was generated by the broken symmetry (BS) approach.^{18–20} The triplet state had a lower energy than the BS-singlet state. The energy difference between the triplet and the BS-singlet state was 1.98 kcal/mol, which corresponds to $J/k_B = +498$ K or $J/k_B = +987$ K, depending on the estimation methodologies.^{19,20}

In sum, we have found that 1^+ is a stable triplet species with strong intramolecular ferromagnetic coupling. The following additional findings are noteworthy: (1) the corresponding 5,10-dimethyl derived radical cation was unstable and slowly decomposed even under inert atmosphere. (2) The radical cation of the 2,7-bis[(nitronyl nitroxide)-2-yl]-substituted 1^+ -analogue had a clean EPR spectrum with a quartet pattern but was too unstable to isolate in pure form. The details will be published elsewhere. Preparation of charge-transfer complexes and related magnetic materials based on 1^+ is in progress.

Supporting Information Available: X-ray crystallographic files (CIF) and a list of spin-densities (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) For general approaches: (a) Lahti, P. M.; Ed. *Magnetic Properties of Organic Materials*; Marcel Dekker: New York, 1999. (b) Amabilino, D.

- B.; Veciana, J. In *Magnetism: Molecules to Materials II*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: New York, 2001; pp 1–60. For ferrimagnetic approaches: (c) Hosokoshi, Y.; Katoh, K.; Nakazawa, Y.; Nakano, H.; Inoue, K. *J. Am. Chem. Soc.* **2001**, *123*, 7921–7922. (d) Shiomi, D.; Kanaya, T.; Sato, K.; Mito, M.; Takeda, K.; Takui, T. *J. Am. Chem. Soc.* **2001**, *123*, 11823–11824. For CT approaches: (e) Breslow, R. In *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999; pp 27–60. (f) Sugimoto, T. In *Molecular Magnetism*; Itoh, K., Kinoshita, M., Eds.; Kodansha or Gordon and Breach: Tokyo, 2000; pp 223–239.
- (2) (a) Yamaguchi, K.; Namimoto, H.; Fueno, T. *Chem. Phys. Lett.* **1990**, *166*, 408–414. (b) Yamaguchi, K.; Okumura, M.; Fueno, T.; Nakasuji, K. *Synth. Met.* **1991**, *41–43*, 3631–3634.
- (3) (a) Sugano, T.; Fukasawa, T.; Kinoshita, M. *Synth. Met.* **1991**, *41–43*, 3281–3284. (b) Sakurai H.; Izuoka A.; Sugawara T. *J. Am. Chem. Soc.* **2000**, *122*, 9723–9734.
- (4) Nakamura, Y.; Koga, N.; Iwamura, H. *Chem. Lett.* **1991**, 69–72.
- (5) (a) Nakazaki, J.; Ishikawa, Y.; Izuoka, A.; Sugawara, T.; Kawada, Y. *Chem. Phys. Lett.* **2000**, *319*, 385–390. (b) Nakazaki, J.; Matsushita, M. M.; Izuoka, A.; Sugawara, T. *Tetrahedron Lett.* **1999**, *40*, 5027–5030. (c) Kumai, R.; Matsushita, M. M.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **1994**, *116*, 4523–4524. (d) Kumai, R.; Izuoka, A.; Sugawara, T. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 151–154.
- (6) (a) Sugimoto, T.; Yamaga, S.; Nakai, M.; Ohmori, K.; Tsuji, M.; Nakatsuji, H.; Fujita, H.; Yamauchi, J. *Chem. Lett.* **1993**, 1361–1364. (b) Sugimoto, T.; Yamaga, S.; Nakai, M.; Tsuji, M.; Nakatsuji, H.; Hosoito, N. *Chem. Lett.* **1993**, 1817–1820.
- (7) Nordio, P. L.; Soos, Z. G.; McConnell, H. M. *Annu. Rev. Phys. Chem.* **1966**, *17*, 237–260.
- (8) Izuoka, A.; Hiraishi, M.; Abe, T.; Sugawara, T.; Sato, K.; Takui, T. *J. Am. Chem. Soc.* **2000**, *122*, 3234–3235.
- (9) Okamoto, T.; Terada, E.; Kozaki, M.; Uchida, M.; Kikukawa, S.; Okada, K. *Org. Lett.* **2003**, *5*, 373–376.
- (10) Cauquis, G.; Delhomme, H.; Serve, D. *Tetrahedron Lett.* **1971**, 4649–4652.
- (11) Crystallographic data for **1**: monoclinic, space group $C2/c$, $a = 37.16(1)$ Å, $b = 6.127(2)$ Å, $c = 24.091(9)$ Å, $\beta = 111.392(7)^\circ$, $V = 5106.8(3)$ Å³, $Z = 8$, $\rho_{\text{calcd}} = 1.273$ g/cm³, $T = 113$ K, $R = 0.070$, $R_w = 0.088$, GOF = 1.142. Crystallographic data for $1^+\cdot\text{ClO}_4^-\cdot\text{CH}_2\text{Cl}_2$, Triclinic, space group $P-1$, $a = 10.282(1)$ Å, $b = 11.232(1)$ Å, $c = 15.539(2)$ Å, $\alpha = 80.70(1)^\circ$, $\beta = 77.67(1)^\circ$, $\gamma = 64.483(7)^\circ$, $V = 1577.2(3)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.419$ g/cm³, $T = 113$ K, $R = 0.045$, $R_w = 0.065$, GOF = 0.988.
- (12) Caneschi, A.; Laugier, J.; Rey, P. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1077–1079.
- (13) Two additional short contacts were observed between atoms bearing smaller spin densities: One was between the neighboring dimers through the O2 and the C3-attached hydrogen (2.85 Å), resulting in a dimer chain in the [011] direction. The other was between the O2 atom and the C13-attached hydrogen (2.41 Å) of another neighboring 1^+ , giving a 1^+ chain in the [101] direction.
- (14) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.
- (15) The $\chi_p T$ values in the high-temperature region (>100 K) were reproducible with $J_1/k_B \geq +700$ K. The unsatisfactory fitting of the low-temperature region (<50 K) may be due to the other contacts described in ref 13 being neglected. Trials with some accessible conventional models taking into account weaker contacts, i.e. a two-spin singlet–triplet model with a mean field (θ) or an $S = 1$ chain model did not improve the fitting.
- (16) Dihydrophenazine radical cation has nonalternant spin distribution, where both the nitrogen and the C2-carbon have large positive spin densities. See also Supporting Information.
- (17) The total energy E (hartree) and S^2 before spin projection were $E = -1567.36685314$ with $S^2 = 2.0685$ for triplet state, $E = -1567.36369601$ with $S^2 = 1.0594$ for the BS-singlet state using *Gaussian 98*, revision A.9; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian, Inc.*, Pittsburgh, PA, 1998.
- (18) (a) Yamaguchi, K. *Chem. Phys. Lett.* **1975**, *33*, 330–335. (b) Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737–5743. (c) Adao, C.; Barone, V.; Bencini, A.; Totti, F.; Ciofini, I. *Inorg. Chem.* **1999**, *38*, 1996–2004. (d) Okada, K.; Nagao, O.; Mori, H.; Kozaki, M.; Shiomi, D.; Sato, K.; Takui, T.; Kitagawa, Y.; Yamaguchi, K. *Inorg. Chem.* **2003**, *42*, 3221–3228.
- (19) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comput. Chem.* **1999**, *20*, 1391–1400.
- (20) (a) Yamanaka, S.; Kawakami, T.; Nagao, H.; Yamaguchi, K. *Chem. Phys. Lett.* **1994**, *231*, 25–33. (b) Yamaguchi, K. *Int. J. Quantum Chem.* **2002**, *90*, 370–385.

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