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## Syntheses of Piperidinyloxyl Diradicals Containing Squaric Acid Moieties and Their Magnetic Properties

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Received February 19, 1993

Four compounds containing two 2,2,6,6-tetramethylpiperidin-1-yloxyl radicals were synthesized. They are all chemically bonded with squaric moieties. The diradical compounds show fundamentally the paramagnetic behaviors satisfying the theoretical magnetic susceptibility according to Curie's law. A diradical compound of salt-form **4** however shows a relatively strong antiferromagnetic interaction in comparison with other reported organic radicals. The antiferromagnetic interaction of diradical **4** approximates a value of  $J/k = -50$  K by the theoretical analysis of its temperature dependence.

### Introduction

Unpaired electrons in atoms and molecules cause several kinds of magnetic properties. They are divided into paramagnetism, ferromagnetism and antiferromagnetism according to the direction and strength among the individual magnetic moments. The ferromagnetism usually occurs with the transition metals or their oxides. In the case of organic compounds, parallel arrangements of electron spins, which can eventually result in ferromagnetism, have usually no success because of their low symmetry and degeneracy. Several theoretical models solving these difficulties and aiming at the organic ferromagnetism are proposed in the literatures.<sup>1-7</sup> However no valuable pure organic ferromagnet has been reported yet.

McConnell noticed the possibility of organic ferromagnetism through the strong spin-polarization of crystalline radical compounds.<sup>1</sup> The magnetic properties of a few well-known stable radicals such as galvanoxyl, verdazyl and hydrazyl were reported to show only paramagnetism with weak antiferromagnetic interaction.<sup>8-10</sup> This paper is a part of our studies on the way toward organic ferromagnetism.<sup>11,12</sup> We report here the magnetic properties of a different type of stable radicals. The piperidinyloxyl radicals have been conventionally named as nitroxyl. Their derivatization with

squaric acid was selected because it has the intrinsic polarity as well as aromaticity.<sup>13-15</sup>

### Results and Discussion

Figure 1 shows the synthetic route for diradical compounds **4**, **5**, **6** and **7**, which contain nitroxyl diradical and cyclobutene skeleton from squaric acid **1**. 2,2,6,6-Tetramethylpiperidin-1-yloxyl radical is abbreviated into a TEMPO as in the conventional way. The reaction conditions to link the TEMPO unit were referred to the similar reaction of squaric acid with amine and alcohol in literatures.<sup>16-19</sup> In contrast with squaric acid which is a strong organic acid, the nitroxyl radical is weakly basic.<sup>20</sup> The salt form **4** is formed by simple mixing of squaric acid with  $\text{H}_2\text{N-TEMPO}$  under mild condition. However a direct condensations to obtain bisamide forms **5**, **6** and bisester form **7** are not successful because they cause the destruction of nitroxyl radical center. Consequently, 1,2-bisamide form **5** and 1,2-bisester form **7** were synthesized by the indirect condensation *via* diethyl ester **2**. 1,3-Bisamide form **6** was synthesized for the same reason by transamidization from compound **3**.

Hot DMSO around 100° C is the only solvent for bisamide compounds **5** and **6**. In comparison with that, the salt compound **4** is soluble in water and the bisester compounds

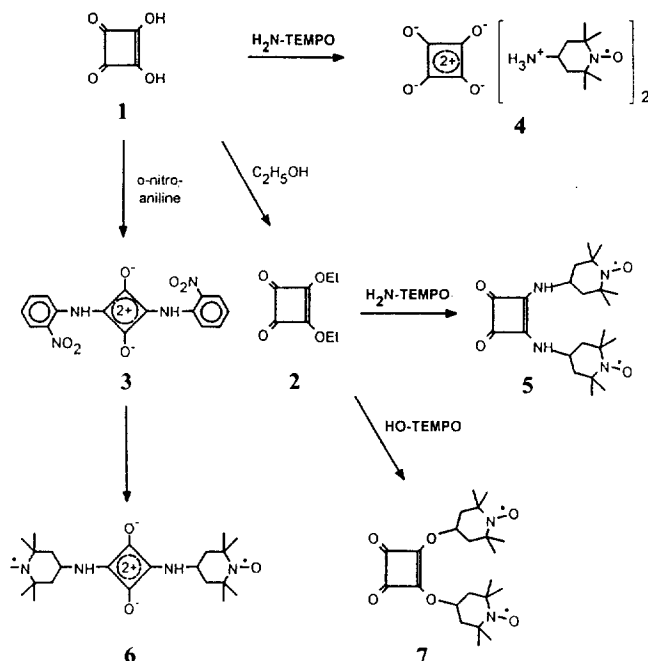


Figure 1. Reaction schema for the synthesis of nitroxyl diradicals.

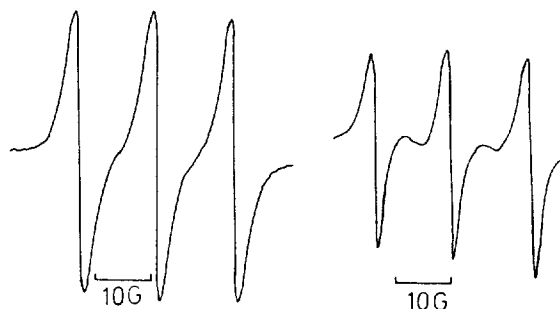


Figure 2. ESR spectra of diradical **4** in methanol (left) and **7** in chloroform (right).

**7** in usual organic solvents such as diethyl ether and chloroform.

Structure confirmations by spectroscopic method are detailed in experimental part. NMR is not applicable for that because of the interference from electron spins. ESR spectra of compounds **4** and **7** show typical 1:1:1 triplet splitting caused by nuclear spin quantum number  $I=1$  of nitrogen (Figure 2). This means additively that there is no strong electron-electron exchange energy between two radicals. Table 1 shows the molar magnetic susceptibilities of four compounds at room temperature, which are corrected with the diamagnetic contribution through Pascal's constants.<sup>21</sup>

The molar magnetic susceptibilities  $\chi_M$  of **5**, **6** and **7** approach the theoretical molar paramagnetic susceptibility  $2.5 \times 10^{-3}$  emu/mole at 300 K. The value can be calculated from the following Curie's law.

$$\chi_M = C/T \quad (1)$$

where  $C$  is  $0.375 \text{ emu} \cdot \text{K}/\text{mole}$ .<sup>21</sup> A multiplication of obtained value by 2 is necessary because each molecule has two radi-

Table 1. Gram and Molar Magnetic Susceptibilities of Nitroxyl Diradicals at Room Temperature

Compound	M.W. (g/mol)	$\chi_g \times 10^{-6}$ (emu/g) <sup>a</sup>	$\chi_{dia} \times 10^{-3}$ (emu/mol) <sup>b</sup>	$\chi_M \times 10^{-3}$ (emu/mol) <sup>c</sup>
<b>4</b>	456.58	3.170	-0.280	1.974
<b>5</b>	420.55	5.084	-0.262	2.400
<b>6</b>	420.55	5.638	-0.262	2.633
<b>7</b>	422.52	5.283	-0.259	2.491

<sup>a</sup>Measured value with magnetic balance. <sup>b</sup>Diamagnetic contribution calculated with Pascal's constant. <sup>c</sup>Molar paramagnetic susceptibility corrected with the diamagnetic contribution.

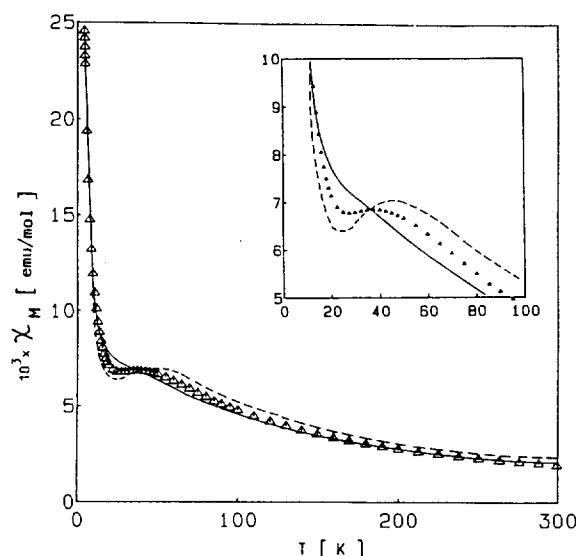
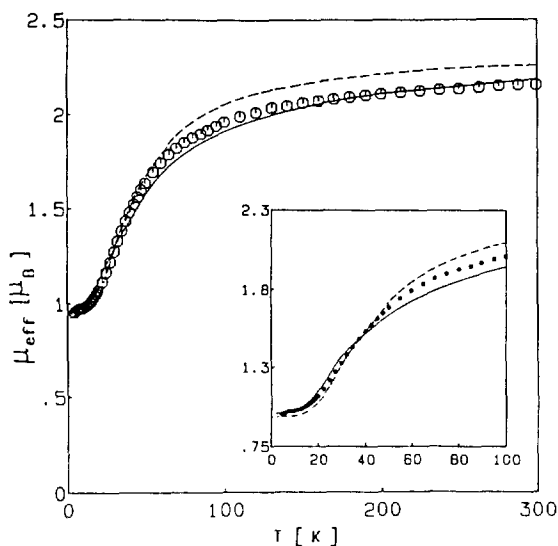


Figure 3. The temperature dependence of molar magnetic susceptibility of diradical **4** at a field strength of 1 Tesla. Triangles are the plot of the experimental data. The Eq. (2) and (3) are shown as a solid line and a broken line respectively.

icals. A decidedly high molar susceptibility at room temperature is necessary to obtain the initially aimed strong ferromagnetic interaction. Such a high molar susceptibility may result in a fairly high Curie's transition temperature to ferromagnet. The measured molar magnetic susceptibilities of compound **5**, **6** and **7** do not satisfy the above prerequisites and predict no possibilities for valuable organic ferromagnets.

The salt-formed diradical **4** shows a far lower molar susceptibility in comparison with the theoretical one. A relatively strong antiferromagnetic interaction causes these phenomena. Its temperature dependence of magnetic susceptibility was analyzed to 4 K. The obtained data was plotted in Figure 3. The shape of measured data deviates from relation 1 under 100 K. The deviation from Curie's law can be estimated through the modified relation i.e. Curie-Weiss law that is represented as  $\chi_M = C/(T - \Theta)$ . The presence of antiferromagnetic interaction and its strength can be given as a negative value of  $\Theta$ . The calculated value of  $\Theta$  of diradical **4** records  $-57.5 \text{ K}$  with regression method.

The molar susceptibility increases again at very low temperature nearing 0 K. Such a phenomenon would be explain-



**Figure 4.** The temperature dependence of effective magnetic moment per a molecule of diradical **4**. Circles are the plot of the experimental data. Solid and broken lines show the calculated curves for it according to the Eq. (2) and (3).

ed though the presence of a small amount of paramagnetic impurities that behave as pure paramagnetic electrons.<sup>22-24</sup> The portion of paramagnetic impurities of compound **4** is relatively high. It is assumed that the acidity of squaric acid acts to decrease the diradical concentration into monoradicals.

Two simple theoretical treatments are selected to estimate magnetic behavior of nitroxyl diradical **4**. One is shown in Eq. (2) derived from a linear Ising model<sup>25,26</sup> and the other by Bleaney-Bower Eq. (3).<sup>22-24</sup>

$$\chi_M = (1-p) \frac{Ng^2\mu_B^2}{2kT} \exp(J/kT) + p \frac{Ng^2\mu_B^2}{4kT} \quad (2)$$

$$\chi_M = (1-p) \frac{Ng^2\mu_B^2}{2kT} \left( \frac{2}{3 + \exp(-2J/kT)} \right) + p \frac{Ng^2\mu_B^2}{4kT} \quad (3)$$

where  $p$ ; fraction of paramagnetic impurities  
 $N$ ; Avogadro's number  
 $g$ ; Landé constant  
 $\mu_B$ ; Bohr magneton  
 $J$ ; magnetic exchange energy

If the fraction of paramagnetic impurities is fixed as 0.16, the best fitting values of magnetic exchange energy  $J$  can be derived from the experimental data of magnetic susceptibility in Figure 3. Its reduced values are usually used by dividing it through Boltzmann constant  $k$ . The obtained value of  $J/k$  is  $-52.1$  K by Eq. (2) or  $-47.5$  K by Eq. (3). Through the other theoretical treatments, we obtained a fast equal magnetic exchange energy of  $-50$  K.<sup>27,28</sup> Figure 4 shows the decrease of effective magnetic moment at low temperature where antiferromagnetic exchange  $J$  plays a significant role in comparison with thermal energy  $kT$ . In the case of pure paramagnetism, the effective magnetic moment retains the value 2.83 irrespective of temperature.

The reported  $J/k$  value of HO-TEMPO lies between  $-4.9$  K and  $-6.5$  K. Diradical **4** shows relatively strong antiferro-

magnetic interaction in comparison with other organic radicals.<sup>25,26</sup> This strong antiferromagnetic interaction is assumed to result from the strong polar and aromatic contribution of the squaric acid dianion  $C_4O_4^{2-}$ .

## Experimental Part

Squaric acid was purified by recrystallization in water. HO-TEMPO and  $H_2N$ -TEMPO were obtained by known oxidation method of corresponding piperidine derivatives.<sup>29,30</sup> The derivatization of squaric acid into 3,4-diethoxycyclobutene-1,2-dione (**2**) and 1,3-bis(2-nitroanilino)-cyclobutenediylum-2,4-diolate (**3**) were performed by the known condensation method.<sup>31-33</sup>

**Bis(4-ammonio-2,2,6,6-tetramethylpiperidin-1-yloxy) cyclobutenediylumtetraolate (4).** Squaric acid **1** (1.17 g, 15 mmol) was dissolved in 45 mL of water at  $70^\circ\text{C}$ . To the solution was added dropwise a solution of 5.14 g (30 mmol)  $H_2N$ -TEMPO in acetone for 2 hours. The mixture was further stirred for 3 hours and then cooled. A precipitated product has a form of yellow powder and separated by filtration. It was further recrystallized from DMSO. A crystal-growth was performed from the evaporation of water solution. Yield: 3.12 g (45.6%), mp.: dec.  $>200^\circ\text{C}$ , IR (KBr): 3000 (br), 1450 (br), UV/VIS (water,  $\epsilon$ ): 433 (20.0), 268 (29, 360), Anal. Calcd. for  $C_{22}H_{40}N_4O_6$ : C, 57.87, H, 8.83, N, 12.27; Found: C, 57.36, H, 8.82, N, 11.98.

**4,4'-(1,2-Dioxo-3-cyclobutene-3,4-diylidiamino)-2,2',2'',6,6,6',6'-octamethylbis(piperidin-1-yloxy) (5).**

3,4-Diethoxycyclobutene-1,2-dione **2** (340.3 mg, 2 mmol) and  $H_2N$ -TEMPO (685.6 mg, 4 mmol) were dissolved in 10 mL of absolute ethanol. The flask was equipped with a drying tube and stand for one day at RT. The reaction ran smoothly giving a orange-coloured precipitate. It was separated, dried and recrystallized from DMSO. Yield: 0.76 g (90.4 %), mp.: dec.  $>200^\circ\text{C}$ , IR (KBr): 3170 (br, s), 2980 & 2950 (sh, s), 1800 (sh, m), 1570 (sh, vs), UV/VIS (KBr, %): 191 (29), 203 (100), 272 (99), Anal. Calcd. for  $C_{22}H_{36}N_4O_4$ : C, 62.83, H, 8.63, N, 13.32; Found: C, 61.83, H, 8.68, N, 12.98.

**4,4'-(1,3-Dioxidocyclobutenediylidino-2,4-diylidiamino)-2,2,2',2'',6,6,6',6'-octamethylbis(piperidin-1-yloxy) (6).**  $H_2N$ -TEMPO (5.13 g, 30 mmol) and **3** (1.77 g, 5 mmol) were dissolved in 60 mL of absolute DMSO. The solution was stirred for 90 min at  $80^\circ\text{C}$ . The dark-red solution was changed into the orange-coloured one as transamidization progressed. The product **6** was obtained as a orange-coloured powder. The product was recrystallized from DMSO. Yield: 1.87 g (89 %), mp.: dec.  $>200^\circ\text{C}$ , IR (KBr): 3400 & 3100 (br, m), 2970 & 2920 (sh, s), 1560 (br, vs), UV/VIS (KBr, %): 201 (78), 263 (58), 316 (100), Anal. Calcd. for  $C_{22}H_{36}N_4O_4$ : C, 62.83, H, 8.63, N, 13.32; Found: C, 61.72, H, 8.63, N, 13.07.

**4,4'-(1,2-Dioxocyclobutene-3,4-diylidioxo)-2,2,2',2'',6,6,6',6'-octamethylbis(piperidin-1-yloxy) (7).** HO-TEMPO (6.89 g, 40 mmol) and **2** (2.55 g, 15 mmol) were put into the 50 mL one-neck flask and a catalytic amount of sodium ethoxide was added. The flask was equipped with a condenser. At the top of the condenser, an aspirator and an inlet of nitrogen were connected. The mixture was stirred for 17 hours at  $70^\circ\text{C}$ . The formed ethanol was evaporated shortly with aspirator and the reaction flask was washed

thoroughly with nitrogen every step. Then the mixture was cooled and dissolved with 10 mL of acetone. A small amount of water was dropped into the solution until a homogeneous mixture of water and acetone was prepared. Then a red and viscous oil was separated. The oil was dissolved again in acetone to which a small amount of water was added repeatedly. The main portion of product remained in the yellow solution. To the combined yellow solution, a sufficient water was dropped under mild stirring. A yellow and fine crystal was obtained. It was separated and dried. A crystal-growth was performed by the ambient evaporation of diethyl ether solution. Yield: 1.42 g (22.4%), mp.: 151.0°C, IR (KBr): 2990 & 2950 (sh, m), 1810, 1740 & 1600 (sh, s), 1080 & 1020 (sh, m), UV/VIS (methanol,  $\epsilon$ ): 212 (10,750), 249 (27,650), 449 (23.0), Anal. Calcd. for  $C_{22}H_{34}N_2O_6$ : C, 62.54, H, 8.11, N, 6.63, found: C, 62.39, H, 8.11, N, 6.54.

**Measurements of Magnetic Susceptibility.** The magnetic susceptibility at RT was measured with a Johnson-Matthey balance. Its temperature dependence was measured with a S.H.E. VTS SQUID magnetometer.

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