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Structural and magnetic studies of quinoline and *N*-methyl quinolinium-substituted nitronyl nitroxides

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Abstract

Quinoline and *N*-methyl quinolinium-substituted nitronyl nitroxides **1** and **2** were prepared, and their crystal structures were determined. Thermal variance of their molar magnetic susceptibilities was measured with SQUID, and the results indicated that they both showed antiferromagnetic behavior. Atomic spin density in **1** and **2** was calculated with ab initio method, and magneto-structural correlation was discussed.

Keywords: Quinoline; Antiferromagnetic; Nitronyl nitroxide

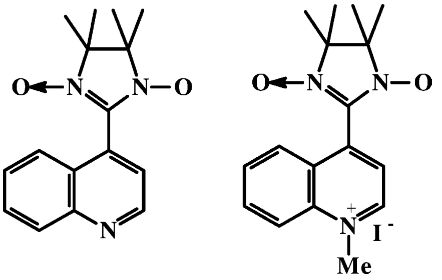
1. Introduction

Theoretical studies indicate that the SOMO–SOMO (spin occupied molecular orbital) overlap leads to spin–spin antiferromagnetic interactions, and SOMO–NHOMO (next highest occupied molecular orbital) or SOMO–NLUMO (next lowest unoccupied molecular orbital) interactions result in spin–spin ferromagnetic coupling [1]. A lot of efforts have been made to adjust the intermolecular arrangements of nitronyl nitroxide derivatives in order to achieve ferromagnetic spin–spin interactions and even bulk organic ferromagnetism. For instance, Awaga et al. [2] proposed that *N*-alkylpyridinium nitronyl nitroxide cation radicals could produce an intermolecular arrangement which satisfied the empirical condition for ferromagnetic coupling of neighboring nitronyl nitroxides. Since then, pyridine and *N*-alkylpyridinium-substituted nitronyl nitroxides were extensively studied in this regard [3]. Besides, pyridine with nitroxides were used as ligands to assemble metallic complexes which displayed interesting magnetic behaviors [4]. On the other hand, *N*-alkylpyridinium nitronyl nitroxide were combined with various anions to afford new organic–inorganic hybrid materials. Molecular-based magnets [5] and antiferromagnetic spin-ladder [6] were obtained by this approach. These studies indicate that pyridine and *N*-alkylpyridinium units play an important role in determining intermolecular arrangements and hence the magnetic properties of the molecular materials containing pyridine and *N*-alkylpyridinium-substituted nitronyl nitroxides. Replacement of pyridine and *N*-alkylpyridinium by their analogues such as quinoline and *N*-methyl quinolinium will lead to new nitronyl nitroxide derivatives, from which new magnetic materials can be generated, and new structural and magnetic data will be provided for studies of magneto-structural correlation in a systematical way. Herein we report structural and magnetic studies of quinoline and *N*-methyl quinolinium-substituted nitronyl nitroxides **1** and **2** (see Scheme 1).

2. Experimental

2.1. Materials

Compound **1** was prepared starting from 4-quinolinecarboxaldehyde and 2,3-bis(hydroxylamino)-2,3-dimethylbu-



Scheme 1. Chemical structures of **1** and **2**.

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Table 1
Crystallographic and refinement data of **1** and **2**

	1	**2**
Chemical formula	$C_{16}H_{18}N_3O_2$	$C_{17}H_{21}IN_3O_2$
Formula weight	284.33	426.27
Crystal system	Triclinic	Monoclinic
Space group	$P1$	$P2(1)/c$
a (Å)	7.2800(10)	14.169(3)
b (Å)	10.440(2)	9.664(2)
c (Å)	10.660(2)	14.693(3)
α (°)	68.53(3)	90
β (°)	77.68(3)	117.45(3)
γ (°)	77.57(3)	90
V (Å^3)	728.2(2)	1785.4(6)
F (0 0 0)	151	1112
$D_{\text{calc.}}$ (g/cm^3)	0.648	2.175
Z	1	5
μ (mm^{-1})	0.044	3.158
Reflns collected	6961	16700
Reflns unique	5076	6627
Reflns observed $[I \geq 2\sigma(I)]$	1419	2850
R_1[a]	0.0579	0.0412
wR_2[b]	0.1038	0.0514

[a] $R_1 = \left(\sum[|F_o| - |F_c|]\right) / \sum |F_o|$.

[b] $wR_2 = \left\{\sum[w(F_o^2 - F_c^2)] / \sum[w(F_o^2)]\right\}^{1/2}$.

tane according to the reported procedure [7], and compound **2** was obtained by the reaction of **1** and methyl iodide in darkness over 48 h. Their chemical structures and purity were established and checked by FT-IR, FAB-MS, and elemental analyses.[2] Their single crystals of good quality for X-ray structural analysis were obtained by slow evaporation of their dichloromethane solutions at room temperature.

2.2. X-ray crystal structural analysis

The intensity data of **1** and **2** were collected on Enraf-Nonius Kappa CCD with a graphite monochromator for the Mo Kα ($\lambda = 0.71073$ Å) radiation at 293 K. Data reduction, structure solution and refinement were performed using SHELXS97 package. Non-hydrogen atom sites were directly solved, and refined with full least-squares method. Hydrogen atoms were theoretically added and included in the final refinement. The crystallographic and refinement data are summarized in Table 1.

2.3. Magnetic susceptibility measurement

The magnetic susceptibility was measured on the bulk material in the temperature range of 5–300 K for each compound with a SQUID magnetometer (MMPS-7, Quantum Design) under 1 T. The data were corrected for magnetization of the sample holder and the diamagnetism of the constituent atoms using Pascal constants.

Table 2
Theoretically calculated atomic spin densities of **1** and **2**[a]

Compound **1**		Compound **2**	
Atom	Spin density	Atom	Spin density
C(1)	0.010963	C(1)	0.004608
C(2)	−0.010330	C(2)	−0.044612
C(3)	0.009051	C(3)	0.047565
C(4)	−0.009243	C(4)	−0.032240
C(5)	0.012800	C(5)	0.013270
C(6)	−0.026907	C(6)	−0.012375
C(7)	0.058107	C(7)	0.004079
C(8)	−0.046618	C(8)	−0.005700
C(9)	0.018967	C(9)	0.007194
C(10)	−0.262614	C(10)	−0.246869
N(1)	−0.030054	N(1)	0.258147
N(2)	0.268258	N(2)	0.251377
N(3)	0.254756	N(3)	−0.040448
O(1)	0.382166	O(1)	0.395065
O(2)	0.366920	O(2)	0.395113
H(1) [–C(8)]	0.001857	H(1A) [–C(1)]	−0.000084
H(2) [–C(9)]	−0.000866	H(2A) [–C(2)]	0.001880
H(3) [–C(4)]	0.000372	H(5A) [–C(5)]	−0.001554
H(4) [–C(3)]	−0.000351	H(6A) [–C(6)]	0.000525
H(5) [–C(2)]	0.000426	H(7A) [–C(7)]	−0.000124
H(6) [–C(1)]	−0.001335	H(8A) [–C(8)]	0.000247

[a] Calculated with ab initio method (B31YP basis set 6-31G), Gaussian 98 program.

3. Atomic spin density

The atomic spin density in compounds **1** and **2** was theoretically calculated with ab initio method[3], and the results are summarized in Table 2. As for other nitronyl nitroxide derivatives, most spin densities are distributed over the unit: O–N–C–N–O (of the imidazoline ring); nitrogen and oxygen atoms have positive spin densities, while the carbon atom possesses negative spin density [8]. The atoms of quinoline ring (and *N*-methyl quinolinium) only own small spin densities, and the spin density sign (positive or negative) of each atom is alternatively varied due to spin polarization. The spin density signs of hydrogen atoms are just opposite to those of carbon atoms (of quinoline and *N*-methyl quinolinium rings) to which they are attached. Interestingly, compounds **1** and **2** show similar spin density distribution. It seems that the difference of dihedral angle (between the imidazole ring and quinoline plane) between **1** and **2** will not affect the spin density distribution greatly.

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[2] Compound **1**. mp: 190–192 °C; FAB-MS (*m/z*): 284 (*M*), 285 (*M* + 1), 286 (*M* + 2). IR (KBr): $\nu = 1368.8\,\text{cm}^{-1}$ (nitronyl nitroxide). Anal. Cacld. for $C_{16}H_{18}N_3O_2$: C, 67.59; H, 6.38; N, 14.78. Found: C, 67.76; H, 6.41; N, 14.42. Compound **2**. mp: 203–205 °C; FAB-MS (*m/z*): 299 (*M*), 300 (*M* + 1). IR (KBr): $\nu = 1373.7\,\text{cm}^{-1}$ (nitronyl nitroxide). Anal. Calcd. for $C_{17}H_{21}IN_3O_2$: C, 47.90; H 4.97; N, 9.86. Found: C, 48.05; H, 5.06; N, 9.62.

[3] The atomic spin density was calculated with ab initio method (B31YP basis set 6-31G), Guassian 98 program.

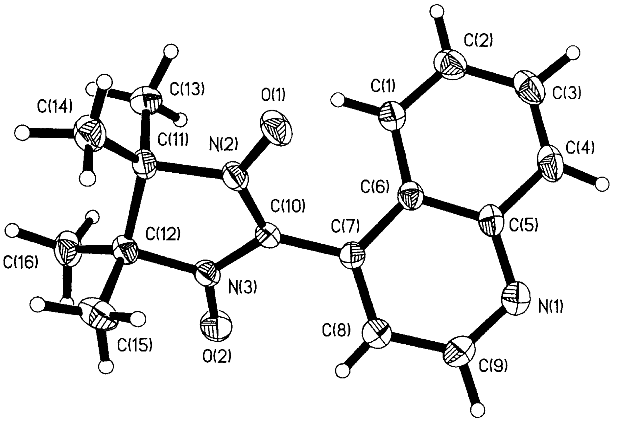


Fig. 1. Molecular structure of **1** with selected bond lengths (Å) and angles (°): O(1)–N(2) 1.281 (2), O(2)–N(3) 1.277 (2), N(2)–C(10) 1.348 (2), N(3)–C(10) 1.363 (2), C(7)–C(10) 1.451 (3), C(5)–N(1) 1.372 (3), N(1)–C(9) 1.314 (3), O(1)–N(2)–C(10) 125.69 (17), O(2)–N(3)–C(10) 125.22 (19), N(2)–C(10)–C(7) 126.40 (18), N(3)–C(10)–C(7) 125.56 (19).

4. Crystal structures

Fig. 1 shows the molecular structure of **1** together with selected bond lengths and angles. As for most of nitronyl nitroxide derivatives, the bond lengths of N(2)–O(1) and N(3)–O(2) are almost the same, due to the fact that the unpaired electron is delocalized over O–N–C–N–O unit. It holds also true for those of C(10)–N(2) and C(10)–N(3). The imidazoline ring forms a dihedral angle of 44° with that of quinoline. The intermolecular arrangements in the crystal lattice of **1** is showed in Fig. 2. Short O(2)–O(2)′ (oxygen atoms of nitronyl nitroxide units) contacts (3.679 Å) were found among the neighboring molecules of **1**, and a dimer was formed through such intermolecular interactions. The dimers are arranged along *b*-axis, and between these dimers there are short O(1)–O(1)′ contacts (4.520 Å). Since both atoms O(1) and O(2) have positive spin densities based on the theoretical calculations (see Table 2), the intermolecular interactions through short interatomic contacts: O(1)–O(1)′ and O(2)–O(2)′ will lead to spin–spin antiferromagnetic coupling.

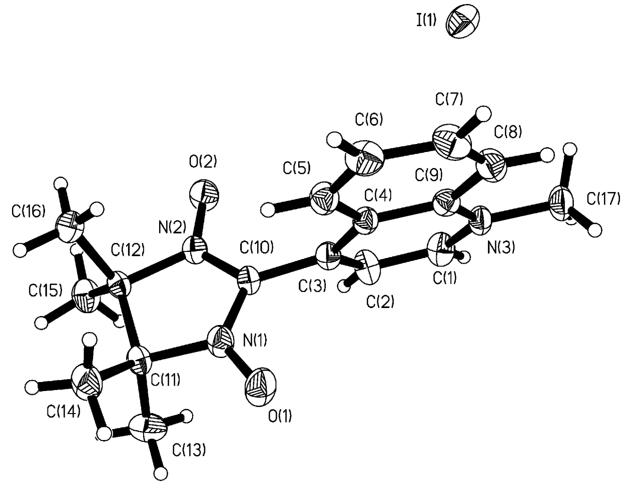


Fig. 3. Molecular structure of **2** with selected bond lengths (Å) and angles (°): N(1)–O(1) 1.283 (2), N(2)–O(2) 1.271 (2), N(1)–C(10) 1.337 (3), N(2)–C(10) 1.333 (3), C(3)–C(10) 1.461 (3), N(3)–C(1) 1.321 (3), N(3)–C(9) 1.388 (3), O(1)–N(1)–C(10) 125.1 (2), O(2)–N(2)–C(10) 124.8 (2), N(2)–C(10)–N(1) 109.9 (2), N(2)–C(10)–C(3) 125.0 (2), N(1)–C(10)–C(3) 125.0 (2).

Fig. 3 shows the asymmetric unit of compound **2** (containing *N*-methyl quinolinium cation and iodide anion) together with selected bond lengths and angles. The dihedral angle between the imidazoline ring and *N*-methyl quinolinium plane is 74°. This may affect electron conjugation between the imidazoline ring and *N*-methyl quinolinium plane in the cation part of **2**. In the crystal lattice, *N*-methyl quinolinium-substituted nitronyl nitroxides are dimerized

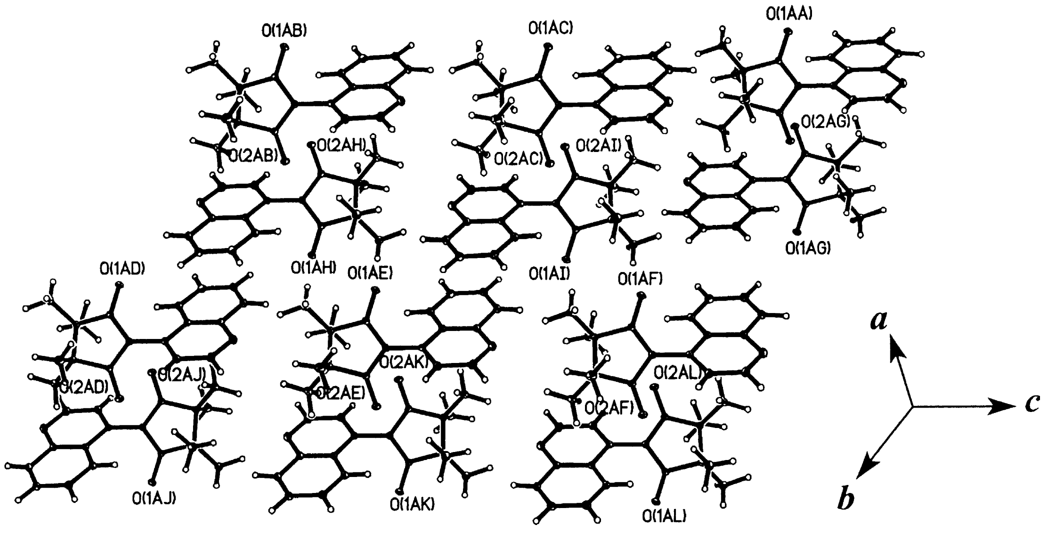


Fig. 2. Intermolecular arrangements in the *bc* plane in the crystal lattice of **1**.

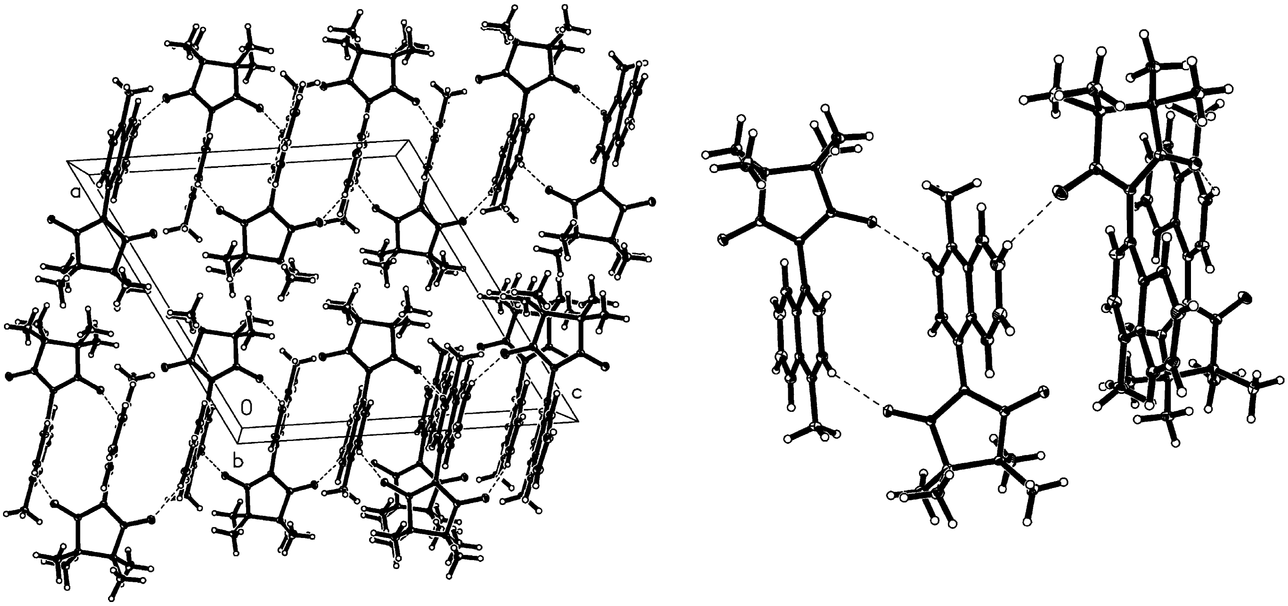


Fig. 4. Molecular packing in the crystal lattice of **2** (left) and the formation of dimers through hydrogen bonds (right).

through the hydrogen bond: O(2)–H(1A)^{i} 2.189 Å (i: $-x$, $-y$, $-z$) (see Fig. 4). The dimers were further linked through the interatomic contacts: O(1)–H(7A)^{ii} 2.531 Å (ii: $-x$, $-0.5+y$, $-0.5-z$); O(1)–O(2)^{iii} 3.137 Å (iii: $2-x$, $1-y$, $-z$); O(1)–N(2)^{iii} 4.059 Å. According to the spin density distribution in **2** (see Table 2), atoms H(1) and H(7) have negative spin densities, while atoms O(1), O(2) and N(2) own positive spin densities. Consequently, it can be predicted that spins of intra-dimers are ferromagnetically coupled while inter-dimer spin–spin interactions are dependent on competition among the interactions through the short interatomic contacts as listed above.

5. Magnetic studies

Fig. 5 shows the temperature dependence of molar magnetic susceptibility for **1**. On the basis of crystal structure of **1**, the spin–spin interactions can be described by Scheme 2, i.e. one-dimensional alternating antiferromagnetic chain. Efforts were made to fit the experimental thermal variance of its molar magnetic susceptibility with the corresponding theoretical equation for one-dimensional alternating antiferromagnetic chain model [9]. But, no reasonable results can be resulted. Instead, the experimental data can be well fitted (see Fig. 5) by modified singlet–triplet model with Eq. (1) [9], where J is spin–spin coupling constant in the dimers, and θ accounts for the inter-dimer interactions (the inter-dimer spin–spin coupling is simply expressed by the "mean-field", $k_b\theta$) and other parameters have the conventional meanings. The best fitting gives $2J/k_b = -11.74\,\mathrm{K}$ and $\theta = -4.04\,\mathrm{K}$.

$$\chi = \frac{4C}{T-\theta}\,\frac{\exp(2J/k_bT)}{1+3\exp(2J/k_bT)} \tag{1}$$

Negative values of J and θ indicate the antiferromagnetic spin–spin interactions for both intra-dimers and inter-dimers, which is in agreement with short interatomic contacts [O(2)–O(2)′ and O(1)–O(1)′] along b-axis as detailed above.

Fig. 6 shows the temperature dependence of molar magnetic susceptibility for **2**. The experimental data were fitted by modified singlet–triplet model with Eq. (1) as done for **1**. The best fitting data are $2J/k_b = +13.47\,\mathrm{K}$ and $\theta = -4.22\,\mathrm{K}$. The positive J means the intra-dimer spin–spin interaction is ferromagnetic, which is consistent with the short

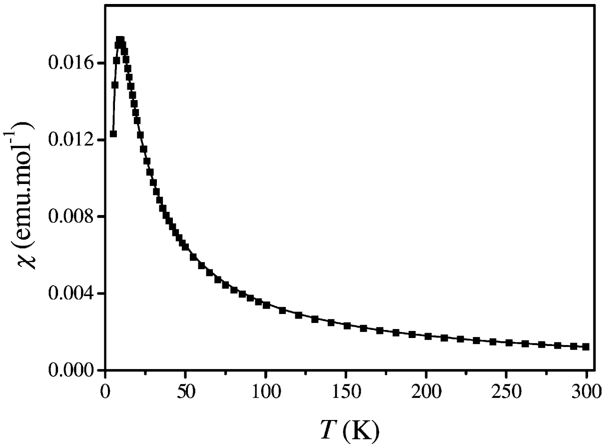
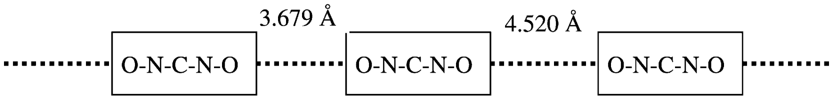


Fig. 5. Temperature dependence of the molar magnetic susceptibility of **1** [the solid line represents the best theoretical fitting (see text)].



Scheme 2. Schematic demonstration of spin–spin interactions of nitronyl nitroxides along the *b*-axis in the crystal of **1**.

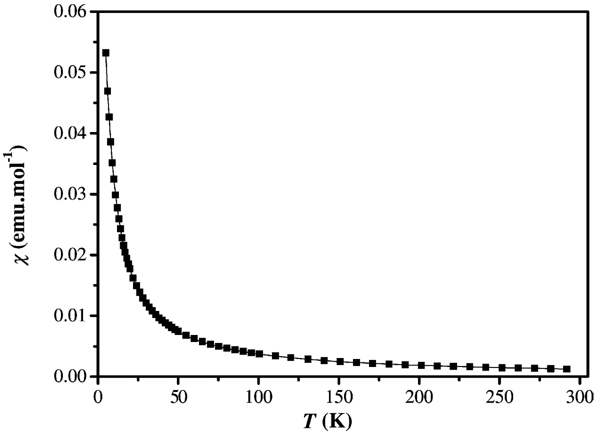


Fig. 6. Temperature dependence of the molar magnetic susceptibility of **2** [the solid line represents the best theoretical fitting (see text)].

interatomic contacts [O(2)–H(1A)′] in the dimers as mentioned above.

6. Summary

Quinoline and *N*-methyl quinolinium-substituted nitronyl nitroxides **1** and **2** were prepared, and their crystal structures were determined. Their magnetic properties were measured with SQUID, and the magneto-structural correlation was studied in combination with atomic spin densities in **1** and **2** calculated with ab initio method. Employment of **1** and **2** as spin components to construct molecular systems with interesting structures and magnetic behaviors is subjected to further studies.

Acknowledgements

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