

Crystal Structure and Magnetic Studies of a New Nitronyl Nitroxide Compound

Liang DING, De Qing ZHANG, Bin ZHANG, Dao Ben ZHU*

Organic Solids laboratory, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080

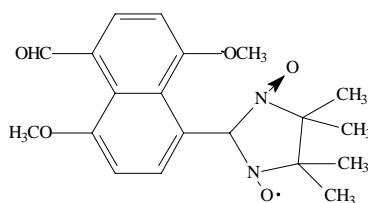
Abstract: Compound **1** was first synthesized and characterized. Its crystal structure and magnetic property were determined and investigated. Discussion about the molecule packing in crystal and the macroscopic magnetism was also presented, in combination with computing study of the spatial distribution over the molecule.

Keywords: Nitronyl nitroxide, crystal structure, spin density, magneto-structural relationship.

Continuing efforts have been taken to explore organic magnets both experimentally and theoretically¹. For organic materials, bulk magnetism depends upon the specific electronic molecular structure and the molecular packing in solid state. Scientists are encouraged by the discovery of the first pure organic ferromagnet in 1991², but under the current circumstances relatively little is known as to the relationship between the molecular structure, the stacking pattern of molecules in solid state and the exhibited magnetic properties³. In our research project, we design and synthesize nitronyl nitroxide compounds with different chemical structures to study the mechanism by which spin-spin interaction takes place, hoping to find promising organic ferromagnets in the future⁴.

In compound **1**, nitronyl nitroxide is incorporated into the naphthalene ring substituted by three functional groups: one formyl and two methoxy groups. Functional groups are considered important and effective in arranging the molecules in solid states, whereas the aromatic rings with alternating spatial distribution can act as coupling units and may lead to intermolecular ferromagnetic interaction according to McConnell's theory⁵. This compound is the first attempt to employ the naphthalene ring as the coupling unit, and we hope that our study may lead to interesting results.

Figure 1. The chemical structure of compound **1**



Compound **1** was obtained after five steps of reaction followed by tedious purification over silica gel. Its chemical structure and purity were determined and checked by spectral and elemental analysis⁶. Dark-red single crystals of compound **1** were grown from dichloromethane and ethyl acetate solution. A crystal of the dimension 0.35×0.35×0.20mm³ was selected for X-ray crystal structural analysis⁷.

Figure 2. The molecular structure of compound **1**

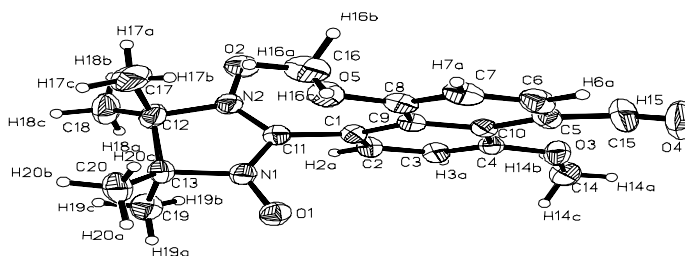


Figure 2 shows the molecular structure of compound **1**. The imidazoline ring is almost planar. The dihedral angle between this plane and the aromatic ring is 81.87(05)°, the greatest ever found in the nitronyl nitroxide family. The large dihedral angle strongly weakens the cross-conjugation for compound **1**. This is consistent with its UV spectrum in dichloromethane solution with a long wavelength peak at 566.5 nm, which is significantly shifted hypsochromically as compared with UV spectra of other aromatic nitronyl nitroxide compounds⁸. Consequently compound **1** forms red solution in dichloromethane in contrast to the blue color of other nitronyl nitroxide compounds in the same solvent. The bond length of O1-N1 is 1.282(2) Å, longer than that of O2-N2 Å, which is 1.275(2) Å. This may be attributed to the influence of the neighboring methoxy group. Other bond lengths and angles are all in normal range.

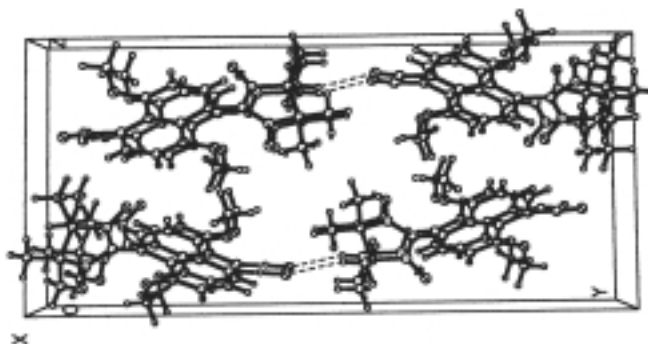
In order to shed light on the spin distribution over the molecule, calculation is performed with density functional method (B3LYP/6-31G) on the optimized structure by semi-empirical PM3 method. The calculated result is listed in **Table 1**. The spin is mainly located on the nitronyl nitroxide moiety. The spin densities on the two nitrogen atoms are positive and prominent, while the carbon atom (sp₂) carries big negative spin density. The little difference of the spin densities of N1 and N2 is owing to the different chemical environment, which is also true of O1 and O2. However, it is still important to note that the aromatic carbons in the ring adjacent to the nitronyl nitroxide carry larger spin densities than the other aromatic carbons due to the spin dislocation effect. The spin densities on the methyl groups in the nitronyl nitroxide moiety are also of importance in studying the through-space magnetic interaction, though this has not received enough attention yet.

Table 1. The calculated atomic spin densities for compound **1**

| atomic spin density | | atomic spin density | |
|---------------------|-------------|---------------------|---------|
| N1,N2 | 0.285,0.280 | C1 | 0.035 |
| O1,O2 | 0.368,0.369 | C2,4 | -0.010 |
| C11 | -0.315 | C5,7 | 0.002 |
| C12,C13 | -0.017 | O5 | -0.002 |
| C17~20 | 0.010 | O3,,4 | <-0.001 |
| | | H | <-0.001 |

The molecule packing is shown in **Figure 3**. The molecules form columns along *a* axis with “head-head” pattern (nitroxide moiety overlapping with nitroxide moiety). This molecular arrangement will enhance SOMO-SOMO overlap, and hence lead to intermolecular spin anti-ferromagnetic property. But such spin-spin interaction will be considerably weak owing to the long intermolecular distance. Weak hydrogen bonds are found between H20b and O4 in the adjacent molecules on the (0,1,1) plane which to some extent plays a role in arranging the molecules in the crystal. The hydrogen bond length is 2.5796Å, and the C20-H···O4 angle is 149.09°. As mentioned above, the hydrogen atoms on C17, C18, C19 and C20 carry negative spin densities greater than the other hydrogen atoms, and O4 also carries negative spin density. Thus, according to McConnell’s principle, the hydrogen bond may bring weak intermolecular spin-spin anti-ferromagnetic interaction, which is fully consistent with the result of magnetic measurement for compound **1** as discussed below.

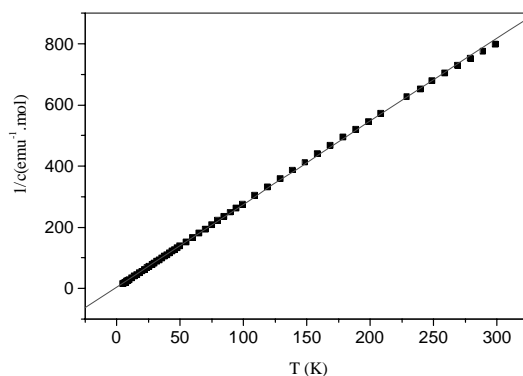
Figure 3. Molecule packing for compound **1**



Magnetic property is investigated with SQUID as shown in **Figure 4** in which the reciprocal magnetic susceptibility (χ^{-1}) versus temperature plot for compound **1** is displayed. Apparently, it follows the Curie-Weiss law with $C=0.369\text{emu}\cdot\text{mol}^{-1}\cdot\text{K}$ and $\theta=-1.215\text{K}$. The small negative value of θ , which reflects the intermolecular spin interaction, indicates the weak anti-ferromagnetic interaction.

Our research work on the nitronyl nitroxide family incorporated into the naphthalene ring is in progress, with emphasis on compounds containing multiple nitronyl nitroxides as well as the corresponding metal-coordinated compounds.

Figure 4. The reciprocal magnetic susceptibility (χ^{-1}) versus temperature plot for compound **1**



Acknowledgement

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References and Notes

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6. Compound **1**: dark-red crystal; mp. 222–223°C; IR 1368.80 and 1141.58 cm⁻¹ (typical adsorption of nitronyl nitroxide compound); FAB-MS 371 (M⁺), 373 (M⁺+2H); Anal. Calc. For C₂₀H₂₃O₅N₂: C 64.68 H 6.24 N 7.54; Found C 64.74 H 6.41 N 7.34; ESR: five peaks, g=2.0005 $\alpha_N=7.497$ G.
7. The crystal data are as follows: monoclinic, P₂(1)/n, a=6.4253(4)Å, b=25.5003(17) Å, c=11.5497(6) Å, $\alpha=90^\circ$, $\beta=95.000(3)^\circ$, $\gamma=90^\circ$, V=1885.2(2) Å³, Z=4, R=0.0620, wR=0.1482. Crystallographic parameters have been deposited in the editorial office of CCL.
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