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Synthesis, solution ESR spectra, and solid-state magnetic property of thieno[3,4-*d*]imidazol-2-yl nitronyl nitroxide

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Abstract

2-(Thieno[3,4-*d*]imidazol-2-yl)-1,3-dihydro-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (**2**) was designed and synthesized. Compound **2** was stable in a solid state but unstable in organic solvents. Solution ESR spectra showed that small spin densities locate on the four methyl groups and the thieno[3,4-*d*]imidazole ring, though most of spin densities localized on the ONCNO moiety. Magnetic susceptibility measurement showed that antiferromagnetic interaction is dominant which could be fitted to the Bonner–Fisher model with $J = -8.8$ cm^{-1}.

Keywords: Molecule-based magnetism; Nitronyl nitroxide; Thieno[3,4-*d*]imidazole; Solution ESR spectra; Magnetic interaction

1. Introduction

No one would deny that dramatic progress has been seen in the field of molecular magnetism in the last decade [1]. After the discovery of purely organic ferromagnet (*p*-NPNN) in 1991 [2], especially, a lot of scientists have discussed magneto-structural correlation of organic radical crystals with the ultimate objective of the development of purely organic magnetic materials.

We have already reported that benzimidazol-2-yl nitronyl nitroxide (**1**) bearing NH proton donor site forms hydrogen-bonded 1-D chain structures accompanying a close contact between magnetic orbitals in its crystal [3] (Fig. 1). Compound **1** shows intermolecular ferromagnetic interaction which can be reproduced by 1-D Heisenberg ferromagnetic chain model with $J = +12$ cm^{-1}. The result suggests that introduction of NH proton donor sites into nitronyl nitroxide is useful for constructing molecular self-assembly exhibiting ferromagnetic interaction.

In the field of organic conductors or superconductors, the introduction of chalcogen atoms such as sulfur, selenium and tellurium have been recognized as an effective way to construct conducting pathways or to control dimensionality through close contact between chalcogen atoms [4]. Also in the field of molecule-based magnetism, *S*-centered stable radicals such as dithiadiazolyl [5], trithiatriazapentalenyl [6], thioaminyl [7] have attracted much attention. These examples prompted us to synthesize a novel nitronyl nitroxide derivative bearing heterocycles containing sulfur atom.

In this paper, we described the synthesis of a new nitronyl nitroxide derivative having a thieno[3,4-*d*]imidazolyl ring, which is isoelectronic to the benzimidazolyl ring, and its solution ESR and solid-state magnetic measurement.

2. Experimental

2.1. Materials and instruments

Diethoxyacetonitrile and 2,3-bis(hydroxyamino)-2,3-dimethylbutane were prepared as described previously [8,9]. Other reagents were commercially available and used without further purification.

ESR spectra of rigorously degassed solutions of **2** were recorded on a JEOL JES-RE3X X-band (9.4 GHz) spectrometer. Magnetic susceptibilities were measured

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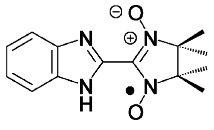

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Fig. 1. Chemical structure of **1**.

using a Quantum Design MPMS-5 SQUID susceptometer at a field strength of 0.5 T in the temperature range of 1.8–300 K. Diamagnetic contributions were corrected using Pacault's constants.

2.2. Computational details

Calculations were made using the GAUSSIAN-98 program package [10], employing Becke's 3 parameter functional (B3LYP) [11]. Molecular structure optimization and single point calculations were carried out at a UB3LYP/cc-pVDZ [12] level. Computed isotropic hyperfine coupling constants (hfccs) were taken directly from computed Fermi constant terms.

2.3. Syntheses of compounds

2.3.1. Thieno[3,4-d]imidazole-2-carbaldehyde diethylacetal (4)

To a solution of sodium ethoxide (0.232 g, 3.39 mmol) in dry ethanol (72 ml) was added freshly prepared diethoxyacetonitrile (4.14 g, 32.1 mmol). The reaction mixture was stirred for 1 h at room temperature (r.t.) to form the corresponding imidate. After glacial acetic acid (0.45 g) was added to the solution to adjust the pH at 5–7, 3,4-diaminothiophene dihydrochloride (**3**) (5.00 g, 26.7 mmol) was added and the solution was stirred in the dark at r.t. for 12 h. The solvent was removed in vacuo and the residue was extracted with ethyl acetate. At that time, the water layer was basified by adding sodium carbonate. The organic layer was separated, dried over anhydrous sodium sulfate and evaporated to dryness. Chromatography on silica gel with ethyl acetate/*n*-hexane (1/1) as the eluent yielded **4** (1.87 g, 31%), which was recrystallised as white fine needles from a benzene/*n*-hexane (1/1) solution. M.p.: 123–124 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H ppm: 7.05 (1H, s, Ar–H), 6.58 (1H, s, Ar–H), 5.58 (1H, s, –CH–), 3.66 (4H, m, $-CH_2-$), 1.25 (6H, t, $-CH_3$). FAB MS: observed $(M+1)^+ = 227$ (Calc. for $C_{10}H_{14}N_2O_2S = 226.30$). Elemental analysis Found: C, 53.36; H, 6.17; N, 12.28; S, 14.14. Calc. for $C_{10}H_{14}N_2O_2S$: C, 53.08; H, 6.24; N, 12.38; S, 14.17%.

2.3.2. Thieno[3,4-d]imidazole-2-carbaldehyde (5)

A solution of **4** (3.00 g, 13.3 mmol) in 1 M sulfuric acid (60 ml) was stirred for 1 h at r.t. and then refluxed at 100 °C for 10 min. After the solution was cooled down to r.t., the pH was adjusted to 10 with aqueous sodium carbonate solution. The precipitate was filtered off, washed with water, dried in vacuo to yield **5** (1.90 g, 94%) as a yellow powder. M.p.: > 300 °C. Elemental analysis Found: C, 47.04; H, 2.95; N, 18.07; S, 20.58. Calc. for $C_6H_4N_2OS$: C, 47.36; H, 2.65; N, 18.41; S, 21.07%.

2.3.3. 2-(Thieno[3,4-d]imidazol-2-yl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (6)

To a solution of **5** (0.30 g, 1.06 mmol) in methanol (50 ml) was added 2,3-bis(hydroxyamino)-2,3-dimethylbutane (0.86 g, 5.78 mmol). The mixture was refluxed at 80 °C for 30 min and then stirred at r.t. for 12 h in the dark under nitrogen atmosphere. After the precipitate was filtered off, the filtrate was concentrated and the residue was washed with dichloromethane and chloroform to yield **5** (0.427 g, 29%). M.p.: approximately 240 °C (dec.). ^{1}H NMR (DMSO-d_6, 300 MHz) δ_H ppm: 7.96 (2H, s, –OH), 7.03 (1H, s, Ar–H), 6.71 (1H, s, Ar–H), 4.66 (1H, d, –CH–), 1.10 (6H, s, $-CH_3$), 1.06 (6H, s, $-CH_3$).

2.3.4. 2-(Thieno[3,4-d]imidazol-2-yl)-1,3-dihydro-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (2)

Compound **6** (0.3 g, 1.06 mmol) was taken up in dichloromethane (200 ml), cooled to 0 °C, and then sodium periodide (1.00 g, 4.67 mmol) in water (200 ml) was added with stirring. The organic layer was washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. Chromatography on silica gel with ethyl acetate as the eluent yielded **2** (5.9 mg, 2%) as a dark green powder. Compound **2** was stable in a solid-state but decomposed easily in organic solvents in several hours. M.p.: approximately 150 °C (dec.). FAB MS: observed $(M+1)^+ = 280$ (Calc. for $C_{12}H_{14}N_5O_2S = 279.34$). Elemental analysis Found: C, 51.89; H, 5.49; N, 19.64; S, 11.37. Calc. for $C_{12}H_{14}N_5O_2S$: C, 51.60; H, 5.41; N, 19.64; S, 11.48%.

3. Results and discussion

3.1. Synthesis

Compound **2** was synthesized from the corresponding aldehyde (**5**), which was prepared from 3,4-diaminothiophene dihydrochloride (**3**) by the procedure used for the preparation of perimidine-2-carbaldehyde from 1,8-diaminonaphthalene and ethyl 2,2-diethoxyacetimidate [13], and 2,3-bis(hydroxyamino)-2,3-dimethylbutane as shown in Fig. 2, following the oxidation procedure described by Ullman et al. [14].

We have used condensation reaction between diamines and ethyl diethoxyacetate under strong basic conditions with sodium ethoxide to form benzimida-

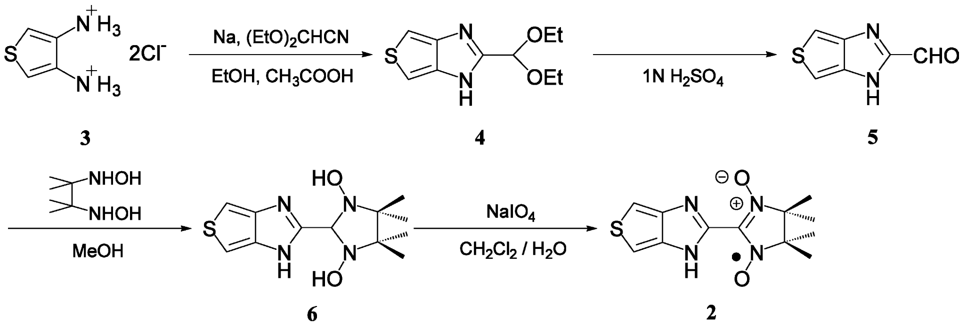

Fig. 2. Synthetic route of **2**.

zole-2-carbaldehyde derivatives [15]. To synthesize thieno[3,4-*d*]imidazole-2-carbaldehyde (**5**), on the other hand, this condition could not be applied because 3,4-diaminothiophene dihydrochloride (**3**) is not stable in strong basic conditions. We found that the same conditions as the condensation between 1,8-diaminonaphthalene and ethyl 2,2-diethoxyacetimidate to form six-membered perimidine derivatives was useful not only to form pyrimidine rings but also to form five-membered imidazole rings. Using this procedure, diamine was added to an ethanol solution of diethoxyacetonitrile containing sodium ethoxide after the pH was adjusted to 5–7 by adding acetic acid. This modification enabled us to synthesize the new nitronyl nitroxide derivative.

3.2. Spin density distribution

The EPR spectra of a 5×10^{-5} M benzene/methanol (39/1) solution and a 5×10^{-5}M benzene/methanol-d_1 (39/1) solution of **2** at r.t. are shown in Figs. 3 and 4. Both the spectra consist of five main lines with relative intensities of 1:2:3:2:1, due to the coupling of the unpaired electron with two equivalent nitrogen nuclei ($I = 1$) of imidazoline ring. The high-resolution spectra of each line reveals a complex pattern, implying the coupling of the unpaired electron to twelve hydrogen nuclei ($I = 1/2$) of the four methyl groups and hydrogen and/or nitrogen nuclei of thienoimidazolyl ring. Careful observation of these spectra found that the complex patterns observed in benzene/methanol and benzene/methanol-d_1 solutions were different from each other. Hfccs obtained by non-linear curve fitting of the spectra are summarized in Table 1. The spectrum of benzene/methanol-d_1 solution can be nicely reproduced using the hfccs for benzene/methanol solution without one hfcc for a proton. When we consider the proton exchange reaction between a hydroxyl proton of methanol and a NH proton of the thienoimidazolyl ring in a methanol solution, the fact suggests that the hfcc for the proton corresponds to that for the NH proton of thienoimidazolyl ring, and the time scale of proton exchange reaction is slower than that of solution ESR time scale of 10^{-8} s.

Hfccs were calculated with density functional theory using GAUSSIAN-98. UB3LYP/cc-pVDZ level calculation for the UB3LYP/cc-pVDZ optimized structure of **2** is compared with the experimental hfccs in Table 1. Experimental and calculated results suggest that small spin densities reside on the methyl groups and thienoimidazolyl ring, though most of the spin density is localized on the ONCNO moiety.

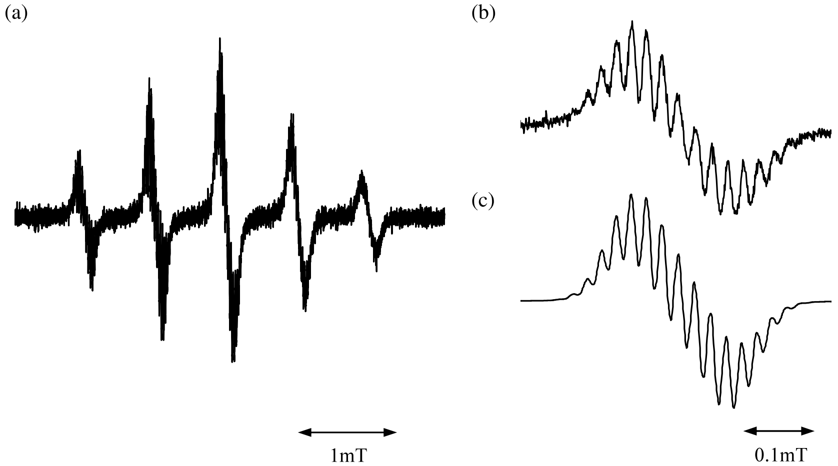

Fig. 3. EPR spectra of **2** in benzene/methanol solution (a); the central line (b) and its simulation (c).

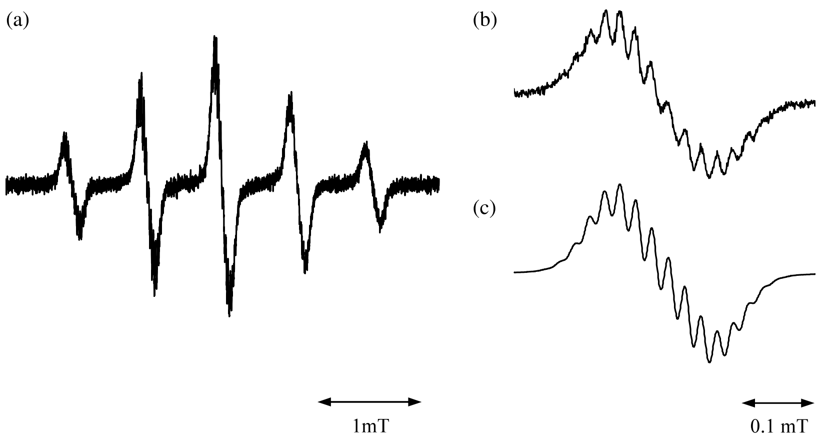

Fig. 4. EPR spectra of **2** in benzene/methanol-d_1 solution (a); the central line (b) and its simulation (c).

Table 1
Experimental and calculated hfcc (mT) for **2**

Position	Expl. hfcc [a]	Expl. hfcc [b]	Calc. hfcc [c]
a_N, Nitroxide N	0.715	0.718	0.797, 0.650
a_N, Thienoimidazole = N–	0.047	0.047	(−)0.126
a_N, Thienoimidazole N(H)	0.012	0.012	(−)0.028
a_H, Methyl H	0.020	0.020	–
a_H, Thienoimidazole (N)H	0.016	–	0.025
a_H, Thienoimidazole 4,6 C–H	[d]	[d]	0.064, (−)0.027

[a] Benzene/methanol soln.
[b] Benzene/methanol-d_1 soln.
[c] UB3LYP/cc-pVDZ/UB3LYP/cc-pVDZ.
[d] The spectrum was not resolved enough to assign.

3.3. Solid-state magnetic measurement

Fig. 5 shows $\chi_m T$ vs. T and χ_m vs. T plots for **2**, where χ_m is molar susceptibility and T is absolute temperature. At 300 K $\chi_m T$ equals to 0.34 emu K mol^{-1}, a little smaller than that expected for isolated monoradical (0.38 emu K mol^{-1}). The value decreases slowly with decreasing temperature, suggesting that antiferromagnetic interaction is dominant between spins. Focusing on the χ_m vs. T plot, χ_m increased gradually with decreasing temperature and had a broad maximum at 7 K, suggesting the magnetic interaction pathway is low-dimensional. The magnetic data can be nicely fit to the Bonner–Fisher model [16] taking account of paramagnetic impurities as described below:

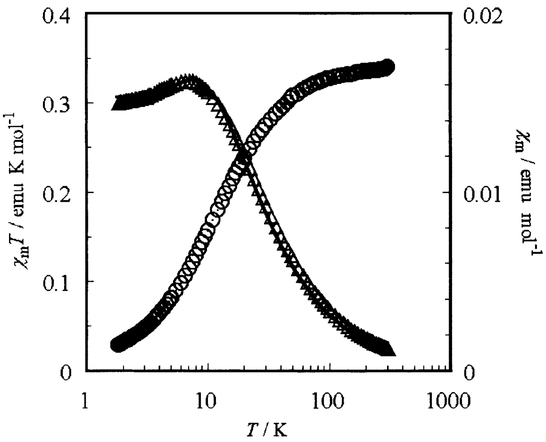

Fig. 5. Temperature dependence of $\chi_m T$ (⊙) and χ_m (△) for **2**. Solid line corresponds to calculated curve (see text).

$$\chi_m = f\left((1-y) \times \left(\frac{N_A g^2 \mu_B^2}{k_B T} \times \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3}\right) + y\left(\frac{C}{T}\right)\right),$$

where f is radical purity, y is the fraction of isolated radicals and $x = |J|/k_B T$. The best-fit parameters are $f = 0.91$, $J = -8.8$ cm^{-1} and $y = 0.02$.

Because **2** is unstable in any organic solvent, we have not succeeded in growing a single crystal suitable for X-ray diffraction yet. Judging from the magnetic susceptibility measurement, **2** probably forms a chain structure in which the one dimensional magnetic interaction is dominant. Further investigations including electrochemical studies are in progress.

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