Crystal Structures and Magnetic Studies of Naphthalene Derivatives Containing Nitronyl Nitroxides

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Crystal structures of new nitronyl nitroxide derivatives **1**, **2** and **3** were determined with X-ray diffraction analysis: **1**, monoclinic, C_2/c, $a = 1.2404(5)$ nm, $b = 0.9730(5)$ nm, $c = 2.7049(10)$ nm, $\beta = 98.189(15)°$, $V = 3.2315(24)$ nm^3, $Z = 8$; **2**, orthorhombic, $Pbca$, $a = 0.61262(2)$ nm, $b = 1.11426(6)$ nm, $c = 2.30543(13)$ nm, $V = 1.57373(13)$ nm^3, $Z = 4$; **3**, monoclinic, $P2(1)/n$, $a = 0.64253(4)$ nm, $b = 2.55003(17)$ nm, $c = 1.15497(6)$ nm, $\beta = 95.000(3)°$, $V = 1.8852(2)$ nm^3, $Z = 4$. Their magnetic properties were measured with SQUID and analyzed based on their crystal structures with simple singlet-triplet, modified one dimensional antiferromagnetic chain and modified singlet-triplet models respectively: **1**, $J/k_b = -2.5$ K; **2**, $J/k_b = 7.8$ K, $\theta = 2.8$ K; **3**, $J/k_b = -0.96$ K, $\theta = 0.21$ K.

Keywords   nitronyl nitroxide, naphthalene, magneto-structural correlation

Introduction

In recent years, great attention has been paid to organic ferromagnetism,[1] mainly stimulated by the discovery of the first genuine organic ferromagnet (*p*-NPNN) in 1991.[2] In fact, by now tens of organic ferromagnets have been synthesized and well characterized,[3-5] but their ferromagnetic transition temperatures are still low. Most of the studies in this field are concentrated on nitronyl nitroxide derivatives. On one hand, various multi-nitronyl nitroxide compounds have been prepared[6] with the hope to increase the intermolecular spin-spin interactions and dimensions of the resulting magnetic materials, and consequently obtaining new organic ferromagnets with higher transition temperatures. On the other hand, model compounds[7] have been designed and synthesized for investigations on magneto-structural correlation with the end to find guiding principle for rational design of organic ferromagnets. Several theoretical models for organic ferromagnetism were proposed.[8] However, as to the exact mechanism controversy still exists.[9] In order to study the magneto-structural relations, compounds with similar chemical structures are mostly suited. With this in mind, three naphthalene derivatives each with one nitronyl nitroxde unit are designed. Here, the crystal structures and magnetic properties as well as the magneto-structural correlation for compounds **1**, **2** and **3** (Fig. 1) are described.

Experimental

Materials

Compounds **1**, **2** and **3** were prepared starting from the corresponding aldehydes according to the reported procedure.[10] Their chemical structures and purity were established and checked by FT-IR, FAB-MS, EPR and elemental analyses.
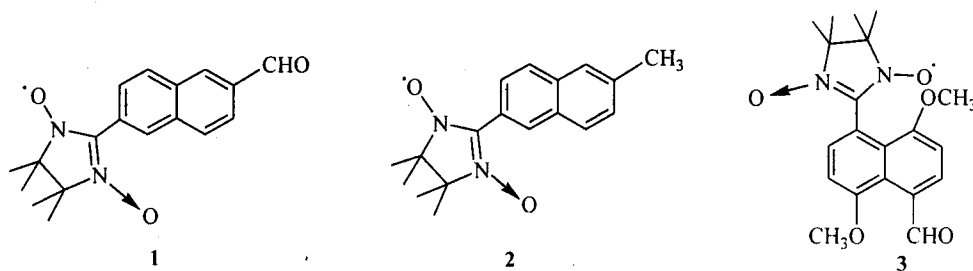

Fig. 1   Chemical structures of compounds **1**, **2** and **3**.

1　　　Blue crystal; m.p. 167—169 ℃; IR (KBr) ν: 1368, 1141 cm^{-1}(typical adsorption bands of nitronyl nitroxide), 1687 (C = O); ESR (CH$_3$CN): five peaks, g = 2.0116, α_N = 7.25 G; FAB-MS m/z: 311 (M$^+$), 312 (M + H), 313 (M + 2H). Anal. calcd for C$_{18}$H$_{19}$N$_2$O$_3$: C 69.44, H 6.15, N 9.00; found C 69.17, H 6.19, N 9.02.

2　　　Blue crystal; m.p. 176—178 ℃ (dec.); IR (KBr) ν: 1367, 1137 cm^{-1}; ESR (CH$_3$CN): five peaks, g = 2.0065, α_N = 7.25 G; FAB-MS m/z: 297 (M$^+$), 298 (M + H), 299 (M + 2H). Anal. calcd for C$_{18}$H$_{21}$N$_2$O$_2$: C 72.70, H 7.12, N 9.42 ; found C 72.58, H 7.10, N 9.31.

3　　　Dark-red crystal; m.p. 222—223 ℃; IR (KBr) ν: 1369, 1142 cm^{-1}; ESR (CH$_2$Cl$_2$): five peaks, g = 2.0005, α_N = 7.50 G; FAB-MS m/z: 371 (M), 372 (M + H), 373 (M + 2H). Anal. calcd for C$_{20}$H$_{23}$N$_2$O$_5$: C 64.68, H 6.24, N 7.54; found C 64.74, H 6.41, N 7.34.

X-*Ray crystal structural analysis*

Their single crystals of good quality were obtained by slow evaporation of their dichloromethane solutions at room temperature. The intensity data of **1** and **2** were collected on a Rigaku AFC6S diffractometer, and those of **3** on an Enraf-Nonius Kappa CCD with a graphite monochromator for the Mo Kα (λ = 0.071073 nm) 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 fulm least-squares method. Hydrogen atoms were theoretically added and included in the final refinement. Due to the poor quality of the single crystal, intensities of the most reflections were weak, which led to large values of R_1 and wR_2 for compound **1**. The crystallographic and refinement data are summarized in Table 1.

Magnetic susceptibility measurement

The magnetic susceptibility was measured on the bulk material in the temperature range of 5—300 K for each compound with an 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.

Results and discussion

Crystal structure

Fig. 2 shows the molecular structure of **1**, and the selected bond lengths and angles are listed in Table 2. The naphthalene and imidazoline planes are not coplanar and they form a dihedral angle of 27.7(5)°. In the crysual, molecules are dimerized as indicated in Fig. 3. Short interatomic contacts are found in the dimers: O(2)—H(1)^i(0.248 nm), O(2)—H(5)^i(0.242 nm), O(2)—C(1)^i(0.332 nm), O(2)—C(5)^i(0.316 nm)[symmetry code^i: 1 – x, – y,

Table 1　Crystallographic and structural refinement data of **1**, **2** and **3**

Compound	1	2	3
Formula	C$_{18}$H$_{19}$N$_2$O$_3$	C$_{18}$H$_{21}$N$_2$O$_2$	C$_{20}$H$_{23}$N$_2$O$_5$
Formula weight	311.35	297.37	371.40
Temperature (K)	293(2)	293(2)	293(2)
$\lambda_{rad.}$ (nm)	0.071073	0.071073	0.071073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	*C2/c*	*Pbca*	*P2(1)/n*
a (nm)	1.2404(5)	0.61262(2)	0.64253(4)
b (nm)	0.9730(5)	1.44426(6)	2355003(17)
c (nm)	2.7049(10)	2.30543(13)	1.15497(6)
α (°)	90	90	90
β (°)	98189(15)	90	95.000(3)
γ (°)	90	90	90
V (nm^3)	3.2315(24)	1.57373(13)	1.8852(2)
Z	8	4	4
$D_{calc.}$ (g/cm^3)	1.280	1.255	1.309
No. of unique data	2117	2164	4383
No. of obsd. data [$I > 2\sigma(I)$]	754	1515	2872
$R_1{}^a$	0.0913	0.0520	0.0620
$wR_2{}^b$ [$I > 2\sigma(I)$]	0.2534	0.1071	0.1482

$^a R_1 = \dfrac{\sum[|F_o| - |F_c|]}{\sum|F_o|}$. $^b wR_2 = \left\{ \dfrac{\sum[w(F_o^2 - F_c^2)]}{\sum[w(F_o^2)]} \right\}^{1/2}$.

**Table 2** Selected bond lengths (nm) and angles (°) of compounds **1**, **2** and **3**

1		2		3	
O(1)—N(1)	0.1279(10)	O(1)—N(1)	0.1275(3)	O(1)—N(1)	0.1282(2)
O(2)—N(2)	0.1267(10)	O(2)—N(2)	0.1281(3)	O(2)—N(2)	0.1275(2)
O(3)—C(1)	0.1207(13)	N(1)—C(12)	0.1358(4)	O(4)—C(15)	0.1190(3)
N(1)—C(12)	0.1327(12)	N(2)—C(12)	0.1347(3)	N(1)—C(11)	0.1343(2)
N(2)—C(12)	0.1320(12)	C(2)—C(11)	0.1501(4)	N(2)—C(11)	0.1331(3)
C(9)—C(12)	0.1457(14)	C(6)—C(12)	0.1454(4)		
N(2)-C(12)-N(1)	108.2(8)	N(2)-C)12)-N(1)	107.8(2)	N(2)-C(11)-N(1)	109.76(17)
N(2)-C(12)-C(9)	128.0 (10)	N(2)-C(12)-C(6)	125.9(2)	N(2)-C(11)-C(1)	125.92(18)
N(1)-C(12)-C(9)	123.8(10)	N(1)-C(12)-C(6)	126.3(2)	N(1)-C(11)-C(1)	123.62(18)
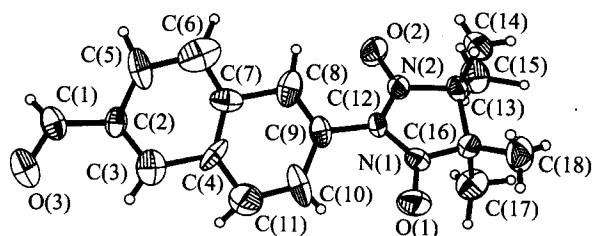
Fig. 2 Molecular structure of **1**.
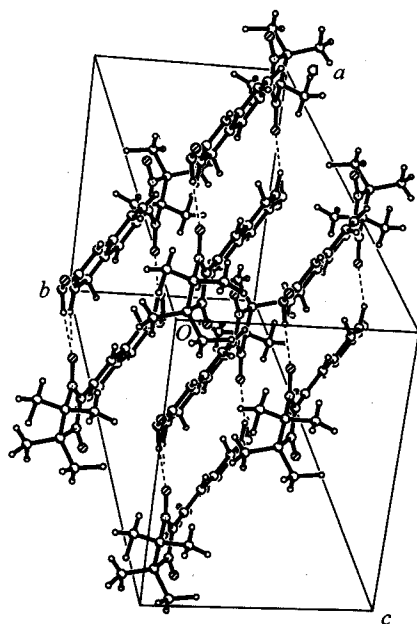
Fig. 3 Molecular packing pattern in the crystal of **1**.

1 − z]. Both experimental and theoretical results[11] point out that oxygen and nitrogen atoms of nitsonyl nitroxide moiety have positive spin densities for nitronyl nitroxide derivatives. According to spin polarization mechanism atoms C(1) and C(5) possess small positive spin densities, while atoms H(1) and H(5) own small negative spin densities. On the basis of McConnell principle[12] the interatomic contacts O(2)—H(1)^i and O(2)—H(5)^i lead to spin-spin ferromagnetic coupling, while those of O(2)—C(1)^i and O(2)—C(5)^i result in anti-ferromagnetic coupling. There are no significant short inter-atomic distances among the dimers. Consequently, the spin-spin interactions among the dimers should be rather weak. Hence, the magnetic behavior of **1** in the solid state should

solely depend on the competition between spin-spin interactions in the dimers.

The molecular structure of **2** is displayed in Fig. 4, and the important bond lengths and angles are included in Table 2. The bond length of N(1)—O(1) is almost equal to that of N(2)—O(2). It also holds true for N(1)—C(12) and N(2)—C(12). The naphthalene and nitronyl nitroxide rings form a dihedral angle of 26.8(1)°. Fig. 5 shows the inter-molecular arrangements in the crystal of **2**. Short interatomic distances (ca. 0.384 nm) are found between the oxygen atoms [O(1)] of nitronyl nitroxide units and carbon atoms [C(3)] of naphthalene rings which are next to the carbon atoms directly linked to methyl groups for the adjacent molecules. Atom C(3) has small positive spin density on the
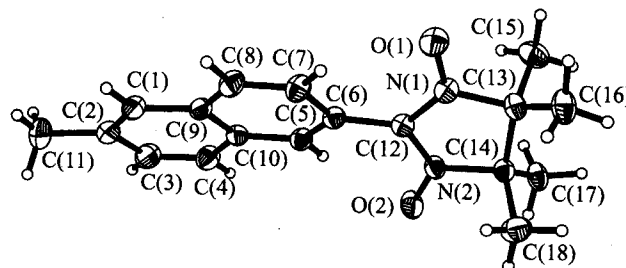
Fig. 4 Molecular structure of **2**.
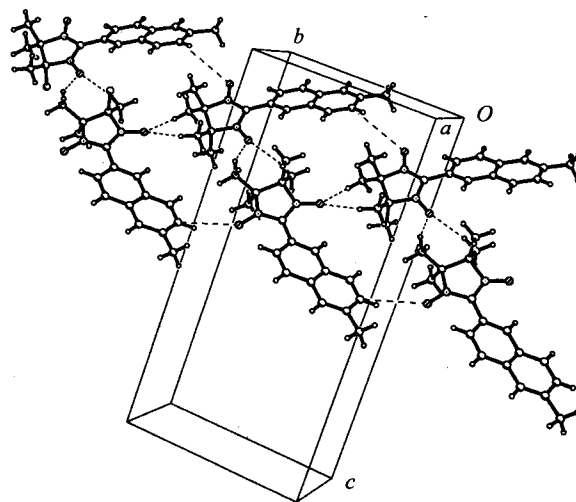
Fig. 5 Intermolecular arrangements in the crystal of **2**.

basis of spin polarization mechanism, and consequently inter-actions through these interatomic contacts will contribute to intermolecular spin-spin antiferromagnetic coupling. Such kind of intermolecular interaction is extended as manifested in Fig. 5, and thus an antiferromagnetic chain is formed. Besides, there are short interatomic contacts between the oxygen atoms and hydrogen atoms of methyl groups in the nitronyl ni-troxide units among the neighboring molecules (0.232 nm). As indicated previously,[13] such interaction will result in spin-spin ferromagnetic coupling among the neighboring antiferro-magnetic chians.

Fig. 6 shows the molecular structure of **3** and the select-ed bond lengths and angles are presented in Table 2. Proba-bly due to the steric hindrance of neighboring methoxyl group, the dihedral angle formed between the nitronyl nitroxide and naphthalene planes is exceptionally large, being $81.9(1)°$, the highest for the known nitronyl nitroxide derivatives. Ac-cordingly, the conjugation between the nitronyl nitroxide and naphthalene units is significantly weakened. This is fully in accordance with the fact that **3** displays red in conventional solvents, in contrast to most of nitronyl nitroxide substituted aromatic compounds which are blue in organic solvents. In the crystal, as showed in Fig. 7 molecules of **3** are dimerized through the interatomic contacts: $O(1)$—$C(2)^{ii}$ (0.338 nm) and $O(1)$—$C(3)^{ii}$ (0.334 nm) [symmetry code[ii]: $-1 + x$, y, z]. On the basis of spin polarization mechanism atom $C(2)$ possesses small negative spin density. On the contrary, atom $C(3)$ has positive spin density. Thus, the interactions due to the short interatomic contacts $O(1)$—$C(2)^{ii}$ and $O(1)$—$C(3)^{ii}$ lead to ferromagnetic and antiferromagnetic spin-spin couplings respectively. Consequently, the net spin-spin coupling behavior in the dimers should depend on the relative importance of these two interactions. Short interatom-ic contacts are found among the dimers: $O(4)$—$H(20A)^{iii}$ (0.285 nm), $O(4)$—$H(20B)^{iv}$ (0.258 nm) [symmetry codes[iii]: $0.5 + x$, $-0.5 - y$, $-0.5 + z$; [iv]$0.5 - x$, $0.5 + y$, $0.5 - z$]. Theoretical calculation result establishes that atom $O(4)$ of the aldehyde group has small negative spin density.[14] Because the hydrogen atoms of methyl group in the nitronyl nitroxide unit have small negative spin density, the spin-spin interaction among the dimers should have ferromag-netic property, which is consistent with the experimental re-sult as discussed below.
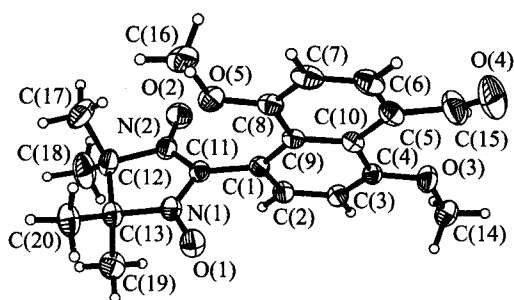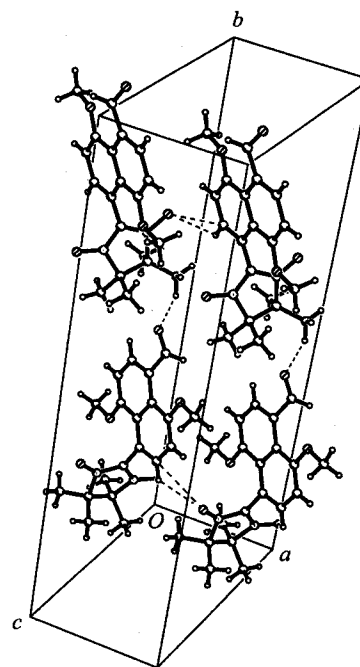

Fig. 7   Molecular packing pattern in the crystal of **3**.

Magnetic study

On the basis of the crystal structure of **1**, the tempera-ture dependence of its magnetic susceptibility showed in Fig. 8 can be interpreted in terms of singlet-triplet model,[15] using the Eq. (1)

$$\chi = \frac{4C}{T} \frac{\exp(2J/k_b T)}{1 + 3\exp(2J/k_b T)} + \frac{C_{def}}{T} \qquad (1)$$

where C_{def} accounts for the crystallattice effect, C, k_b and J are the Curie-Weiss constant, Boltzmann constant and the in-termolecular spin-spin coupling constant, respectively. The best theoretical fit gives $J/k_b = -2.5$ K, $C = 0.375$ emu·K·mol^{-1} (fixed) and $C_{def} = 0.06$ emu·K·mol^{-1}. Negative value of J implies spin-spin antiferromagnetic coupling in the dimers.
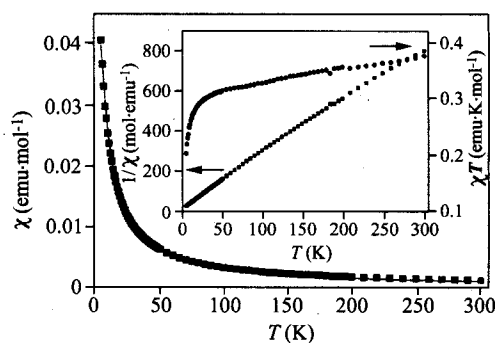

Fig. 6   Molecular structure of **3**.

Fig. 8   Temperature dependence of molar magnetic susceptibility of **1** (the solid line represents the best theoretical fitting). Inset shows the plots of $1/\chi$ ($\blacklozenge$) and χT ($\bullet$) versus T respective-ly.

Fig. 9 displays the plot of magnetic susceptibility versus temperature for compound **2**. Based on the crystal structural result, an antiferromagnetic chain is formed through the intermolecular contacts as showed in Fig. 4. Therefore, the experimental magnetic data was fitted to one dimensional antiferromagnetic chain model with the following equation [Eq. (2)],[16]

$$\chi = \frac{Ng^2\beta^2}{k_b(T-\theta)}\frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3}$$

$$x = |J|/k_bT \tag{2}$$

where J ($H = -J\sum S_1 \cdot S_2$) stands for the spin-spin exchangeconstant, θ accounts for the interchain interaction (the interchain spin-spin coupling is simply expressed by the "mean-field", $k_b\theta$), N is Avogadro constant and β is the Bohr magneton. The best fit (Fig. 9) gives $|J|/k_b = 7.8$ K, and $\theta = 2.8$ K (the g factor was fixed to 2.0).[17] Positive θ value indicates the interchain spin-spin coupling is ferromagnetic.
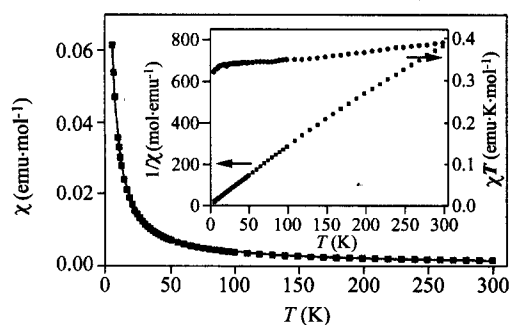

Fig. 9 Temperature dependence of molar magnetic susceptibility of **2** (the solid line represents the best theoretical fitting); Inset shows the plots of $1/\chi$ (◆) and χT (●) versus T respectively.

Fig. 10 shows the temperature dependence of magnetic susceptibility of **3**, which can be well fitted with modified singlet-triplet model,[15] using the following equation [Eq. (3)]

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

where θ measures the property and strength of spin-spin interaction among thedimers, and J has the meaning as mentioned for compound **1**. The best fitting results are $C = 0.375$ emu· K·mol^{-1}(fixed), $J/k_b = -0.96$ K, $\theta = 0.21$ K. Negative J means antiferromagnetic spin-spin interaction in the dimers, and positive θ hints the neighboring dimers interact ferromagneticallly.

Summary

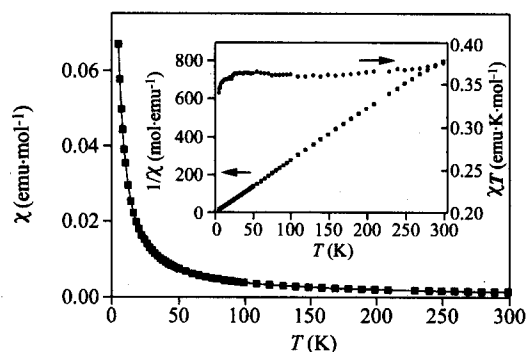Three new nitronyl nitroxide derivatives **1**, **2** and **3** were

Fig. 10 Temperature dependence of molar magnetic susceptibility of **3** (the solid line represents the best theoretical fitting); Inset shows the plots of $1/\chi$ (◆) and χT (●) versus T respectively.

prepared and characterized. Their crystal structures were determined and analyzed in terms of intermolecular spin-spin interactions. Their magnetic properties were measured with SQUID and interpreted with singlet-triplet, modified one dimensional antiferromagnetic chain and modified singlet-triplet models respectively. Further investigations including preparation and studies of multinitronyl nitroxide substituted naphthalene derivatives are in progress.

References and notes

1   See for example, *The Conference Proceedings of ICMM'98*, Sept. France, **1998**.

2   Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *186*, 401.

3   Nakatsuji, S.; Anzai, H. *J. Mater. Chem.* **1997**, *7*, 2161.

4   (a) Chiarelli, R.; Novak, M. A.; Rassat, A.; Tholence, J. L. *Nature* **1993**, *363*, 147.
(b) Banister, A. J.; Bricklebank, N.; Lavender, I.; Rawson, J. M.; Gregory, C. I.; Tanner, B. K.; Clegg, W.; Elsegood, M. R. J.; Palacio, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2533.

5   Allemand, P. M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Grüner, G.; Thompson, J. D. *Science* **1991**, *253*, 301.

6   (a) Dulog, L.; Kim, J. S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 415.
(b) Mitsumori, T.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1995**, *117*, 2467.
(c) Akabane, R.; Tanaka, M.; Matsuo, K.; Koga, N.; Matsuda, K.; Iwamura, H. *J. Org. Chem.* **1997**, *62*, 8854.
(d) Tanaka, M.; Matsuda, K.; Itoh, T.; Iwamura, H. *J. Am. Chem. Soc.* **1998**, *120*, 7168.
(e) Itoh, T.; Matsuda, K.; Iwamura, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1791.
(f) Hayami, S.; Inoue, K. *Chem. Lett.* **1999**, 545.

7   (a) Awaga, K.; Yamaguchi, A.; Okuno, T.; Inabe, T.; Nakamura, T.; Matsumoto, M.; Maruyama, Y. *J. Mater. Chem.* **1994**, *4*, 1377.
(b) Nakatsuji, S.; Saiga, M.; Haga, N.; Naito, A.; Nakagawa, M.; Oda, Y.; Suzuki, K.; Enoki, T.; Anzai, H. *Mol. Cryst. Liq. Cryst.* **1997**, *306*, 279.

8 Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385.

9 (a) Deumal, M.; Cirujeda, J.; Veciana, J.; Novoa, J. J. *Adv. Mater.* **1998**, *10*, 1461.
   (b) Deumal, M.; Cirujeda, J.; Veciana, J.; Novoa, J. J. *Chem. Eur. J.* **1999**, *5*, 1631.

10 Ullman, E. F.; Osiecki, J. H.; Brocock, D. G. B.; Darcy, R. *J. Am. Chem. Soc.* **1972**, *94*, 7049.

11 (a) Neely, J. W.; Hatch, G. F.; Kreilick, R. W. *J. Am. Chem. Soc.* **1974**, *96*, 652.
   (b) D'Anna, J. A.; Wharton, J. H. *J. Chem. Phys.* **1970**, *53*, 4047.
   (c) Zheludev, A.; Barone, V.; Bonnet, M.; Delley, B.; Grand, A.; Ressouche, E.; Rey, P.; Subra, R.; Schweizer, J. *J. Am. Chem.* Soc. **1994**, *116*, 2019.
   (d) Yamaguchi, K.; Okumura, M.; Nakano, M. *Chem. Phys. Lett.* **1992**, *191*, 237.

12 McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

13 (a) Hernàndez, E.; Mas, M.; Molins, E.; Rovira, C.; Ve-
ciana, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 882.
   (b) Cirujeda, J.; Ochando, L. E.; Amigó, J. M.; Rovira, C.; Ruis, J.; Veciana, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 55.

14 The spin density distribution for molecule **3** was theoretically estimated with semi-empirical method (AM1). As expected, the nitrogen and oxygen atoms of nitronyl nitroxide unit have positive spin densities, while the carbon atom between the two nitrogen atoms owns the negative spin density: N(1) 0.442561, N(2) 0.437399, O(1) 0.447333, O(2) 0.443910, C(11) 0.785539. The oxygen atom of the aldehyde group has the small negative spin density: O(4), 0.062088.

15 Otsuka, T.; Okuno, T.; Awaga, K.; Inabe, T. *J. Mater. Chem.* **1998**, *8*, 1157.

16 Otsuka, T.; Okuno, T.; Awaga, K.; Inabe, T. *J. Mater. Chem.* **1998**, *8*, 1157, further references therein.

17 The fitting values of θ and J are in the same order, and thus theoretical fitting with this model is rather approximate.