JOURNAL OF Materials CHEMISTRY

Synthesis, crystal structures and magnetic properties of Schiff bases with α-nitronyl aminoxyl

Deqing Zhang,[a] Wensheng Zhou[b] and Daoben Zhu*[a]

[a]Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China. E-mail: zdq@mimi.cnc.ac.cn
[b]Department of Physics, Peking University, Beijing 1000871, China

Received 29th March 1999, Accepted 7th April 1999

Schiff bases with α-nitronyl aminoxyl **1a**–**1f** were prepared and characterized with EA, MS, ESR and X-ray diffraction analysis. Magnetic investigations indicated that compounds **1b**, **1c** and **1e** showed ferromagnetic properties while compounds **1a**, **1d** and **1f** displayed antiferromagnetic behavior. Discussions in connection with the magneto-structural relation are also presented.

1 Introduction

Interest in the chemistry of stable radicals has been stimulated by the assumption that some radicals might be possible organic ferromagnets.[1] However, the temperature dependence of the static magnetic susceptibility of pure organic free radicals in the solid state generally follows the Curie–Weiss law with zero or negative Weiss constants indicating independent spins or predominant antiferromagnetic interactions in the solid state.[1–3] Positive constants are not common.[4] Thus, how to control and enhance the interaction among spins is becoming the essential point for designing new organic ferromagnets. In our research program, we proposed a new kind of organic compound consisting of the backbone of some liquid crystal molecules (Schiff base) and α-nitronyl aminoxyl†, taking advantage of the stronger interaction among Schiff base molecules to improve the interactions among spins and hoping to get new organic ferromagnets. In fact, purely organic ferromagnets with similar chemical structures were discovered by Nogami *et al.*[5] Besides, concerning the liquid crystal properties, these compounds are also very interesting. To our best knowledge, molecules containing stable organic radicals with liquid crystal properties have not been reported in the literature, and ferromagnetic liquid crystals have only been discussed theoretically.[6] In this paper, the syntheses, crystal structures and magnetic properties of these Schiff bases with α-nitronyl aminoxyl (**1a**–**1f**) will be reported.

2 Experimental

2.1 Synthesis

General. Elemental analyses: Heraeus Chn-Rapid. IR: Perkin-Elmer 2000 (KBr platelets). FAB-MS: KYKY Zhp-5 double-focusing mass spectrometer. ESR: Bruker ESP 300 (in ethyl acetate or dichloromethane, $\sim 10^{-5}$ M).

Compounds 1a–1f. To the solution of compound **2** (see Scheme 1, 10 mmol) and aniline or substituted aniline/β-naphthylamine (10 mmol) in 30–50 ml of anhydrous benzene, anhydrous sodium sulfate (1 g) and a catalytic amount of toluene-*p*-sulfonic acid were added. The resulting mixture was refluxed for 4–6 h. Then, solvents were evaporated under reduced pressure to afford a dark-blue oil, which was washed with petroleum 3–5 times. To the residue 30–50 ml of ethyl acetate were added and the mixture was filtered. The solvents of the filtrate were removed and the resulting oil was crystallized from a mixture of hexane and ethyl acetate yielding needle crystals of **1a**–**1f** (yield: 10–30%).

1a. IR: 1365 cm^{-1} (characteristic of α-nitronyl aminoxyl); EPR: five lines (1:2:3:2:1), $a_N = 7.3$ G; FAB-MS: 366 (M), 367 (M+1), 368 (M+2); Anal. Calc. for $C_{21}H_{24}N_3O_3$: C, 68.85; H, 6.55; N, 11.47; Found: C, 68.82; H, 6.37; N, 11.52%.

1b. IR: 1370 cm^{-1}; EPR: five lines (1:2:3:2:1), $a_N = 7.4$ G; FAB-MS: 350 (M), 351 (M+1), 352 (M+2); Anal. Calc. for $C_{21}H_{24}N_3O_2$: C, 72.00; H, 6.86; N, 12.00; Found: C, 71.82; H, 7.08; N, 11.75%.

1c. IR: 1368 cm^{-1}; EPR: five lines (1:2:3:2:1), $a_N = 7.4$ G; FAB-MS: 336 (M), 337 (M+1), 338 (M+2); Anal. Calc. for $C_{20}H_{22}N_3O_2$: C, 71.43; H, 6.55; N, 12.50; Found: C, 71.30; H, 6.75; N, 12.13%.

1d. IR: 1371 cm^{-1}; EPR: five lines (1:2:3:2:1), $a_N = 7.3$ G; FAB-MS: 370 (M), 371 (M+1), 372 (M+2); Anal. Calc. for $C_{20}H_{21}N_3O_2Cl$: C, 64.77; H, 5.71; N, 11.33; Found: C, 65.19; H, 5.87; N, 11.14%.

1e. IR: 1372 cm^{-1}; EPR: five lines (1:2:3:2:1), $a_N = 7.5$ G; FAB-MS: 414 (M), 415 (M+1), 416 (M+2), 417 (M+3); Anal. Calc. for $C_{20}H_{21}N_3O_2Br$: C, 57.84; H, 5.10; N, 10.12; Found: C, 57.88; H, 5.15; N, 9.94%.

1f. IR: 1367 cm^{-1}; EPR: five lines (1:2:3:2:1), $a_N = 7.4$ G; FAB-MS: 386 (M), 387 (M+1), 388 (M+2); Anal. Calc. for $C_{24}H_{24}N_3O_2$: C, 74.61; H, 6.22; N, 10.88; Found: C, 74.55; H, 6.17; N, 10.73%.

2.2 Magnetic studies

With the extracting sample magnetometer, magnetic properties of polycrystalline samples of compounds **1a**–**1f** and **2** were investigated. The contributions of the sample holder and diamagnetism were subtracted in order to obtain the corrected data. The total content of Fe, Co, Ni of these samples under magnetic measurement was evaluated using an atomic absorption spectrometer to be less than 5 ppm. Thus, the magnetic contribution due to the contamination of transition metals can be neglected.

2.3 Crystal structures

Single crystals of **1b**, **1f** and **2** for X-ray diffraction analysis were obtained by recrystallization from the mixture of hexane

---

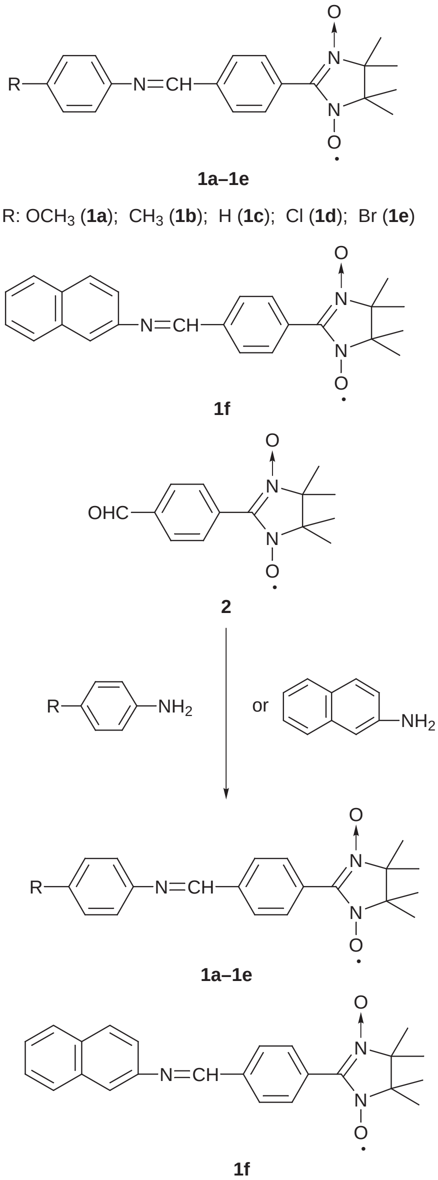
†Aminoxyls were formerly known as nitroxides, but this term is now no longer recommended.

and ethyl acetate in a refrigerator. X-Ray diffraction data were collected at room temperature with Rigaku RASA IIS (for **1b** and **2**) and Rigaku-AFC5R (for **1f**) diffractometers using graphite-monochromatized MoKa radiation (w–2θ scan technique). For all reflections the PL factor correction was made. The absorption correction was made for **1f** and **2**, and was not made for **1b**. The observed reflections [$I>3\sigma(I)$ for **1b** and **1f**; $I>2\sigma(I)$ for **2**] were used for structural analysis. Their crystal structures were solved by direct methods.[7] The structures were refined by a full matrix least-squares method on F^2. Anisotropic thermal parameters were adopted for non-hydrogen atoms, and hydrogen atoms were included by difference Fourier synthesis according to ideal geometry. The calculations were carried out on a PANAFCOM-1500 computer for **1b** and **2**, and a Micro VAXII computer for **1f**.

3 Results and discussion

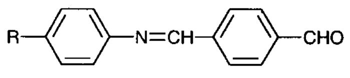
3.1 Synthesis

Schiff bases with α-nitronyl aminoxyl **1a**–**1f** were prepared by condensation of compound **2**, which could be synthesized according to the procedure reported previously,[8] with aniline, the corresponding substituted aniline and β-naphthylamine respectively as shown in Scheme 1. This condensation reaction was catalyzed by toluene-*p*-sulfonic acid. These compounds could not be isolated with conventional column chromatography since they were easily decomposed on a silica column. Fortunately, pure **1a**–**1f** could be obtained by recrystallization from a mixture of ethyl acetate and hexane in a refrigerator. The yields vary with different reactants in the range of 10–30%.

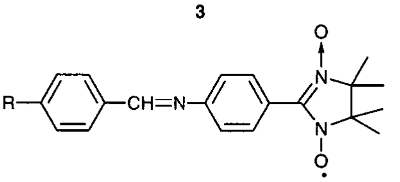


Scheme 1 Syntheses of compounds **1a**–**1f**.

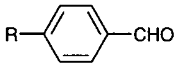
Other routes were also tried for the preparation of these novel compounds and proved to be unsuccessful. These included the reaction between **3** and 2,3-dimethyl-2,3-bis(hydroxyamino)butane, and oxidation by $NaIO_4$. The reaction was conducted under several conditions. Unfortunately, both the FAB mass spectrum and other physical data indicated that the desired compound was not produced in each case. In addition, compounds **4**, isomers of compounds **1a**–**1f**, could not be prepared similarly by the condensation of compounds **5** and **6**.



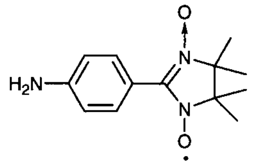
3



4



5



6

3.2 Magnetic studies

The paramagnetic susceptibilities (χ) of these samples were found to follow the Curie–Weiss law in the measuring temperature range except for **1b**, **1c** and **1e** for which slight deviation from the Curie–Weiss law was observed at lower temperature (<5 K), with $\theta = -1.9$, 1.9, 0.9, -1.6, 0.7, -0.8 and -6.9 K for compounds **1a**–**1f** and **2** respectively. Thus, it may be concluded that compounds **1b**, **1c** and **1e** possessed ferromagnetic properties while compounds **1a**, **1d**, **1f** and **2** showed antiferromagnetic behavior in the solid state at low temperature.

The temperature dependence of paramagnetic susceptibilities of **1d**, **2**, **1e** and **1b** is shown in Fig. 1 (A–D), where χT is plotted as a function of temperature. For **1d** (Fig. 1A), the product χT remains almost constant above 10 K, and below 10 K the product χT decreases sharply with decreasing temperature, demonstrating the antiferromagnetic interaction among spins in the solid state at low temperature. For **2** (Fig. 1B) the product of χT decreases gradually with lowering temperature above 10 K, then decreases sharply with decreasing temperature below 10 K, indicating a stronger antiferromagnetic interaction for **2** in the solid state as compared to **1d**.

In contrast to **1d** and **2**, for **1e** (Fig. 1C), however, below 10 K the product χT increases with decreasing temperature reaching the maximum at 5.7 K, which indicates that the ferromagnetic interaction among spins is realized in the solid state. However, below 5.7 K the product χT decreases with decreasing temperature for **1e**. Thus, it is very probable that for **1e** in the solid state, spins interact ferromagnetically forming molecular pairs or chains, and spin interactions between molecular pairs or chains lead to antiferromagnetic behaviour at low temperature. Similar magnetic behavior was found for **1b**, that is, the product χT increases with decreasing

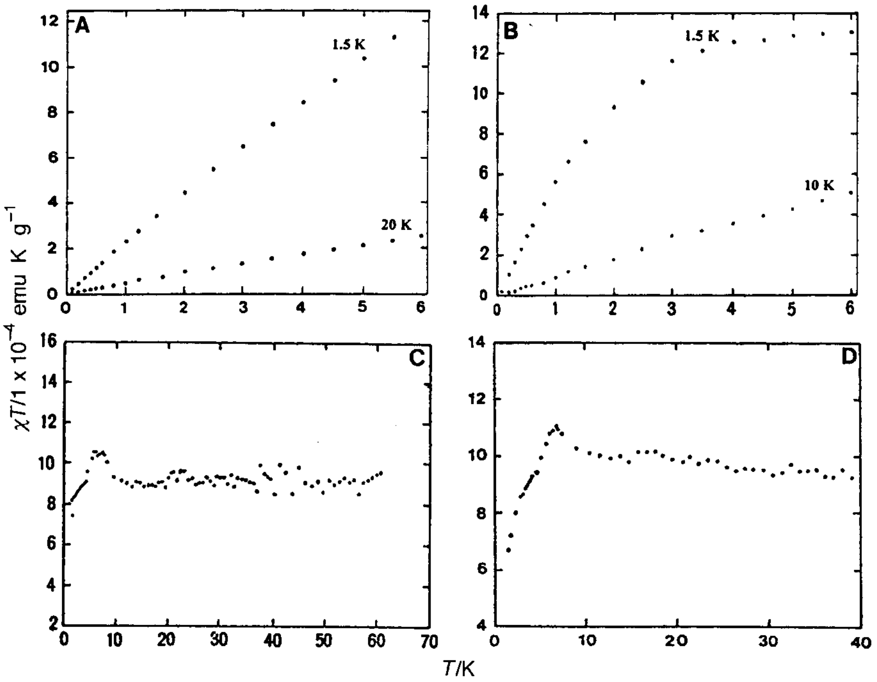


Fig. 1 Product of magnetic susceptibility with temperature *versus* temperature for **1d** (A), **2** (B), **1e** (C) and **1b** (D).

temperature below 10 K, reaching a maximum at 7.1 K and then decreasing with lowering temperature as shown in Fig. 1D.

The results of the field dependent magnetization confirmed the above results. For example, for **1d** the magnetization increases with increasing external field in a nearly linear manner at both 1.5 K and 20 K (Fig. 2A). On the other hand, a magnetic saturation effect was observed for **1e** at 1.5 K, but the magnetization increased with external field at 10 K as shown in Fig. 2B.

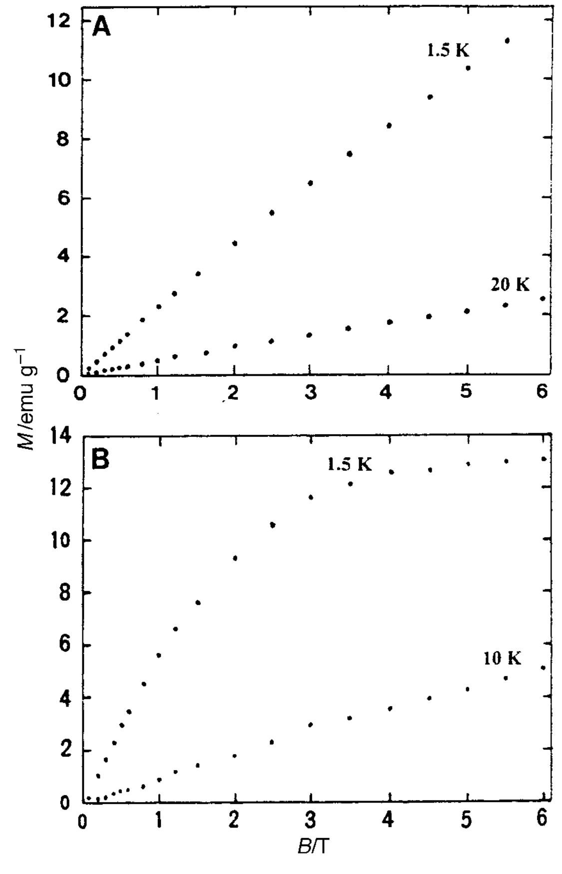


Fig. 2 Field dependent magnetization of **1d** (A) and **1e** (B).

The magnetic properties of **1a** and **1f** are similar to those of **1d**, and those of **1c** are similar to those of **1b** and **1e**. Thus, the magnetic behavior of **1a**, **1f** and **1c** will not be detailed here.

3.3 Crystal structures and magneto-structural relations

The crystal structures of **1b** and **1f** were solved. Some of the structural details of **1f** were reported previously.[9] Here, we only report its molecular packing pattern in the crystal for the magneto-structural discussion. In addition, the crystal structure of the intermediate compound **2** was also determined. Therefore, we will report the crystal structures of **1b** and **2** in detail.‡

The crystallographic data are summarized in Table 1. Selected bond lengths and angles of **1b** and **2** are listed in Table 2-1 and Table 2-2 respectively, and their molecular structures (atomic numbering scheme) are shown in Fig. 3. All the

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

Compounds	**1b**	**2**
Chemical formula	$C_{21}H_{24}N_3O_2$	$C_{14}H_{17}N_2O_3$
Formula weight	350.43	261.30
Crystal system	Monoclinic	Triclinic
a/Å	21.425(6)	7.860(2)
b/Å	9.133(5)	12.660(4)
c/Å	9.942(5)	7.375(2)
α (°)	90	103.40(4)
β (°)	102.03(4)	105.37(3)
γ (°)	90	93.61(3)
V/Å^3	1902.6(2)	682.3(3)
T/K	293	293
Space group	$P2_1/n$	$P\bar{1}$
Z	4	2
μx(MoKα)/cm^{-1}	0.7	0.91
Reflections measured	3742	1575
Independent reflections	3742	1575
Reflections $I \geqslant 2\sigma(I)$	2804 [$I \geqslant 3\sigma(I)$]	1054
R	0.065	0.0598

---

‡CCDC reference number 1145/153.

Table 2-1 Selected bond lengths (Å) and angles (°) of **1b**

N2–O1 1.269(3)	N3–O2 1.265(3)	C14–N2 1.339(2)	C14–N3 1.345(1)
C15–N2 1.510(1)	C18–N3 1.509(3)	C15–C18 1.542(1)	C11–C14 1.479(1)
N1–C4 1.413(2)	N1–C7 1.256(2)	C7–C8 1.483(1)	C1–C21 1.514(1)
N2–C14–N3 108.3(3)	C14–N2–C15 112.2(4)	N2–C15–C18 99.3(3)	C15–C18–N3 99.9(5)
C18–N3–C14 110.1(2)	C3–C4–N1 119.1(3)	C4–N1–C7 (117.7(5)	C7–C8–C9 121.9(4)

Table 2-2 Selected bond lengths (Å) and angles (°) of **2**

N1–O3 1.279(2)	N1–C8 1.343(3)	N1–C9 1.499(3)	N2–O2 1.282(3)
N2–C8 1.337(3)	N2–C10 1.494(4)	C9–C10 1.540(4)	C1–C2 1.475(4)
O1–C1 1.196(4)	C5–C8 1.456(4)	O3–N1–C8 125.9(2)	O3–N1–C9 121.2(2)
C8–N1–C9 112.6(2)	O2–N2–C8 125.7(2)	O2–N2–C10 120.9(2)	C8–N2–C10 113.4(2)
O1–C1–C2 125.6(3)	C1–C2–C7 121.2(3)	C4–C5–C8 120.2(2)	

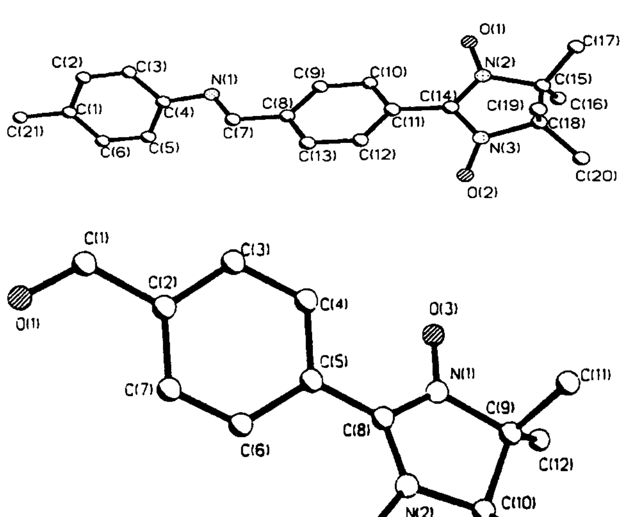


Fig. 3 Molecular structures of **1b** (upper) and **2** (lower) with atomic numbering used in the tables.

bond lengths and angles are in the normal region. As to the 'radical head', the O–N–C–N–O part of the imidazoline ring, the bond lengths of the two N–O bonds and those of the N–C bonds are almost the same, demonstrating that the electrons are delocalized over the O–N–C–N–O part of the imidazoline ring. In contrast to the expectations, for these molecules the three important planes, *i.e.* the imidazoline ring, the benzene ring connecting with the imidazoline ring and the other benzene ring or naphthalene ring, are not coplanar. For example, for **1b** the dihedral angle between the two benzene rings is 54.1° and 9.77° between the imidazoline ring and the benzene plane bonding with the imidazoline ring. As for *p*-nitrophenyl nitronyl aminoxyl (*p*-NPNN), the imidazoline ring and the benzene plane of **2** are twisted with a dihedral angle of 30.5°.

The magnetic properties of these compounds in the solid state can be understood on the basis of their crystal structures. Before discussing the crystal structures and the correlation between magnetic properties and crystal structures, we would like to point out some general principles for organic ferromagnetism. Extensive studies on *p*-NPNN and Galvinoxyl, which show ferromagnetic properties or even bulk ferromagnetic behavior, indicated that for organic molecules containing stable radicals to show ferromagnetic properties they must satisfy the following conditions: (1) Large spin polarization within the molecules; (2) Small SOMO–SOMO overlap, but large SOMO–NHOMO/NLUMO overlap, where SOMO, NHOMO and NLUMO mean spin occupied molecular orbital, next highest occupied molecular orbital, and next lowest unoccupied molecular orbital respectively.[10] For α-nitronyl aminoxyl derivatives, neutron diffraction results indicate that the spin densities of the molecule are mainly confined to the O–N–C–N–O part of the imidazoline ring.[11] Namely, the SOMO of an α-nitronyl aminoxyl molecule is principally determined by the O–N–C–N–O part of the imidazoline ring.

The molecular packing patterns in the crystals of **1b**, **1f** and **2** are shown in Fig. 4 and Fig. 5. For **1b**, molecules stack along the *b*-axis forming a column. In each molecular column, molecules are dimerized with two different modes of molecular overlap, *i.e.* parallel (the intermolecular distance being about 3.40 Å), and perpendicular (fairly short interatomic distances within the molecular pair: C1–C12′, 3.49 Å; C2–O1′, 3.47 Å). Furthermore, the parallel and perpendicular molecular pairs are arranged alternately. In the parallel molecular pair, molecules displace each other to some extent, so that the radical part overlaps with the rest of the molecule. Such a molecular arrangement favors the inter-

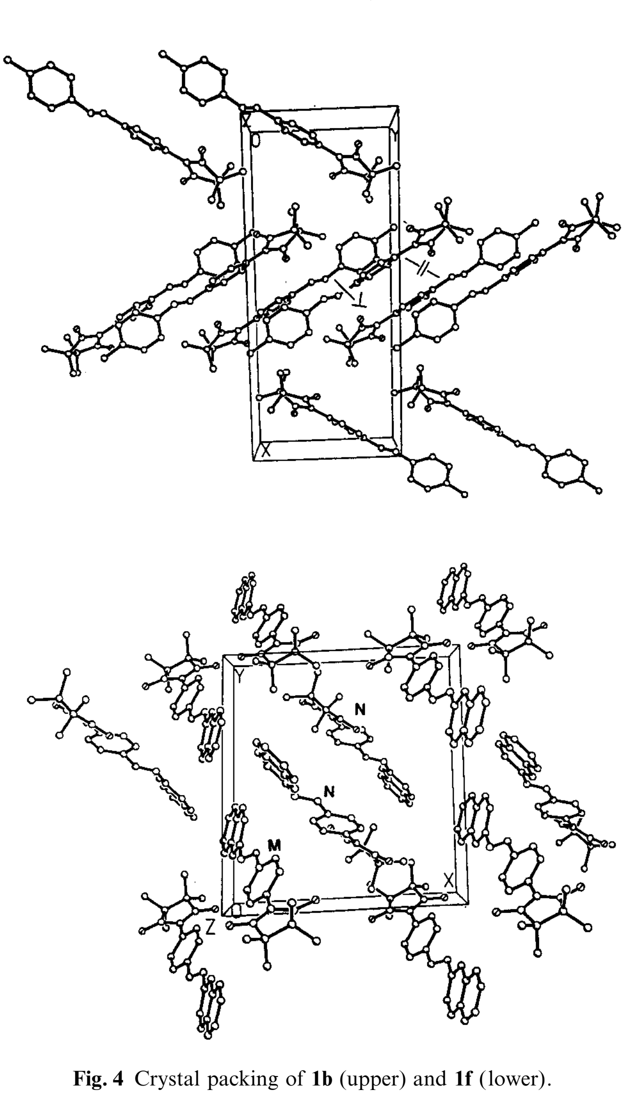


Fig. 4 Crystal packing of **1b** (upper) and **1f** (lower).

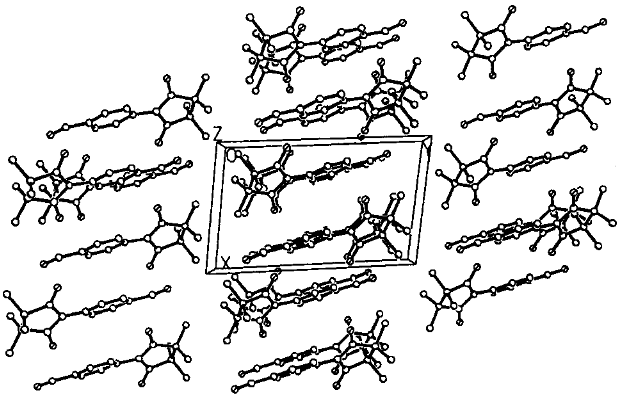


Fig. 5 Crystal packing of **2**.

molecular SOMO–NHOMO/NLUMO overlap resulting in ferromagnetic spin interaction. In contrast, for the perpendicular molecular pair there is no overlap between the radical part and the rest of the molecule, so this molecular overlap mode disfavors the intermolecular SOMO–NHOMO/NLUMO overlap. Along the *c*-axis molecules form a column, and the intermolecular distance is approximately 9.94 Å. Thus, the intermolecular spin interaction along the *c*-axis must be very weak because of the large intermolecular separation. Accordingly, the ferromagnetic properties of **1b** should be due to the ferromagnetic spin interaction within the parallel molecular pair in the molecular column along the *b*-axis.

There are two independent molecules (M and N) in the crystallographic unit cell of **1f**. Along the direction [110] molecules of the same type are dimerized and related by central symmetry. Molecular pairs of M and N are arranged alternately. Fairly short intermolecular contact (3.14–3.33 Å) was found in the neighboring molecules. In each column, the molecular overlap between different types of molecules (M–N) favors SOMO–SOMO overlap while that between the same type of molecules (M–M, N–N) favors SOMO–NHOMO/NLUMO overlap. Besides this, molecules M and N stack separately along the *c*-axis. In analogy to **1b**, the large intermolecular distance ($\sim$10 Å) ruled out possible intermolecular spin interaction within the molecular column along the *c*-axis. Therefore, the antiferromagnetic properties of **1f** at low temperature may be explained by the fact that the molecular overlap of M–N predominates over those of M–M and N–N.

For **2**, molecules stack along the *a*-axis with a 'head-to-tail' arrangement, *i.e.* the radical head of one molecule facing the tail of the neighboring molecule. Short interatomic distances were found between the 'radical head' and 'tail' in the adjacent molecules: N2–C1′, 3.5 Å; O2–C1′, 3.3 Å. Its antiferromagnetic behaviour can be accounted for by McConnel's proposal[12] in combination with intramolecular spin polarization.[13] In accordance with the principle of spin polarization, the carbonyl group of **2** may have a small positive spin density as the nitro group of *p*-NPNN.[11b] Thus, the 'head' and 'tail' of the molecule have the same sign of spin density. According to the McConnel proposal, such 'head-to-tail' molecular arrangement will lead to antiferromagnetic spin interaction.

4 Summary

Schiff bases with α-nitronyl aminoxyl (**1a**–**1f**) were synthesized, and their chemical structures were confirmed by spectroscopic data and elemental analysis. Crystal structure analyses for **1b**, **1f** and **2** were performed. The magnetic properties of these compounds in the solid state were investigated. A possible correlation between crystal structures and magnetic properties for these compounds was also discussed. From these results, it can be concluded that the molecular packing pattern in the crystal plays a very important role in determining the magnetic behavior for these compounds in the solid state. Therefore, further investigations should concentrate on the magneto-structural relation from which we may derive some useful principles that will guide further research in the field.

As to the liquid crystal properties, some of the above compounds were tested and it was found that they did not show any liquid crystal properties. However, preliminary results indicated that the Schiff bases with α-nitronyl aminoxyl having a long alkyl group showed some liquid crystal properties. Further investigations of this aspect are in progress.

Acknowledgement

This work was financially supported by the National Natural Science Foundation of China and the Chinese Academy of Sciences. The authors thank Professor Zhe-Sheng Ma of the Chinese University of Geosciences and Dr Zhang Bin for their kind help with crystal structure analysis.

5 References

1 (*a*) A. Rassat, *Pure Appl. Chem.*, 1990, **62**, 233; (*b*) S. Nakatsuji and H. Anzai, *J. Mater. Chem.*, 1997, **7**, 2161.
2 A. L. Buchachkenko, *Mol. Cryst. Liq. Cryst.*, 1989, **176**, 307.
3 H. Iwamura, *Adv. Phys. Org. Chem.*, 1990, **26**, 179.
4 (*a*) K. Awaga and Y. Maruyama, *Chem. Phys. Lett.*, 1989, **158**, 556; (*b*) D. Zhang, W. Zhou, H. Wang and D. Zhu, *Synth. Met.*, 1993, **55–57**, 1694.
5 (*a*) T. Nogami, K. Tomioka, T. Ishida, H. Yoshikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda and M. Ishikawa, *Chem. Lett.*, 1994, 29; (*b*) T. Ishida, H. Tsuboi, T. Nogami, H. Yoshikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda and M. Ishikawa, *Chem. Lett.*, 1994, 919.
6 M. Buivydas, *Phys. Status Solidi B*, 1991, **168**, 577.
7 With the program SHELXS-86, G. M. Sheldrick, Program for the solution of crystal structures, University of Göttingen, Germany, 1985.
8 E. F. Ullman, J. H. Osiecki, D. G. B. Brocock and R. Darcy, *J. Am. Chem. Soc.*, 1972, **94**, 7049.
9 B. Zhang, D. Zhang and D. Zhu, *Chin. J. Struct. Chem.*, 1994, **13**, 180.
10 (*a*) M. Kinoshita, *Mol. Cryst. Liq. Cryst.*, 1993, **232**, 1; (*b*) M. Kinoshita, *Jpn. J. Appl. Phys.*, 1994, **33**, 5718.
11 (*a*) A. Zheludev, V. Barone, M. Bonnet, B. Delley, A. Grand, E. Ressouche, P. Rey, R. Subra and J. Schweizer, *J. Am. Chem. Soc.*, 1994, **116**, 2019; (*b*) A. Zheludev, E. Ressouche, J. Schweizer, P. Turek, M. X. Wan and H. L. Wang, *J. Magn. Magn. Mater.*, 1995, **140–144**, 1441.
12 H. M. McConnel, *J. Chem. Phys.*, 1963, **39**, 1910.
13 R. S. Drago, *Physical Methods of Chemistry*, Saunders, Philadephia, PA, 1977, p. 329.

Paper 9/02490E