

Triphenylamine Derivatives Containing Nitronyl Nitroxide and Iminyl Nitroxide—Syntheses, Characterization, Crystal Structures, and Magnetic Studies

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New triphenylamine derivatives 1, 2, 3, and 4 were synthesized and characterized by IR, FAB-MS, EPR and EA. All of them displayed similar absorption and fluorescence spectra except compound 1, for which a possible explanation was proposed. Quasi-reversible oxidation waves at about 0.76 V (vs. SCE) and 1.1 V for nitronyl nitroxide and iminyl nitroxide respectively as well as irreversible one at about 1.5 V for triphenylamine group were detected with cyclic voltammetry for compounds 1, 2, 3 and 4. Crystal structures of 2 and 4 were determined by X-ray diffraction analysis. Their crystal data are as follows: for 2: monoclinic, $C2/c$, $a = 1.69914(4)$, $b = 1.37435(5)$, $c = 1.24621(5)$ nm, $\beta = 106.553(2)^\circ$, $V = 2.7896(2)$ nm³, $Z = 4$; for 4: orthorhombic, $Pbca$, $a = 1.95970(6)$, $b = 1.33096(4)$, $c = 4.84691(14)$ nm, $V = 12.6421(7)$ nm³, $Z = 8$. Magnetic studies indicated that all of them showed antiferromagnetic properties in solid state, but with strong intermolecular spin-spin coupling as indicated by the relatively large values of θ , in particular for 4 ($\theta = -12$ K). Possible spin-spin interaction mechanism was suggested based on the crystal structures of 2 and 4.

Keywords Radicals, nitronyl nitroxide/iminyl nitroxide, magnetic properties, crystal structure

Introduction

Organic materials are usually diamagnetic because

electrons of most of them are paired. Since the discovery of the first genuine organic ferromagnet in 1991,¹ organic ferromagnetism has emerged as one of the important interdisciplinary research fields of modern chemistry and physics.² For organic molecular aggregates to be bulk ferromagnets, they should follow these criteria: (1) strong inter- and/or intramolecular exchange coupling among the spins; (2) high dimensional arrangement in space. In recent years molecules with multi-nitronyl nitroxides/nitroxides have received great attention due to the fact that they may result in the enhancement of intermolecular spin-spin interaction and the dimensionality of the magnetic materials.³ Furthermore, nitronyl nitroxide/nitroxides of these molecules can form coordination bonds with suitable metallic ions, which can also strengthen the intermolecular spin-spin coupling and increase the dimensionality of the resulting magnets.⁴ Actually, several new molecular magnets with significantly high ferromagnetic transition temperature (T_c) were obtained by these approaches.⁵

In recent years multi-functional molecular materials have been paid more and more attention to. Molecular materials with both electrical and magnetic as well as electrical and optical properties have been prepared and studied.⁶ Triphenylamine derivatives have been inten-

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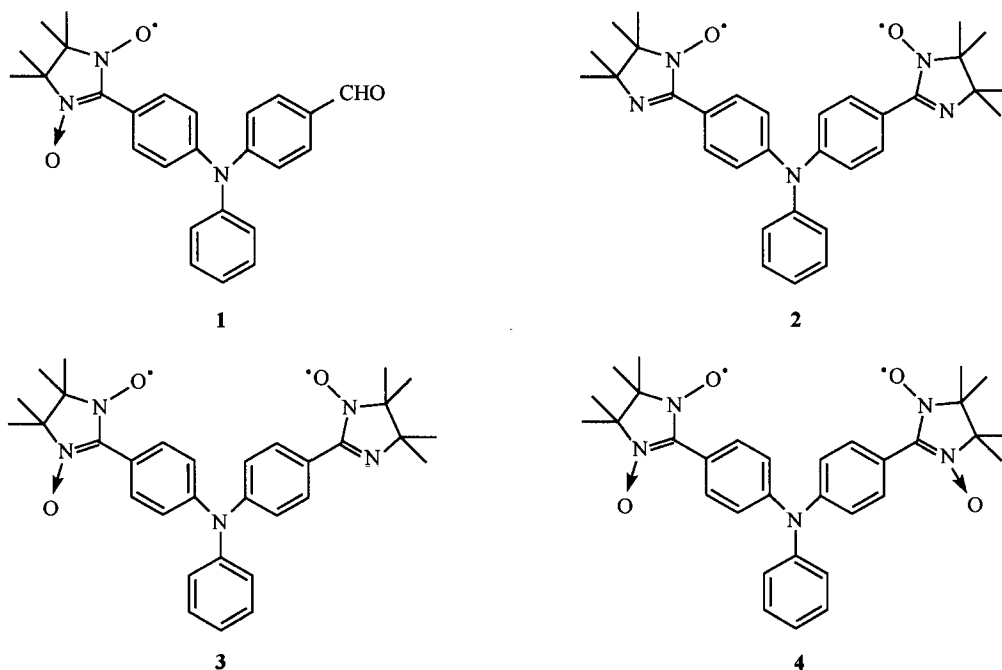
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sively investigated as possible photo-conductors and recently as novel materials for LED (light-emitting-diode) devices.⁷ Thus, triphenylamine derivatives with stable radical substituents would be interesting in this regard. Indeed, a new triphenylamine derivative with three nitroxides has been recently described by Iwamura *et al.*^{3f}

In our research project, new triphenylamine derivatives containing nitronyl nitroxide and iminyl nitroxide were designed. Here, we will report the syntheses, characterization, crystal structures and magnetic properties of novel triphenylamine compounds **1**, **2**, **3** and **4** (Scheme 1).

Scheme 1 Chemical structures of compounds **1**, **2**, **3** and **4**



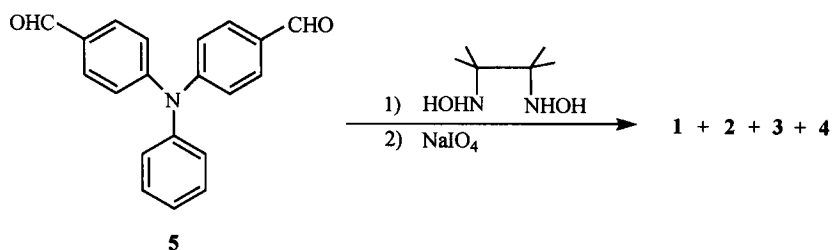
Results and discussion

Synthesis and characterization

The synthesis started from the condensation between **5** and 2,3-bis(hydroxylamino)-2,3-dimethylbutane (Scheme 2), which was prepared first according to the reported procedures.⁸ Compound **1** contains one nitronyl

nitroxide moiety and one unreacted aldehyde group. As reported previously,^{3c,8} besides compound **4** with two nitronyl nitroxide units, compound **2** with two iminyl nitroxides and **3** with one nitronyl nitroxide and one iminyl nitroxide were yielded. Efforts were made to optimize reaction conditions with the aim to increase the yield of one product and to suppress the generation of other products. Unfortunately, the results were discouraging.

Scheme 2 Synthetic approach to compounds **1**, **2**, **3** and **4**



The chemical structures of **1**, **2**, **3** and **4** were established by IR (infrared spectroscopy), FAB-MS (fast-atom-bombardment mass spectroscopy), EPR (electron paramagnetic resonance) and EA (elemental analysis). As to EPR spectra, due to the coupling of two and four identical nitrogen atoms five ($\alpha_N = 7.75$ G) and nine ($\alpha_N = 3.75$ G) signals were observed for compound **1** and **4**, respectively. The patterns of EPR spectra of **2** (> 11 peaks) and **3** (> 8 peaks) are complex owing to the presence of unequal nitrogen atoms.

Like other nitronyl nitroxide/iminylnitroxide substituted compounds, broad absorption bands ($n \rightarrow \pi^*$ transition) in the range of 430–760 nm were detected as manifested in Fig. 1. There are slight differences in the short-wavelength parts of their absorption spectra. Fig. 2 shows the fluorescence spectra of **1**, **2**, **3** and **4**. It can be seen clearly that the fluorescence spectra of compounds **2**, **3** and **4** are similar with fluorescence maxima at ~ 410 nm. As compared with these of **2**, **3**

and **4**, the fluorescence spectrum of **1** is red-shifted ($\lambda_{\max} = 488$ nm). This may be due to the photo-induced electron transfer effect for compound **1**, which contains both electron donating (triphenyl amine) and withdrawing (aldehyde) units.

As an example, the cyclic voltammogram of **3** is showed in Fig. 3, and the numerical data are summarized in Table 1. Compound **3** displays two quasi-reversible oxidation waves, while compounds **1**, **2** and **4** have only one. Based on the previous studies,^{3e,9} it may be concluded that the two nitronyl nitroxides in **4** and two iminylnitroxides in **2** are simultaneously oxidized in a two-electron quasi-reversible process to corresponding dications. For **3**, however, the oxidation may proceed sequentially: first the nitronyl nitroxide and second the iminylnitroxide. The potential value (1.23 V) of **3** is about 0.1 V higher than the corresponding value (1.1 V) of **2**, which is due to the fact that **3** has a positive charge after the oxidation of nitronyl nitroxide, and therefore it is harder for it to be oxidized further because of the Coulombic repulsion. Besides, an irreversible oxidation peak at ~ 1.5 V and an irreversible reduction one at *ca.* -1.3 V were observed for **1**, **2**, **3** and **4** (see Table 1), which were considered to be the oxidation of triphenylamine and the reduction of nitronyl nitroxides/iminylnitroxides respectively.

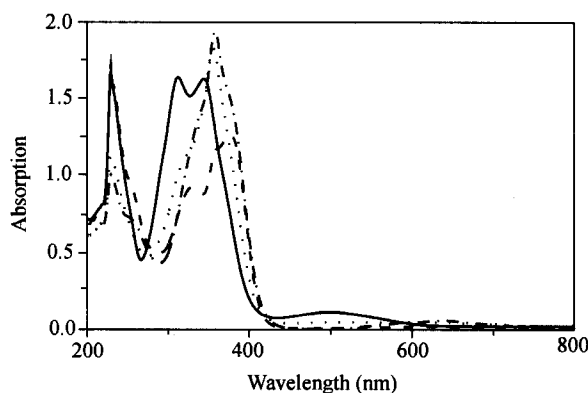


Fig. 1 Absorption spectra of **1**, **2**, **3** and **4**: **1** (dash), **2** (solid), **3** (dot) and **4** (dash dot).

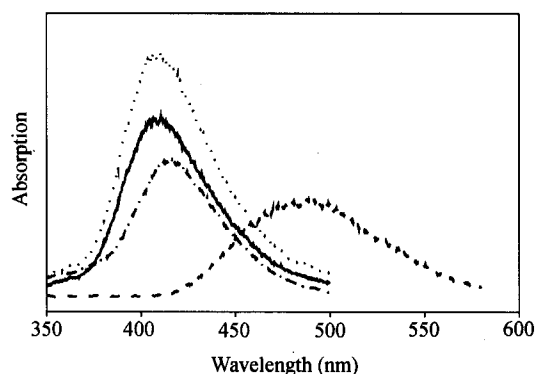


Fig. 2 Fluorescence spectra of **1**, **2**, **3** and **4**: **1** (dash), **2** (solid), **3** (dot) and **4** (dash dot).

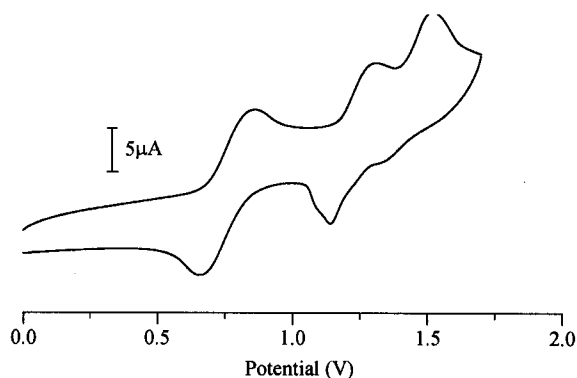


Fig. 3 Cyclic voltammogram of **3**.

Table 1 Oxidation and reduction potentials of **1**, **2**, **3** and **4** (potentials vs. SCE)

	$E_{1/2}^1$ (Oxidation)	$E_{1/2}^2$ (Oxidation)	E^3 (Oxidation)	E^4 (Reduction)
1	0.762	—	1.456	<i>ca.</i> -1.309
2	—	1.101	1.507	<i>ca.</i> -1.240
3	0.757	1.234	1.518	<i>ca.</i> -1.303
4	0.756	—	1.562	<i>ca.</i> -1.315

Crystal structures of **2** and **4**

Fig. 4 shows the molecular structure of **4**. The asymmetric unit contains two crystallographic independent molecules of **4** together with one and half molecules of CH_2Cl_2 in which disorder was found for one carbon atom and one hydrogen atom. Selected bond lengths and angles are listed in Table 2. For most of nitronyl nitroxide derivatives, bond lengths of two N—O bonds as well as those of two C—N bonds of the imidazoline ring are almost the same due to the electron delocalization over the O-N-C-N-O unit. For example, the bond lengths of N(4)—O(3) and N(5)—O(4) are 0.1282(2) and 0.1281(2) nm respectively, and those for C(26)—N(4) and C(26)—N(5) are 0.1357(3) and 0.1353(3) nm respectively. The imidazoline planes and correspond-

ing benzene planes to which they are attached are not coplanar, and the dihedral angles between the benzene plane C(7)–C(8)–C(9)–C(10)–C(11)–C(12), C(20)–C(21)–C(22)–C(23)–C(24)–C(25), C(39)–C(40)–C(41)–C(42)–C(43)–C(44) or C(52)–C(53)–C(54)–C(55)–C(56)–C(57), and corresponding imidazoline plane are 33.6°, 25.3°, 7.7° and 27.2° respectively. The angles around atom N(1) are as follows: 118.7(2)° for C(20)–N(1)–C(4), 122.0(2)° for C(20)–N(1)–C(7) and 119.2(2)° for C(4)–N(1)–C(7). Apparently, atom N(1) is on the plane formed by atoms C(4), C(7) and C(20) in contrast to the pyramidal geometry owned usually by amine compounds. It also holds true for atom N(6). Other bond lengths and angles are in normal range.

Fig. 5 displays the molecular packing pattern of **4**

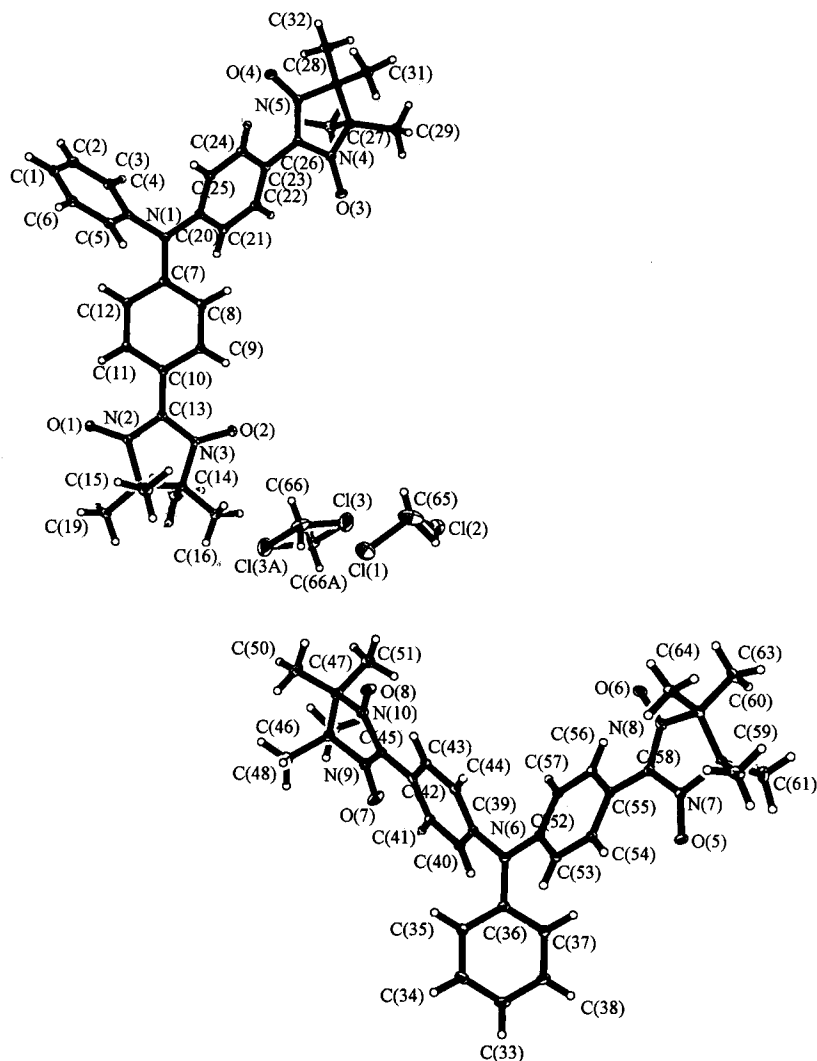
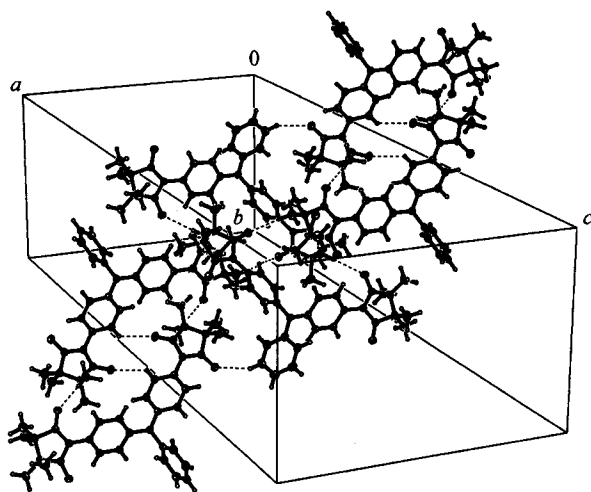


Fig. 4 Crystallographic asymmetric unit of **4**.

Table 2 Selected bond lengths (10^{-1} nm) and angles (deg.) of **2** and **4**

2		4	
Bond lengths			
C(4)—N(1)	1.417(3)	C(5)—N(1)	1.424(2)
C(8)—C(11)	1.475(2)	C(11)—N(13)	1.355(3)
C(11)—N(12)	1.390(3)	O(11)—N(13)	1.262(3)
N(12)—C(12)	1.493(4)	N(13)—C(14)	1.492(3)
C(12)—C(14)	1.557(4)	C(22)—N(23)	1.495(4)
C(22)—C(24)	1.545(5)	C(24)—N(22)	1.505(4)
O(21)—N(23)	1.274(4)	N(2)—O(1)	1.283(2)
		C(13)—N(3)	1.354(3)
		N(4)—O(3)	1.282(2)
		C(26)—N(4)	1.357(3)
		N(7)—O(5)	1.284(2)
		C(58)—N(7)	1.354(3)
		N(9)—O(7)	1.282(3)
		C(45)—N(9)	1.356(3)
		N(3)—O(2)	1.284(2)
		C(13)—N(2)	1.356(3)
		N(5)—O(4)	1.281(2)
		C(26)—N(5)	1.353(3)
		N(8)—O(6)	1.286(2)
		C(58)—N(8)	1.354(3)
		N(10)—O(8)	1.285(2)
		C(45)—N(10)	1.355(3)
Bond angles			
N(13)—C(11)—N(12)	110.3(2)	C(20)—N(1)—C(4)	118.7(2)
N(13)—C(11)—C(8)	128.2(2)	C(20)—N(1)—C(7)	122.0(2)
N(12)—C(11)—C(8)	121.5(2)	C(7)—N(1)—C(4)	119.2(2)
N(22)—C(11)—N(23)	116.0(2)	C(52)—N(6)—C(36)	119.4(2)
N(22)—C(11)—C(8)	124.3(2)	C(39)—N(6)—C(36)	120.0(2)
N(23)—C(11)—C(8)	119.2(2)	C(39)—N(6)—C(52)	120.6(2)
C(4)—N(1)—C(5a)	120.8(8)		
C(4)—N(1)—C(5)	120.8(8)		
C(5)—N(1)—C(5a)	118.5(2)		

**Fig. 5** Molecular packing pattern for **4**.

in the crystal. It belongs to orthorhombic system (*Pbca*) with exceptional large unit cell dimensions (see Table 3). On one hand, short interatomic contacts (0.242–0.256 nm) were found between oxygen atoms of nitronyl nitroxide units and hydrogens (H_{ortho}) attached to aromatic carbon atoms, which are next to these aromatic carbon atoms directly linked with imidazole ring. Both experimental and theoretical results¹⁰ indicate that oxygen

atoms of nitronyl nitroxide unit possess positive spin densities, and due to spin polarization H_{ortho} hydrogens also contain small positive spin densities. According to McConnell principle,¹¹ such an intermolecular interaction will lead to spin-spin antiferromagnetic coupling. On the other hand, short interatomic contacts (0.252 nm) were found between the oxygen atoms and hydrogen atoms of methyl groups among the neighboring nitronyl nitroxides. Hydrogen atoms of methyl groups in the nitronyl nitroxide have small negative spin densities,¹⁰ and thus such interactions will induce spin-spin ferromagnetic coupling. The antiferromagnetic property of compound **4** (see below) in the solid state implies that antiferromagnetic interactions are dominant over the ferromagnetic ones for **4**.

Molecule **2** possesses C_2 symmetry as clearly indicated in Fig. 6. Atomic disorders were found for the iminyl nitroxide parts of the molecule. Such disorders exist even at 120 K. Each of the four nitrogen atoms [N(12), N(13), N(12A) and N(13A) versus N(22), N(23), N(22A) and N(23A)] as well as the two oxygen atoms [O(11) and O(11A) versus O(21) and O(21A)] occupies two positions with equal probability. It also holds true for each of the four carbon atoms [C(12), C(14), C(12A), C(14A) versus C(22), C(24), C(22A) and C(24A)] covalently connected with

corresponding nitrogen atoms. Selected bond lengths and angles are included in Table 2. Like **4**, the N(1) atom lies on the plane of C(4), C(5) and C(5A) since the

sum of the angles [C(4)-N(1)-C(5) 120.8(1)°, C(4)-N(1)-C(5A) 120.8(1)° and C(5)-N(1)-C(5A) 118.5(2)°] is nearly 360°.

Table 3 Crystal data and refinement conditions for **2** and **4**

	2	4
Formula	C ₃₂ H ₃₇ N ₅ O ₂	C _{65.5} H ₇₇ Cl ₃ N ₁₀ O ₈
Formula weight	523.67	1238.7
Crystal system	monoclinic	orthorhombic
Space group	<i>C2/c</i>	<i>Pbca</i>
<i>T</i> (K)	120(2)	120(2)
<i>a</i> (10 ⁻¹ nm)	16.9914(4)	19.5970(6)
<i>b</i> (10 ⁻¹ nm)	13.7435(5)	13.3096(4)
<i>c</i> (10 ⁻¹ nm)	12.4621(5)	48.4691(14)
α (deg.)	90	90
β (deg.)	106.553(2)	90
γ (deg.)	90	90
<i>V</i> (10 ⁻³ nm ³)	2789.56(16)	12642.1(7)
<i>Z</i>	4	8
<i>D</i> (calc.) (g/cm ³)	1.247	1.302
μ (mm ⁻¹)	0.079	0.208
radiation	Mo <i>K</i> _α (0.071073 nm)	Mo <i>K</i> _α (0.071073 nm)
no. collected	19248	137982
no. unique (<i>R</i> _{int})	3324(0.0459)	14862(0.089)
no. observed [<i>I</i> > 2 (<i>I</i>)]	2635	10553
<i>R</i>	0.0564	0.0646
<i>wR</i>	0.1417	0.1389

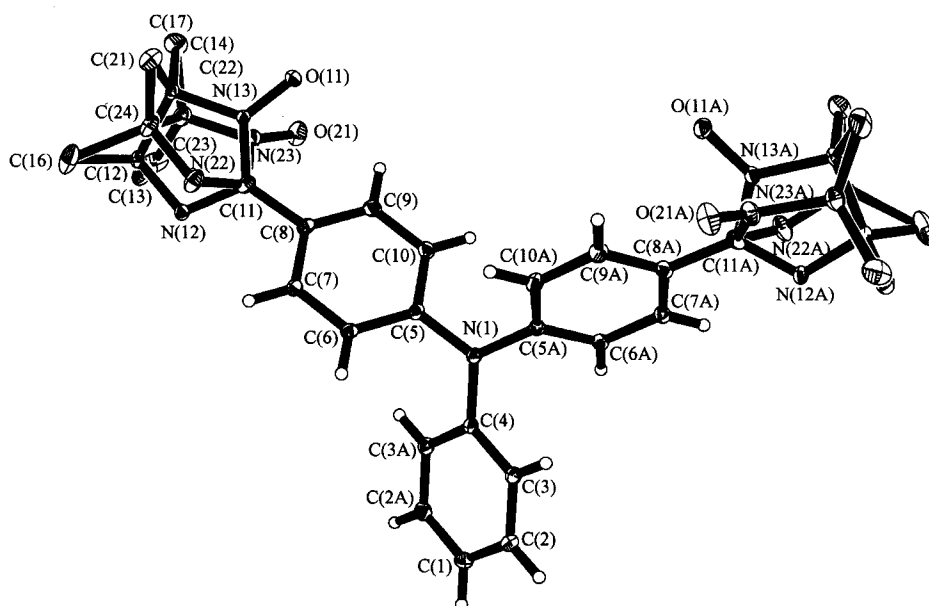


Fig. 6 Molecular structure of **2**.

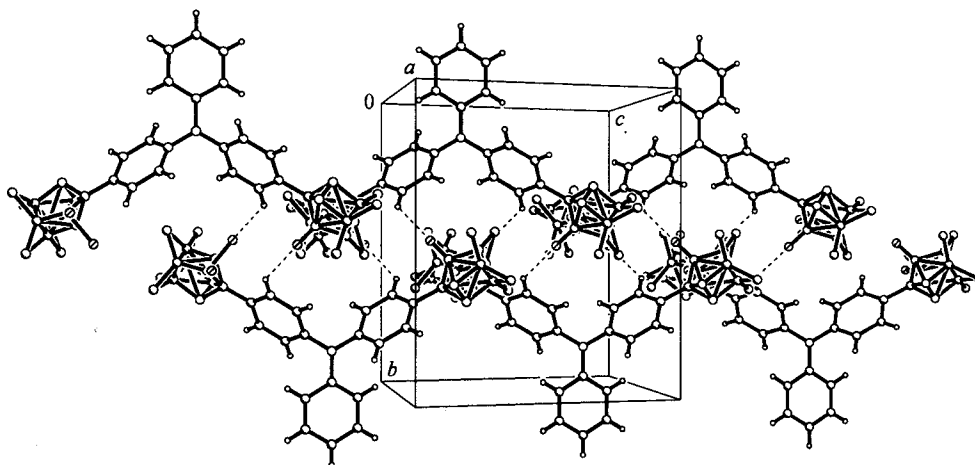


Fig. 7 Molecular packing pattern for **2**.

Intermolecular arrangement of **2** in the crystal is showed in Fig. 7. There are short interatomic contacts among the H_{ortho} atoms and oxygen atoms of iminyl nitroxide moieties. In particular, intermolecular packing pattern is advantageous for the overlap among the iminyl nitroxide units. Thus, it can be predicted that compound **2** in the solid state will display spin-spin antiferromagnetic coupling, which is fully consistent with the result of magnetic studies (see below).

Magnetic properties

Fig. 8 shows the temperature dependence of the product of molar magnetic susceptibility with temperature ($\chi \cdot T$) and reciprocal molar magnetic susceptibility ($1/\chi$) respectively for **1**, **2**, **3** and **4**. At 300 K, the values of $\chi \cdot T$ for **2**, **3** and **4** are 0.746, 0.747 and 0.749 $\text{emu} \cdot \text{mol}^{-1} \cdot \text{K}$ respectively, being almost equal to the theoretical datum (0.750 $\text{emu} \cdot \text{mol}^{-1} \cdot \text{K}$) for two isolated $S = 1/2$ spins or degenerate singlet-triplet systems, while that of **1** is 0.373 $\text{emu} \cdot \text{mol}^{-1} \cdot \text{K}$, as expected for one spin ($S = 1/2$) system. The products ($\chi \cdot T$) decrease gradually from room temperature to ~ 50 K for **2**, **3**, **4** and 13 K for **1**, and hereafter they sharply decrease with further decrease of the temperature. Their paramagnetic susceptibilities follow the Curie-Weiss law as indicated by the good linear relationship between the reciprocal molar magnetic susceptibility and the absolute temperature. The well-fitted values of Curie constants (C) and Curie-Weiss temperatures (θ) are listed in Table 4. These results clearly indicate antiferromagnetic interac-

tion among the spins for these compounds in the solid state. However, the relatively large values of θ , especially for **4** ($\theta = -12$ K), imply that the intermolecular spin-spin coupling for these compounds is strong.

Besides the intermolecular spin-spin antiferromagnetic coupling based on the crystal structures of **2** and **4** as detailed above, intramolecular spin-spin interaction should be also contributed to their magnetic behaviors in the solid state. Such intramolecular spin-spin coupling may be deduced from low-temperature EPR studies, and investigations in this respect are in progress.

Table 4 Curie constants and Curie-Weiss temperatures of **1**, **2**, **3** and **4**

	1	2	3	4
C ($\text{emu} \cdot \text{mol}^{-1} \cdot \text{K}$)	0.365	0.740	0.745	0.748
θ (K)	-6.2	-7.7	-4.9	-12
Fitting factor (R)	0.9985	0.9990	0.9996	0.9989

Conclusion

Four triphenylamine derivatives with one or two nitronyl nitroxides/iminyl nitroxides were synthesized and characterized. Crystal structures of **2** and **4** were determined and analyzed. Magnetic studies indicated that all of them showed antiferromagnetic properties in solid state, but with strong intermolecular spin-spin coupling as indicated by the relatively large values of θ , in particular for **4**. Possible spin-spin interaction mechanism was

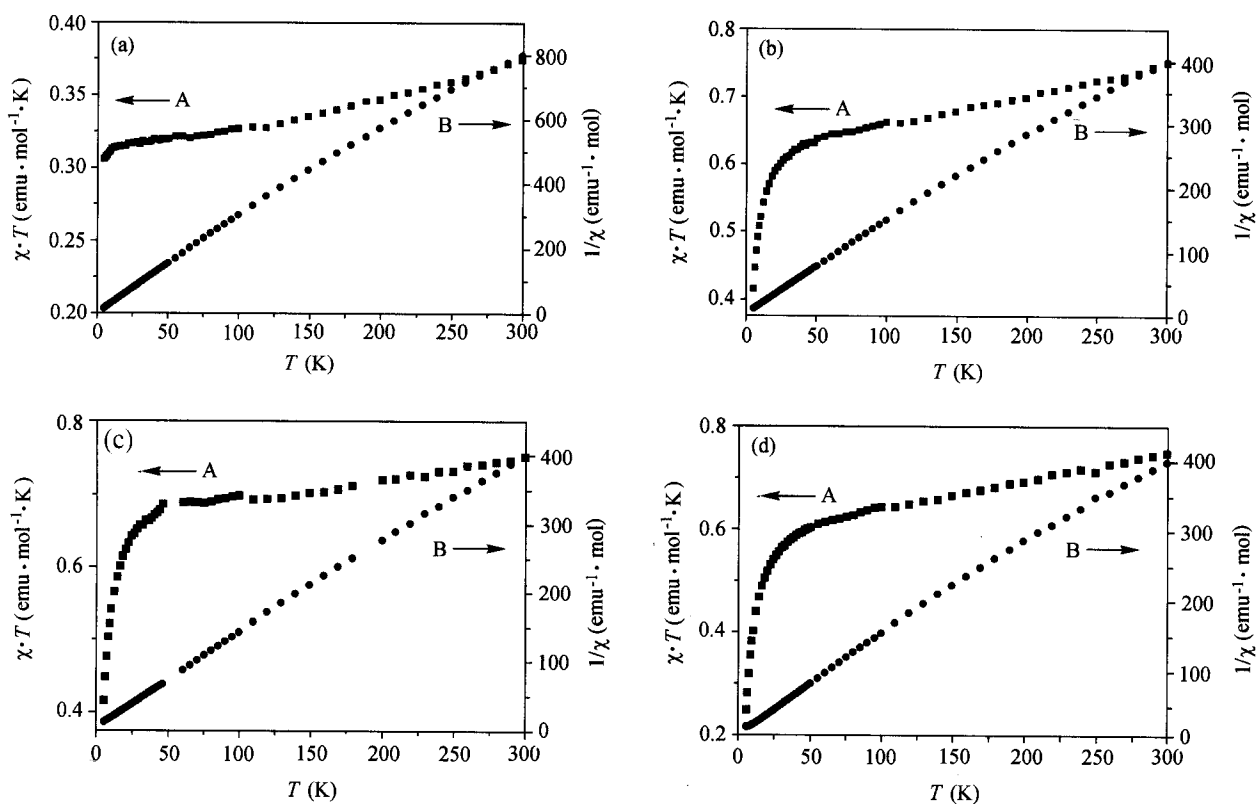


Fig. 8 Temperature dependence of paramagnetic susceptibilities: A— $\chi \cdot T$ vs. T ; B— $1/\chi$ vs. T with theoretical fitting for 1 (a), 2 (b), 3 (c) and 4 (d).

suggested based on the crystal structures of **2** and **4**. Further investigations will include the preparation of interesting metallic coordination compounds of **1**, **2**, **3** and **4** as well as corresponding physical studies.

Experimental

General

Melting points were measured with XT₄-100_X, and not corrected. The IR spectra were recorded on Pekin-Elmer 2000 in the form of KBr platelets. The FAB-MS spectra were obtained with KYKY Zhp-5 double-focusing mass spectrometer. The EPR spectra were recorded on a Varian E-109 spectrometer; the samples were dissolved in CH₂Cl₂ with the concentration of $\sim 10^{-5}$ mol/L. Absorption and fluorescence spectra were measured with Hitachi U-3010 and F-4500, respectively; the samples were dissolved in CH₂Cl₂, $\sim 10^{-5}$ mol/L. Elemental analysis was performed with Heraeus Chn-Rapid. The cyclic voltammetric measurements were made with CHI

705A (Electrochemical Analyzer) using Platinum as working electrode, SCE as reference electrode, TBAPF₆ as electrolyte.

Syntheses of compounds 1, 2, 3, and 4

The mixture of **5** (1.0 g, 3.32 mmol) and 2,3-bis(hydroxylamino)-2,3-dimethylbutane (1.0 g, 6.75 mmol) suspended in 160 mL of anhydrous benzene was stirred at 80°C for 6 h under N₂ atmosphere. After that, there were pale-yellow precipitates out of the reaction mixture. Total of 40 mL of absolute anhydrous methanol was added successively to the reaction flask at an interval of 3 h. Water generated from the condensation reaction was removed azeotropically. Then, the reaction mixture was cooled down to room temperature. The residue after removing most of the solvents in vacuum was suspended in 300 mL of chloroform which was cooled by ice-water bath. To the above suspension 4 g of NaIO₄ in 40 mL of water was added and stirred for 30 min. The organic phase was separated and aqueous so-

lution was further extracted with chloroform (3×40 mL). The organic phase was combined and dried over anhydrous MgSO_4 . The solvents were evaporated under reduced pressure and the resulting raw products were subjected to column chromatography on silica gel with the mixture of dichloromethane and ethyl acetate (2:1) as eluants, yielding **1**, 170 mg (12%); **2**, 260 mg (15%); **3**, 196 mg, (11%); and **4**, 221 mg (18%).

1 m.p. 119°C; IR ν : 1362.8 cm^{-1} ; λ_{max} (CH_2Cl_2): 230 ($\log\epsilon$ 4.6), 329 (4.4), 376 (4.5), 638 (2.8) nm; Fluorescence, λ_{max} (CH_2Cl_2): 488 nm; FAB-MS m/z (%): 428 (M), 429 (M + 1), 430 (M + 2); EPR: five peaks ($\alpha_{\text{N}} = 7.75$ G), $g = 2.0060$; Anal. calcd for $\text{C}_{26}\text{H}_{26}\text{N}_3\text{O}_3$: C 72.88, H 6.12, N 9.81; found C 72.98, H 6.36, N 9.47.

2 m.p. 263–264°C; IR ν : 1367.4 cm^{-1} ; λ_{max} (CH_2Cl_2): 230 ($\log\epsilon$ 4.7), 312 (4.7), 345 (4.7) 513 (3.5) nm. Fluorescence, λ_{max} (CH_2Cl_2): 409 nm; FAB-MS, m/z (%): 523 (M), 524 (M + 1), 525 (M + 2); EPR: multi-peaks, $g = 2.0055$; Anal. calcd for $\text{C}_{32}\text{H}_{37}\text{N}_5\text{O}_2$: C 73.39, H 7.12, N 13.37; found C 72.95, H 7.25, N 12.98.

3 m.p. 202°C (dec.); IR ν : 1363.8 cm^{-1} ; λ_{max} (CH_2Cl_2): 230 ($\log\epsilon$ 4.4), 318 (4.4, sh.), 356 (4.6), 501 (2.1), 639 (3.1) nm; Fluorescence, λ_{max} (CH_2Cl_2): 409 nm; FAB-MS m/z (%): 539 (M), 540 (M + 1), 541 (M + 2); EPR: multi-peaks, $g = 2.0056$; Anal. calcd $\text{C}_{32}\text{H}_{37}\text{N}_5\text{O}_3$: C 71.22, H 6.91, N 12.98; found C 70.83, H 6.92, N 12.87.

4 m.p. 243°C (dec.); IR ν : 1361.8 cm^{-1} ; λ_{max} (CH_2Cl_2): 230 ($\log\epsilon$ 4.0), 358 (4.3), 639 (2.8); Fluorescence, λ_{max} (CH_2Cl_2): 414 nm; FAB-MS m/z (%): 555 (M), 556 (M + 1), 557 (M + 2); EPR: nine-peaks ($\alpha_{\text{N}} = 3.75$ G), $g = 2.0061$; Anal. calcd for $\text{C}_{32}\text{H}_{37}\text{N}_5\text{O}_4 \cdot 3/4\text{CH}_2\text{Cl}_2$: C 63.52, H 6.22, N 10.94; found C 63.65, H 6.24, N 11.37.

X-ray crystallographic analysis

Crystals of the sizes $0.38 \times 0.38 \times 0.35$ mm³ of **2** and $0.29 \times 0.24 \times 0.24$ mm³ of **4** were obtained by slow evaporation of saturated solutions of **2** and **4** in the mixture of dichloromethane and hexane at room temperature. The X-ray diffraction data were collected on an Enraf-Nonius Kappa CCD diffractometer using graphite-monochromatized $\text{Mo } K_{\alpha}$ radiation ($\lambda = 0.071073$ nm)

at 120(2) K. Absorption correction was not applied. Data reduction was performed with the program HKL Denzo.¹² Unit cell dimensions were determined and refined using 21446 reflections with $3.41^\circ < \theta < 30.01^\circ$ for **2** and 137982 reflections with $3.48^\circ < \theta < 27.86^\circ$ for **4** with the program HKL Scalepack. The crystal structure was solved by direct method (SHELXS-97),¹² and refined by full-matrix-least squares method on F^2 . Anisotropic thermal parameters were employed for non-hydrogen atoms. The positions of hydrogen atoms were added with Fourier-difference maps and refined isotropically except those of dichloromethane trapped in the crystal lattice, which was refined with isotropic thermal parameters at geometrically restrained positions. The crystallographic data of **2** and **4** are given in Table 3.

Magnetic measurements

Magnetic measurements were performed with SQUID (MMPS-7, Quantum Design) in the temperature range of 5–300 K. The contributions of sample holders and diamagnetism estimated from Pascal's constants were subtracted in order to obtain corrected data.

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