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Crystal Structures and Magnetic Properties of Nitronyl Nitroxide and Imino Nitroxide Radicals Attached to Thieno[3,2-*b*]- and Thieno[2,3-*b*]thiophene Rings

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Nitronyl nitroxide (ONC=NO) and imino nitroxide (NCNO) free radicals joined to isomeric thieno[3,2-*b*]thiophene and thieno[2,3-*b*]thiophene, respectively, were prepared and their crystal structures and magnetic properties were investigated. In all crystals of four free radical species, the ON−C−NO moieties are in the same plane as the thienothiophene ring. The coplanarity is associated with the extremely short intramolecular contact between the oxygen atom in the NO group and the sulfur atom in the thienothiophene ring. The free radicals attached to thieno[3,2-*b*]thiophene are arranged in a chain structure with short intermolecular NO−S contacts, while the free radicals linked to thieno[2,3-*b*]thiophenes make dimers with a face-to-face pairing by the use of the NO−S contacts. Among four radical species, thieno[3,2-*b*]thiophene-substituted nitronyl nitroxide exhibits a weak ferromagnetic interaction ($J = +0.11$ K/k_B, $H = -2JS_iS_j$) below 40 K as revealed by a SQUID susceptometer, while others are antiferromagnetic.

A number of organic free radicals are currently under investigation in the solid state for their magnetic properties in general and ferromagnetism in particular.[1] Several of their radical crystals have been found to exhibit ferromagnetic intermolecular interactions. Among those, nitronyl nitroxide radicals substituted with various aromatic rings are of great interest as highlighted by the discovery of rare organic ferromagnet in *p*-nitrophenyl nitronyl nitroxide crystals.[2] Commonly in these organic solids, the intermolecular interaction between the nitroxide group of one molecule and the substituent aromatic moiety of the adjacent molecule, rather than the direct one between the NO groups, plays critical roles for their bulk magnetic properties.

In an effort to increase intermolecular interactions, nitrogen heteroaromatics have been incorporated in the nitronyl nitroxide radicals. Relevant examples of such nitrogen heterorings are pyridine,[3] pyridinium salt,[4] quinoline,[5] pyrimidine,[6] and 1,2,4-triazole[7] derivatives. In contrast, the nitroxide radicals joined with sulfur heterocycles have never been investigated.[8] The intermolecular interactions between the sulfur and the oxygen of the NO group are anticipated to work as spin-coupling pathways in the solid state. In this paper we report the structural characterization and magnetic properties of two closely related nitronyl nitroxide (ONC=NO) and imino nitroxide (NCNO) free radicals, 4,4,5,5-tetramethyl-3-oxo-1-oxylimidazolin-2-yl (**1N**, **2N**) and 4,4,5,5-tetramethyl-1-oxylimidazolin-2-yl (**1I**, **2I**), each of which is substituted at the 2-position with the isomeric thienothiophenes, thieno[3,2-*b*]thiophene and thieno[2,3-*b*]thiophene, respectively. The constituent thienothiophene moieties are isomeric to each other with similar molecular size and shape and different only in the topology of π conjugation. Therefore, these materials would provide direct insight into magnetostructural relations in the crystalline state, particularly, if isostructural crystals are obtained.[9] Although such a case was not realized, we could deduce characteristic features of the spin interaction between the NO group and the sulfur atom as well as their effects on the bulk magnetic properties.

Results and Discussion

Crystal Structures. Crystal and molecular structures of the four radical species were studied by single-crystal X-ray diffractions. Crystal data are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.[20]

In all the crystals studied, the ON−C−NO moieties that bear the radical center are in the same plane as the thienothiophene ring. As a result of coplanarity of the thienothiophene ring and the ON−C−NO fragment, one

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[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1995.

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(9) A unique example of the isomorphic crystals including thieno[3,2-*b*]thiophene and thieno[2,3-*b*]thiophene frameworks has recently been reported; see: Hayashi, N.; Mazaki, Y.; Kobayashi, K. *J. Chem. Soc., Chem. Commun.* **1994**, 2351.

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Table 1. Crystal Data and Experimental Parameters of X-ray Crystal Analyses of 1N, 1I, 2N, and 2I

	1N	1I	2N	2I
formula	$C_{13}H_{15}N_2O_2S_2$	$C_{13}H_{15}N_2O_1S_2$	$C_{13}H_{15}N_2O_2S_2$	$C_{13}H_{15}N_2O_1S_2$
M	295.37	279.37	295.37	279.37
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	12.560(4)	17.121(5)	24.69(1)	13.330(3)
b, Å	13.853(7)	10.661(3)	9.040(5)	9.301(1)
c, Å	8.676(3)	16.467(4)	13.459(7)	12.994(3)
β, deg	105.62(2)	109.58(2)	73.78(4)	118.22(1)
V, Å^3	1454(1)	2832(1)	2885(3)	1419.5(5)
Z	4	8	8	4
D, g cm^{-3}	1.350	1.311	1.361	1.306
scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
2θ range, deg	4–55	4–55	4–55	4–55
no. of reflections measured	3754	7094	7411	3670
no. of reflections used in refinement $F > 2.5\sigma$	2171	4129	3205	2378
no. of parameters refined	277	446	464	224
R(I)	0.068	0.084	0.087	0.067
R_w(I)	0.076	0.111	0.100	0.093

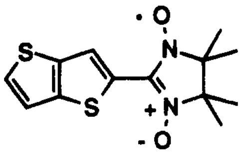
Table 2. Selected Bond Lengths and Angles for 1N, 1I, 2N, and 2I

		1I		2N		
	1N	molecule 1	molecule 2	molecule 1	molecule 2	2I
bond lengths, Å						
C7–N1	1.336(5)	1.385(8)	1.360(7)	1.336(10)	1.352(10)	1.403(5)
C7–N2	1.351(6)	1.275(7)	1.317(8)	1.357(10)	1.365(10)	1.282(5)
N1–O1	1.279(5)	1.256(9)	1.221(8)	1.281(10)	1.282(10)	1.272(4)
N2–O2	1.278(6)			1.277(9)	1.276(9)	
bond angles, deg						
O1–N1–C7	124.7(4)	127.1(6)	128.1(5)	123.2(7)	123.9(7)	125.1(3)
O2–N2–C7	125.6(4)			126.8(7)	125.1(7)	
C1–C7–N1	124.7(4)	122.1(5)	122.9(5)	126.9(7)	126.1(7)	123.3(3)
C1–C7–N2	126.6(4)	123.5(5)	123.6(5)	124.5(7)	125.6(7)	122.7(3)
torsional angles, deg						
O1–N1–C7–C1	−4.5(7)	3.3(9)	1.7(9)	2.4(13)	−3.4(12)	2.3(5)
N1–C7–C1–S1	2.4(6)	−179.7(9)	179.4(9)	−6.9(11)	−2.5(11)	1.6(5)
O2–N2–C7–C1	2.7(7)			−5.8(13)	3.3(12)	
N2–C7–C1–C2	3.0(7)	179.5(7)	−179.0(8)	−8.3(13)	−4.3(13)	7.3(6)

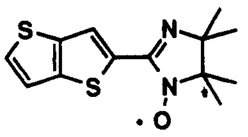
of the NO groups in the nitronyl nitroxides experiences extremely short contact with the sulfur atom of the thienothiophene ring, the intramolecular (N)O—S distance being as short as 2.73 and 2.76 Å in **1N** and **2N**, respectively (Figures 1 and 3). These distances are within the sum of the van der Waals contacts for S—O (3.25 Å). In line with these contacts, nonequivalence of the C(7)–N(1) and C(7)–N(2) bond lengths was revealed in the **1N** crystals; the C(7)–N(1) bond that is arranged in *syn* orientation with respect to the C–S bond of the thienothiophene ring is shorter than the C(7)–N(2) bond of *anti* orientation to the C–S bond. In **1N**, for example, the former is 1.336 Å, while the latter is 1.351 Å (Table 2). The NO—S contacts are considered to arise mainly because of Coulombic attraction; the oxygen atom close to the sulfur atom is equipped with a negative charge, hence increasing the S—O contact via electrostatic interactions.[10,11] In the crystal of **2N**, the two NC bonds are again not equivalent. The one eclipsed to the C–S bond is shorter than the other (Table 2). In contrast to the C–N bonds, there is no remarkable difference of the N–O bond lengths in the nitronyl nitroxides.

The NO bond in imino nitroxide radical **2I** is also oriented in *syn* arrangement to the C–S bond of the thienothiophene ring to retain the planarity of the whole molecule, as shown in Figure 4. On the other hand, the isomeric imino nitroxide **1I**, although the thienothiophene ring is coplanar with the nitrogen five-membered ring, the N–O bond is directed in an *anti* orientation; the imino C(7)–N(2) bond, rather than the NO bond in the five-membered ring, is eclipsed to the S–C bond of the thienothiophene ring (Figure 2). The NO bond length is significantly shorter in the imino nitroxides than in the nitronyl nitroxides.

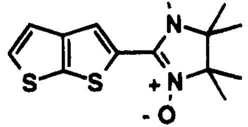
The projections of the crystal structures of **1N**, **1I**, **2N**, and **2I** are shown in Figures 1–4. A trend of the crystal



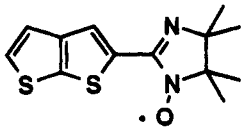
1N



1I



2N



2I

structures is deduced; the crystal structures are dependent on the thienothiophene moiety rather than the radical-bearing fraction, that is, whether the radical moiety is the nitronyl nitroxide or imino nitroxide is not dominant in the crystal packing. Thus, the crystals of thieno[2,3-*b*]thiophene compounds (**2N** and **2I**) are com-

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(10) For leading references and a discussion of intramolecular sulfur–oxygen interactions, see: Burling, F. T.; Goldstein, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 2313.

(11) Desiraju, G. R. *Crystal Engineering*; Elsevier: Amsterdam, 1989; p 203. See also: Mazaki, Y.; Hayashi, N.; Kobayashi, K. *J. Chem. Soc., Chem. Commun.* **1992**, 1381.

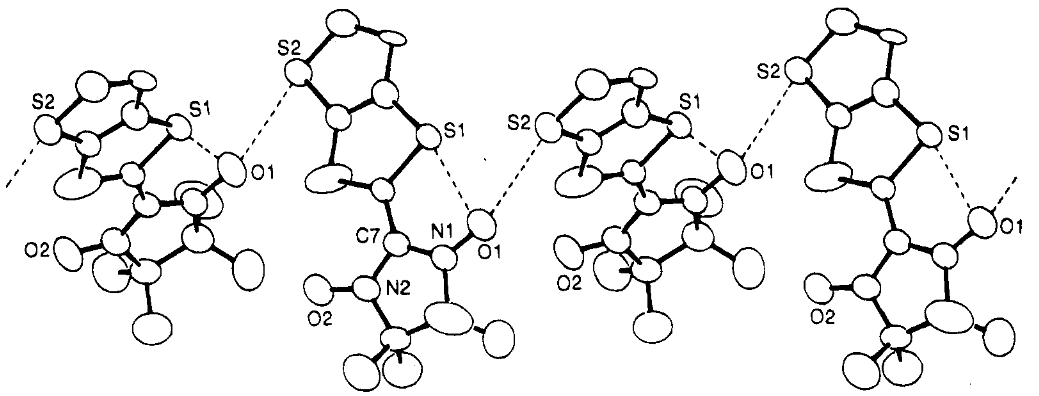

Figure 1. Crystal structure of **1N** showing 1D chain of molecules linked with the short NO—S contacts and the atomic numbering. O1—S1, 2.73 Å; O1—S2, 3.06 Å. The thienothiophene ring shows disorder (see text) and the molecules with higher occupancy factor are illustrated.

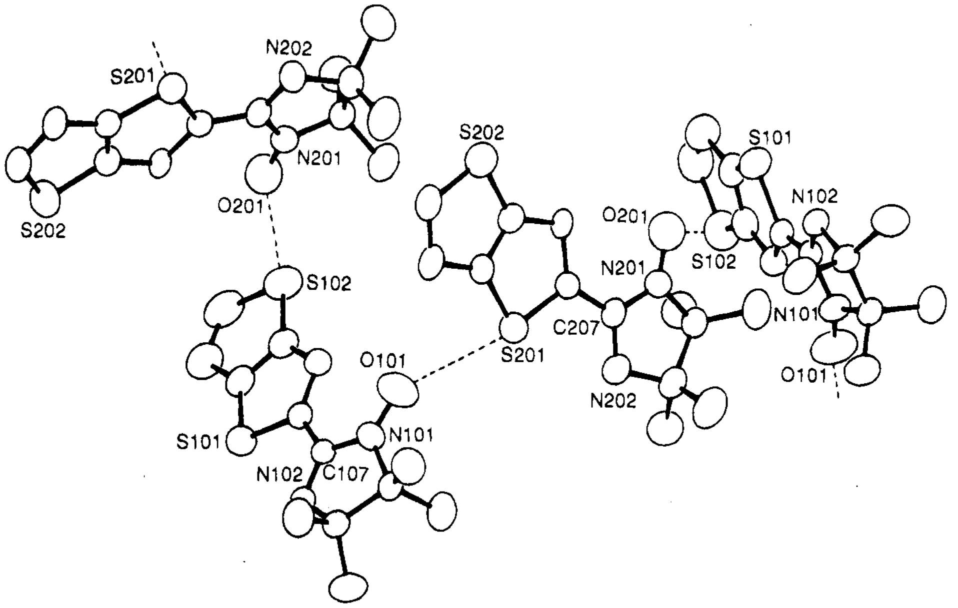

Figure 2. Crystal structure of **1I** showing 1D alternate chain of molecules linked with the short NO—S contacts and indicating the atomic numbering. O101—S201, 3.15 Å; O201—S102, 3.20 Å.

posed of dimeric units of the molecules by their side-by-side and head-to-tail arrangement, whereas thieno[3,2-*b*]thiophene compounds (**1N** and **1I**) form a one-dimensional chain by weak intermolecular contacts between the oxygen atoms in the NO group and the sulfur atoms in the thienothiophene rings.

The dimeric molecules in the **2N** and **2I** crystals are aligned in a plane with two short NO—S contacts. The intermolecular NO—S distances are 3.03 Å in **2N** and 3.09 Å in **2I**. In both crystals there are no short contacts between the dimeric units, as seen in Figure 4 for **2I**. Thus the magnetic interaction is assumed to occur mainly within the dimer.

The molecules of **1N** are linked by a short intermolecular NO—S contact along the *a* axis; one of the oxygen atoms (O1) which is close to the sulfur atom (S1) of the ring has interatomic interaction with the sulfur atom (S2) of the neighboring molecules (3.06 Å). The angle made by the mean planes of two neighboring molecules is 75.5°. For **1N** crystals, the thieno[2,3-*b*]thiophene moiety showed an orientational disorder 180° rotated about the longitudinal axis of the thienothiophene ring. In the least-square refinements the occupancy factors were also refined to be 0.8:0.2. These disordered structures could be ascribed to the similarity of the dimensions related with C—S—C and C=CH—C groups of the thienothiophene moieties.

There are two crystallographically independent molecules of **1I** in the crystal. There are two independent intermolecular short NO—S contacts, one is 3.15 Å and another is 3.20 Å. Through these two contacts, the molecules constitute a zigzag chain structure along the *a/c* diagonal. No short contacts were observed between the chains.

ESR Spectra. For characterization of the free radicals, their ESR spectra have been measured in toluene at room temperature. The coupling constants and the *g* values are summarized in Table 3. The ESR spectra of nitronyl nitroxides **1N** and **2N** are composed of five lines in a ratio of 1:2:3:2:1 as expected for coupling with two equivalent nitrogens. The coupling constant 0.70 mT is somewhat smaller than 0.74 mT reported for 2-aryl nitronyl nitroxides.[12] Imino nitroxides **1I** and **2I** exhibit seven lines resulting from coupling with the two inequivalent nitrogen nuclei (Figure 5). The hyperfine

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[12] Ullman, E. F.; Osiecki, J. H.; Boocock, D. G. B.; Darcy, R. *J. Am. Chem. Soc.* **1972**, *94*, 7049.

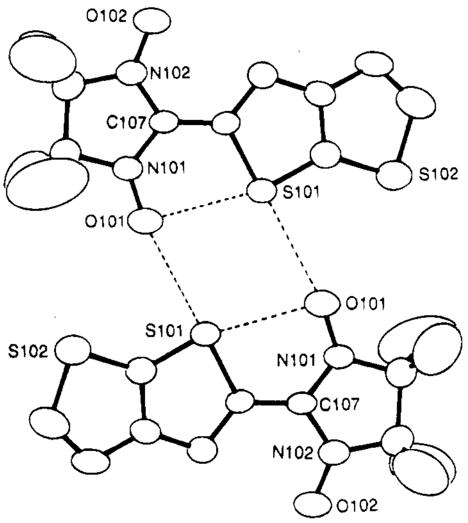

Figure 3. A dimeric pair of **2N** molecules in the crystals showing the short NO—S contacts and the atomic numbering. O101—S101 (intramolecular), 2.76 Å; O101—S101 (intermolecular), 3.03 Å.

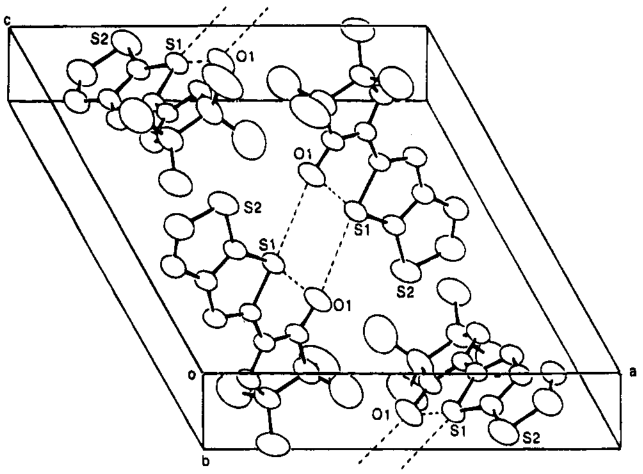

Figure 4. Molecular packing in **2I** crystal with the atomic numbering. The dotted lines indicate the short NO—S contacts. O1—S1 (intramolecular), 2.79 Å; O1—S1 (intermolecular), 3.09 Å.

Table 3. ESR Data for 1N, 1I, 2N, and 2I Measured in Toluene at Room Temperature

compd	*g* value	no. of resolved lines	a_N, mT	a_S, mT
1N	2.0067	5	0.70	–
1I	2.0060	7	0.89, 0.45	0.3
2N	2.0070	5	0.73	–
2I	2.0060	7	0.89, 0.45	0.3

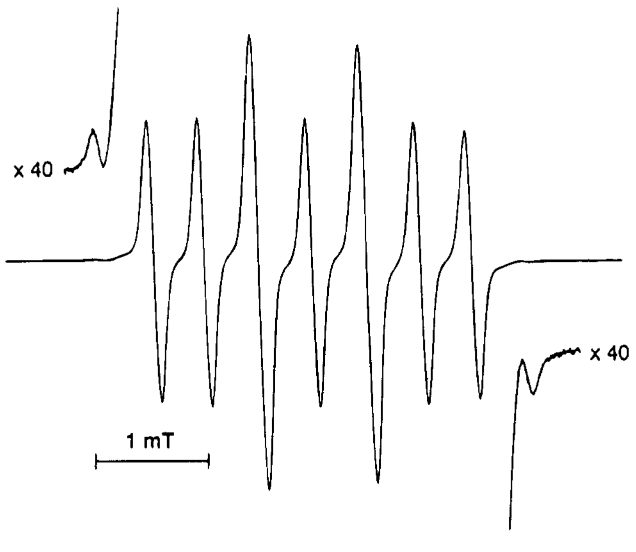

Figure 5. ESR spectrum of imino nitroxide **1I** in toluene at room temperature.

coupling due to the imino nitrogen (0.45 mT) is almost half of that of the nitroxide nitrogen (0.89 mT). These spectra are typical of nitronyl nitroxides and imino nitroxides. Of particular interest in the imino nitroxide radical is the observation of the satellite lines accompanied by the outermost peaks of the seven. These are two lines of very low intensity (ca. 1% of the outermost peak for each); the outer is distinct while the inner is a shoulder peak as shown in Figure 5. We assign the outer satellites to the hyperfine splitting from ^{13}C of the iminyl carbon and the inner shoulders to that from ^{33}S of the thienothiophene ring. The signal due to the hyperfine coupling with sulfur ($I = 3/2$, natural abundance 0.76%) splits into four lines. Thus we can observe the outer lines of an ^{33}S quartet.[13] The spin density on the sulfur atom is estimated on the basis of the observed hyperfine coupling constant (ca. 0.15 mT) to be approximately 5% according to the empirical McConnell-type equation proposed for sulfur nucleus, $a^s = Q_S{}^S \varrho_s{}^p$, where $Q_S{}^S = 3.24$ mT.[14] In contrast to the imino nitroxides, nitronyl nitroxides **1N** and **2N** exhibit no satellite of observable intensities. These results are consistent with the change of the nodal properties of the SOMO on going from imino nitroxide to nitronyl nitroxide; in nitronyl nitroxide radicals the electron spins are more localized at the NO bonds and very little spin density is at the central sp^2 carbon atom bridging the two NO groups, which results in insufficient spin polarization on the thienothiophene ring moiety.

For aryl nitronyl nitroxide radicals, the noncoplanarity of the aromatic ring and the nitroxide moiety would make the spin polarization on the ring even smaller. In the present case, however, the nitroxide moieties tend to be coplanar with the thienothiophene ring, as indicated in the solid state. Therefore, the spin polarization in the thienothiophene derivatives, as compared with the nitronyl nitroxide radicals attached to a benzene ring, should be ensured effectively on the ring, even for the nitronyl nitroxide radical.

The results of MO calculations, which have been carried out for **1N**, **2N**, **1I**, and phenyl nitronyl nitroxide using an MINDO/3 method and the X-ray structural data, support also the delocalization of the spin density on the thienothiophene ring. Figure 6 depicts the orbital coefficients in the SOMO. For **1I** the results of two possible conformation are shown. Between these conformational isomers significant difference of the spin densities has not been found, presumably indicating that the through-bond spin polarization is more important than the through-space one, which might be expected from the short intramolecular NO—S contacts.

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[13] We could also asign the two satellite peaks on each side of the spectrum as the half of the quartet due to ^{33}S. However, it may be not the case since the ESR spectra of nitonyl nitroxides **1N** and **2N** exhibit no such satellite signals in spite of almost the same spin densities at the sulfur as that of **1I** according to the MO calculations (Figure 6).

[14] Sullivan, P. D. *J. Am. Chem. Soc.*, **1968**, *90*, 3618.

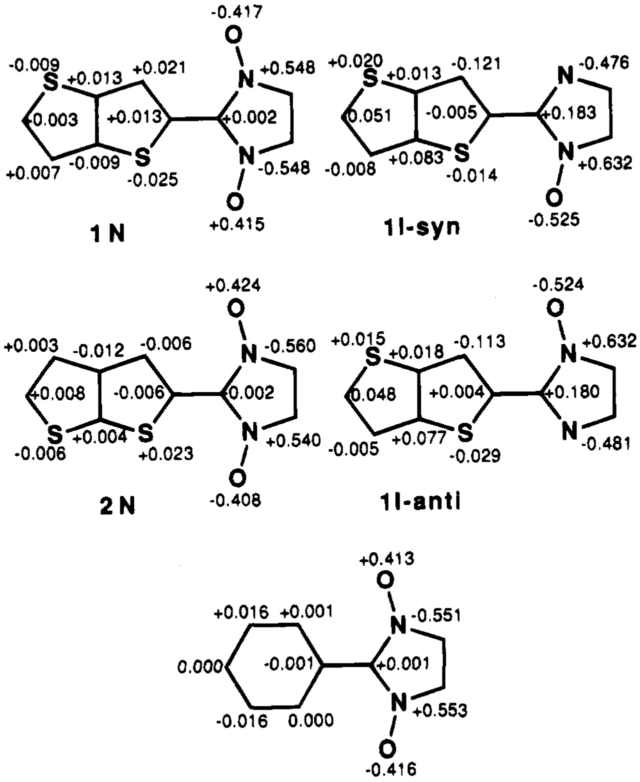

Figure 6. The molecular orbitals of nitronyl nitroxides **1N** and **2N**, two conformers of **1I**, and phenyl nitronyl nitroxide, showing the coefficients of SOMO.

Magnetic Properties. The temperature dependence of the paramagnetic susceptibility of the polycrystalline samples of the compounds was measured by means of a SQUID susceptometer in the temperature range 2–100 K. The molecular diamagnetic contribution is estimated from the plot of the high-temperature data. The magnetic behavior of each compound is depicted in Figure 8 in the form of the temperature dependence of the product of the paramagnetic susceptibility (χ) with the temperature (T). For all the radical samples the room temperature value of χT is about 0.375 emu K mol^{-1} in good agreement with the value expected for uncorrelated spins based on the Curie constant $C = N\mu_B^2 g^2 s(s+1)/3k_B$.

As the temperature is lowered, the χT value of **1N** increases, reaches a maximum at ca. 4 K, and then decreases. This suggests that in **1N** ferromagnetic interaction is predominant at low temperatures and that antiferromagnetic ordering is involved at still lower temperature. On the basis of the crystal structure the magnetic data was analyzed in terms of the one-dimensional Heisenberg model for ferromagnetically coupled linear arrays of spins $^1/_2$.[15] Thus, the ferromagnetic interactions between the neighboring radical sites of $J/k_B = +0.11$ K ($H = -2JS_iS_j$) was obtained. The rapid decrease in χT below 4 K presumably indicates the presence of interchain antiferromagnetic interactions.

The intermolecular NO–S contacts are anticipated to play an important role for the 1D ferromagnetic behavior of **1N**. The unpaired electron occupying the SOMO is localized on the side of the nitronyl nitroxide and has little population in the thienothiophene ring as shown in Figure 6. However, the NHOMO and NLUMO (the highest doubly occupied and the lowest unoccupied MO) are distributed mainly in the thienothiophene ring, as indicated in the results of the MO calculation (Figure 7). Thus, at the contact on the sulfur atom (S2) with the NO group, the intermolecular overlap between SOMO's could be much smaller than those between SOMO–NHOMO and/or between SOMO–NLUMO. It is thought that intermolecular overlaps between SOMO–NHOMO and SOMO–NLUMO lead to ferromagnetic intermolecular interactions.[16]

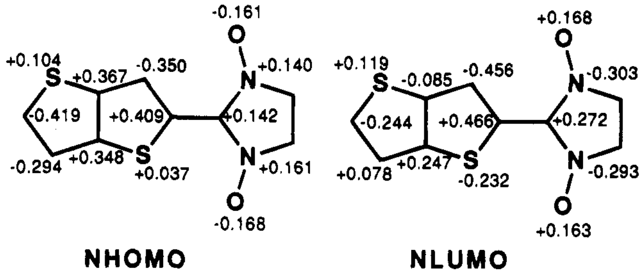

Figure 7. The molecular orbitals of **1N**, showing the coefficients of NHOMO and NLUMO.

Radical **1I** behaves as paramagnetic species down to *ca.* 20 K, as shown by the constant χT value, while it shows a sharp decreases in the χT value at the lowest temperature. This represents an antiferromagnetic coupling between the radical molecules. A Curie–Weiss fit yields the Weiss constant θ of -0.54 K.

The χT *vs* T curve of compounds **2I** and **2N** exhibits also the decrease in χT at low temperatures, suggesting the presence of antiferromagnetic intermolecular interaction in the crystal. According to the crystal structural results that two radical molecules form a dimeric unit, the magnetic data were analyzed in terms of a Bleaney–Bowers expression of the magnetic susceptibility for a pair of spins:[17]

$$\chi = \{Ng^2\mu_B^2/k_B(T-\theta)\}/\{3 + \exp(-2J/k_BT)\}$$

where θ is the Weiss field introduced to describe the weak interaction between the dimeric units and J is that within the dimeric pair. Thus $J/k_B = -2.6$ K and $J/k_B = -4.6$ K with $\theta = -0.5$ K was obtained for **2N** and **2I**, respectively. The magnetic data are summarized in Table 4.

The antiferromagnetic interactions in **2N** and **2I** are rationalized by means of the cyclic dimer structure revealed by the X-ray analyses. These molecules are aligned face-to-face on the same plane with the short NO–S contacts to overlap the SOMO orbitals. Pairing in the thieno[2,3-*b*]thiophene isomers is ascribable to the presence of the two sulfur atoms on the interacting site in a molecule, which can lead to short NO–S contacts (O1–S1) and one relatively short contact (O1–S2). The spins should align antiferromagnetically via the superexchange mechanism. The stronger antiferromagnetic interaction in imino nitroxide **2I** as compared with that in nitronyl nitroxide **2N** could be rationalized by means of the high spin density concentrated in one NO group of imino nitroxide **2I**.

Experimental Section

ESR Spectroscopy and Magnetic Measurements. ESR spectra were recorded on a JEOL JES RE-2X (9GHz) spectrometer. The magnetic susceptibility was measured by the

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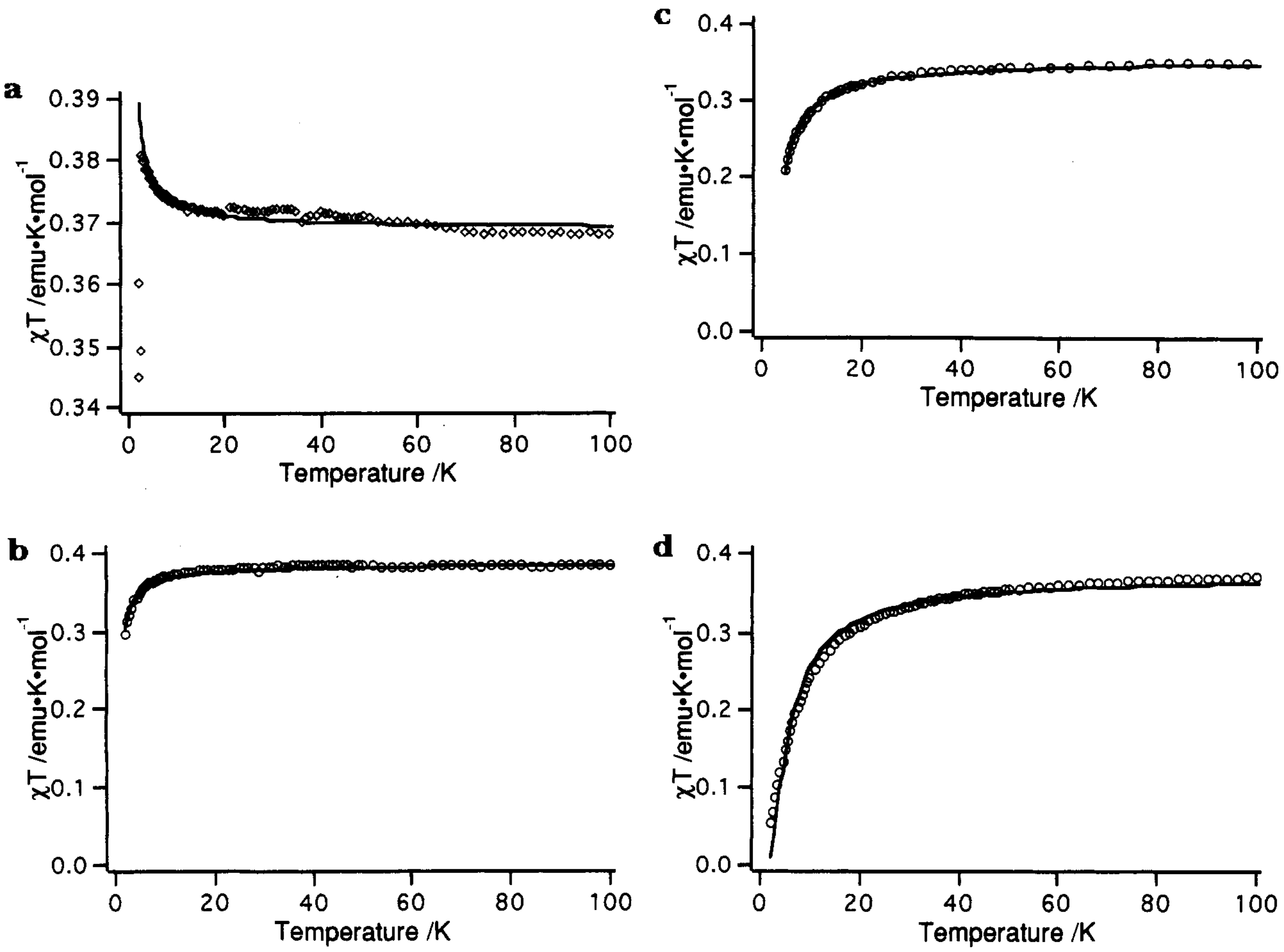

Figure 8. Temperature dependence of χT for the free radical species (a) **1N**, (b) **1I**, (c) **2N**, and (d)**2I**. The solid lines are calculated for each based on an appropriate model described in the text. See also Table 4.

Table 4. Summary of Magnetic Data for 1N, 1I, 2N, and 2I

compd	intramolecular S–O contact, Å	intermolecular configuration	magnetic interaction	
1N	2.73	1D chain	ferromagnetic	$J/k_B = +0.11$ K[a]
1I		alternative 1D chain	antiferromagnetic	$\theta = -0.54$ K[b]
2N	2.76	dimer	antiferromagnetic	$J/k_B = -2.6$ K[c]
2I	2.79	dimer	antiferromagnetic	$J/k_B = -4.6$ K[c]

[a] Fitting for Heisenberg one-dimensional model. [b] Fitting for Curie–Weiss rule. [c] Fitting for Bleaney–Bower rule.

SQUID susceptometer on a Quantum design MPMS2 system with a 1 T superconducting magnet.

X-ray Analysis. Diffraction data were obtained on a Rigaku AFC four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) at room temperature. The structures were solved by direct methods and converged by block-diagonal least-squares analysis using the UNICS-III program.[18] Crystal data are listed in Table 1. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at standard positions and refined isotropically.

Materials. Solvents were used for the reactions and spectral measurements were all distilled under high-purity N_2 after they were dried with sodium/benzophenone ketyl. Anhydrous magnesium sulfate was used as drying agent.

Each thienothiophene isomer was readily formylated at C-2 by the reaction with DMF–$POCl_3$ to give the corresponding aldehyde,[19] which was used as the precursor for the free radical species as follows.

2-(4,4,5,5-Tetramethyl-3-oxo-1-oxylimidazolin-2-yl)thieno[3,2-*b*]thiophene (1N). A suspension of 1.0 g of 2-formylthieno[3,2-*b*]thiophene and 3.0 g of 2,3-bis(hydroxylamino)-2,3-dimethylbutane in 50 mL of dry benzene was refluxed for 3 days under nitrogen. The solvent was evaporated *in vacuo* and the residue was taken up in 200 mL of chloroform. This solution was stirred with a solution of 10 g of sodium periodate in 200 mL of water at room temperature for 5 min. The organic layer was separated, washed with water, dried with magnesium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel with dichloromethane as an eluent and recrystallized from hexane–dichloromethane to give 0.54 g (30%) of **1N** as greenish blue prisms: mp 169.0–170.5 °C; UV (acetone, λ_{max} (log ϵ)) 753 (360), 679 (560), 618 (410), 570 (sh); MS *m/z* 295 (M^+). Anal. Calcd for $C_{13}H_{15}N_2O_2S_2$: C, 52.85; H, 5.12; N, 9.49; S, 21.71. Found: C, 53.00; H, 5.16; N, 9.75; S, 21.79.

2-(4,4,5,5-Tetramethyl-3-oxo-1-oxylimidazolin-2-yl)thieno[2,3-*b*]thiophene (2N). A mixture of 0.80 g of 2-formylth-

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(20) The author has deposited atomic coordinates for these structure with the Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

ieno[2,3-*b*]thiophene, 2.9 g of 2,3-bis(hydroxylamino)-2,3-dimethylbutane, and 150 mL of dry benzene was refluxed for 24 h under nitrogen. The solvent was evaporated *in vacuo* and the residue was taken up in 200 mL of dichloromethane. This solution was stirred with a solution of 10 g of sodium periodate in 200 mL of water at room temperature for 5 minute. The organic layer was separated, washed with water, dried with magnesium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel with dichloromethane as an eluent and recrystallized from hexane–dichloromethane to give 1.1 g (78%) of **2N** as deep blue prisms: mp 167–168 °C; UV (acetone, λ_{max} (log ϵ)) 732 (430), 661 (610), 604 (410), 560 (sh); MS *m/z* 295 (M^+). Anal. Calcd for $C_{13}H_{15}N_2O_2S_2$: C, 52.85; H, 5.12; N, 9.49; S, 21.71. Found: C, 52.80; H, 5.04; N, 9.68; S, 21.73.

2-(4,4,5,5-Tetramethyl-1-oxylimidazolin-2-yl)thieno[3,2-*b*]thiophene (1I). A solution of 0.51 g of **1N** in 250 mL of dichloromethane was stirred vigorously with a solution of 0.30 g of sodium nitrite and 1 mL of acetic acid for 5 min. The organic layer was separated, washed with aqueous sodium hydrogen carbonate and water, dried with magnesium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel with dichloromethane as an eluent and recrystallized from hexane–dichloromethane to give 0.46 g (95%) of **1I** as red prisms: mp 122.0–122.8 °C; UV (acetone, λ_{max} (log ϵ)) 520 (700), 560 (sh), 490 (sh); MS *m/z* 279 (M^+). Anal. Calcd for $C_{13}H_{15}N_2OS_2$: C, 55.89; H, 5.41; N, 10.03; S, 22.97. Found: C, 55.84; H, 5.55; N, 10.19; S, 23.04.

2-(4,4,5,5-Tetramethyl-1-oxylimidazolin-2-yl)thieno[2,3-*b*]thiophene (2I). The procedure described for **1I** was carried out using 0.50 g of **2N** to give 0.42 g (88%) of **2I** as red prisms: mp 101–102 °C; UV (acetone, λ_{max} (log ϵ)) 506 (670), 550 (sh), 470 (sh); MS *m/z* 279 (M^+). Anal. Calcd for $C_{13}H_{15}N_2OS_2$: C, 55.89; H, 5.41; N, 10.03; S, 22.95. Found: C, 56.06; H, 5.35; N, 10.20; S, 23.12.

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