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Intramolecular Spin-Interactions Between Two Nitronyl Nitroxide or Imino Nitroxide Radical Units Linked To Thieno[2,3-*b*]thiophene and Thieno[2,3-*b*]thieno[3',2'-*d*]thiophene Chromophores

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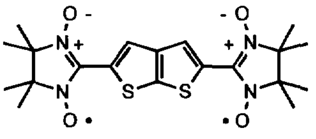
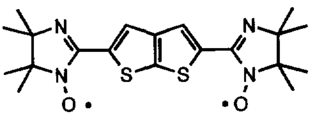
Abstract: Diradical species **1N**, **1I**, **2N**, and **2I**, in which two nitronyl nitroxide (**N**) or imino nitroxide (**I**) radical centers are attached to thieno[2,3-*b*]thiophene (**1**) and thieno[2,3-*b*]thieno[3',2'-*d*]thiophene (**2**) chromophores, respectively, were prepared and their intramolecular exchange interactions were investigated in frozen solutions by means of ESR spectroscopy and magnetic susceptibility measurements at cryogenic temperature. Temperature dependence of the ESR signal intensities due to the triplet state revealed that bis(nitronyl nitroxide) radicals, **1N** and **2N**, are ground-state singlet species with quite small singlet-triplet gaps. In bis(imino nitroxide) radical **1I** the spin interaction was antiferromagnetic and the singlet-triplet gap was estimated to be $2J/k_B = -18$ K. On the other hand, bis(imino nitroxide) **2I** was revealed to be a singlet-triplet degenerate species. These results are discussed in terms of the intramolecular NO---S contact along with corroboration by the semi-empirical MO calculations.

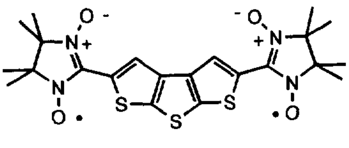
Π-conjugated polyradicals with a high-spin ground state are the focus of contemporary intensive research in relation with bulk ferromagnetism in the molecular solids.[1] To realize a high-spin π-system it is important to understand how two radical centers would couple through a magnetic coupler in diradical species. A number of stable diradicals, in which radical centers are connected through an appropriate π-conjugation, have been investigated.[2,3] Almost of these spin-couplers are hydrocarbon π-systems. Topological consideration based on the valence bond theory developed by Ovchinnikov have been applied to a variety of such hydrocarbon π-systems.[4] On the other hand, heterocyclic π-conjugation has scarcely ever been investigated.[5-9] We now report intramolecular spin-interactions of two nitronyl nitroxide radical units as well as two imino nitroxide radicals in a series of compounds **1N**, **1I**, **2N**, and **2I**, which are constituted of thieno[2,3-*b*]thiophene (**1**) or thieno[2,3-*b*]thieno[3',2'-*d*]thiophene (**2**) rings as intramolecular spin-couplers and are non-Kekulé heterocycles. Diradicals **1N** and **1I** linked by thieno[2,3-*b*]thiophene are heterocyclic vinylogues of pentamethylenepropane (PMP)[10] and **2N** and **2I** are those of hexamethylenebutane (HMB),[11] both of their ground-state spin multiplicity yet being subjects of some controversy in contrast to the well-established triplet of trimethylenemethane (TMM).[12] Thus, it is of interest to see if these diradicals possess triplet ground state or not. We demonstrate herein the results which could be interpreted by the unique intramolecular interactions between the oxygen atom of the NO group and the sulfur atom of the condensed thiophene ring.



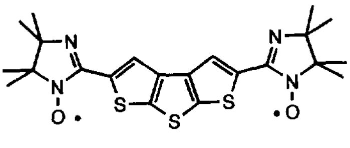
1N



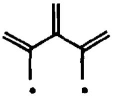
1I



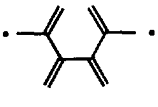
2N



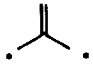
2I



PMP



HMB



TMM

RESULTS

Preparation of Diradicals. Nitronyl nitroxide diradicals **1N** and **2N** were prepared by the condensation reaction of the 2,5-diformyl precursors with 2,3-dimethyl-2,3-bis(hydroxyamino)butane, followed by oxidation with sodium periodate.[3] Imino nitroxides **1I** and **2I** were obtained by reduction of the corresponding nitronyl nitroxides by sodium nitrite under acidic conditions. Their analytically pure samples were obtained by chromatography on silica gel, gel permeation chromatography (GPC), and recrystallization from chloroform-hexane. The diradicals thus obtained were stable at ambient temperature for a few week.

ESR Spectra. The ESR spectra of each diradicals were measured in 2-methyltetrahydrofurane (MTHF) at room temperature. Figure 1 illustrates the typical spectra observed for **1N** and **2I**. The coupling constants with the nitrogen nuclei are summarized in Table 1. The spectra are characterized as biradicals with large electron-electron exchange interactions ($J > a_N$); the hyperfine coupling to all four nitrogens is observed to exhibit nine lines for **1 N** and **2 N** and thirteen lines for **1I** and **2I**.

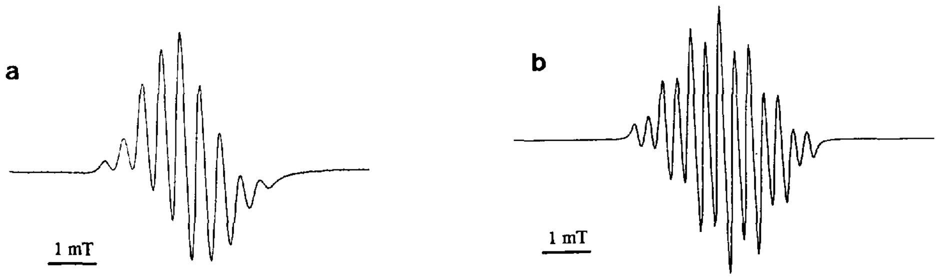
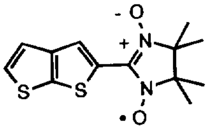


Figure 1. ESR spectra of diradicals **1 N** and **2I** in MTHF at room temperature. (a) **1 N**, (b) **2I**.

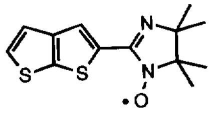
Table 1. ESR data of diradicals and their related monoradicals **3** and **4** measured in MTHF at room temperature.

compd.	resolved	g	a_N /mT
1N	9	2.0070	0.38
1I	13	2.0053	0.45, 0.22
2N	9	2.0063	0.37
2I	13	2.0056	0.46, 0.23
3	5	2.0070[a)]	0.73
4	7	2.0060[b)]	0.89, 0.45

a) in hexane b) in toluene



3



4

The hyperfine splitting with nitrogen in **1N** (0.38 mT) is roughly half 0.73 mT of mono(nitronyl nitroxide) radical **3** attached to thieno[2,3-*b*]thiophene ring (Table 1),[13] indicating that the electron-electron exchange interaction J is greater than the hyperfine coupling a_N. This is also the case for bis(imino nitroxide) radical **1I**, which exhibited the coupling constant (0.45 and 0.22 mT) of an approximately half of the value observed in mono(imino nitroxide) radical **4** (0.89, 0.45 mT).[13]

The cryogenic ESR spectra of each diradical species in an MTHF rigid glass were measured in the temperature range 6-100 K. Typical spectra for **1I** and **2N** are shown in Figure 2. The Δm_S=1 regions of each spectrum at about 5 K consist of the complex pattern with several lines, each of which is rather broad and not symmetry with respect to the mid-point of the spectral band.[14] The spectra could be rationalized by means of the randomly oriented triplet states with the anisotropic g tensors.

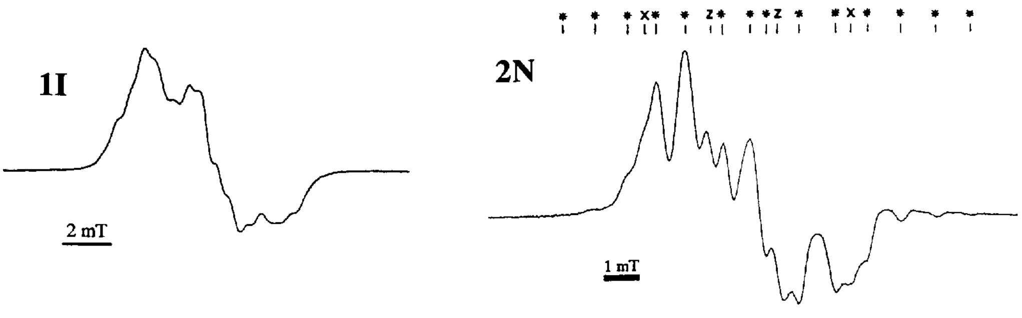


Figure 2. Low temperature ESR spectra of **1I** (18.4 K) and **2N** (6.0 K) in MTHF matrix.

The complexation of the spectra may be attributed to the anisotropic zero-field splitting and the hyperfine splitting of the N nucleus, since D is not significantly large as compared to a_N. For **2N**, however, the several peaks with equidistant separation of ca. 0.9 mT are recognized, which are attributable to the anisotropic coupling with nitrogen nuclei by the y component (perpendicular to the molecular plane). Besides those four peaks can be observable, being assigned to the x and z components. Thus, we can deduce graphically the anisotropic *g* factors, g_x=2.0082, g_y=2.0061, g_z=2.0087 and the zero-field splitting parameters as D=2.9 mT, E=0.4 mT. Small value of D might suggest larger average distances between the "unpaired electrons" in diradicals. The distance between two spin units in **2N** (the average of the N--N, O---O, and N---O distances) was estimated to be 9.75 Å for the structure optimized in terms of a semi-empirical MO calculation. This distance leads to D=3.0 mT based on a point dipole approximation,[15] being consistent with the above assignment of the ESR spectral bands.

For other diradicals, their cryogenic ESR spectra show much more complex patterns than **2N** does, as seen for **1I**. Therefore, the D and E values could not be estimated. However, similarity of the whole spectral profiles to that of **2N** indicates that these spectra can also be assigned to the triplet state. Half-field Δm_S=2 resonances, the indication specifying a triplet, were not observed in the temperature range measured, presumably due to a such long distance between unpaired electrons.

Temperature Dependence of ESR Intensities. To determine which the observed triplet is a ground state or thermally populated excited state, the temperature dependence of the signal intensities was investigated. To avoid saturation of the signal intensities at the lower temperatures, a lower microwave power and modulation were applied. Figure 3 shows the results: for **1N** a plot of the variation in signal intensities due to the triplet radicals *vs* reciprocal temperatures followed the Curie-law down to 10 K. At lower temperatures, the plot deviates slightly from the linear relationship, showing that the ground state is most likely a singlet state. Nitronyl nitroxide radical **2N** exhibited a similar behavior with a more clear convex at about 8 K in the plot, indicating that the observed triplets are thermally excited state.

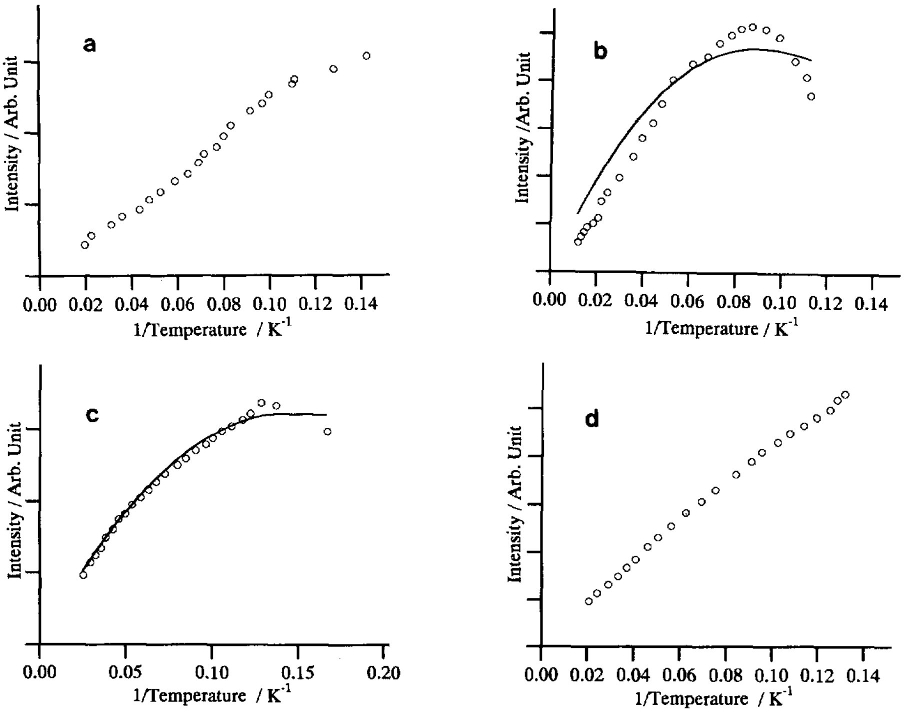


Figure 3. Curie plots of the signal intensity *vs* the reciprocal absolute temperature. The solid line is a simulation curve. (a) **1N**, (b) **1I**, (c) **2N** and (d) **2I**.

The signal intensity of **1I** reaches a maximum at about 16 K and indicates clearly that the radical units in this biradical is connected much more strongly with antiferromagnetic interactions as compared to **1N** and **2N**. The curve fitting to the S-T model yields $2J/k_B$ as the energy gap separating the triplet and singlet states.[16] The fitting expressions have been demonstrated not to be quite different between the $\Delta m_S=2$ and $\Delta m_S=1$ transitions.[17] Thus we used the most intense signal in the $\Delta\ m_S=1$ regions for the estimation; the curve fitting to the S-T model lead to an energy gap of triplet and singlet, $2J/k_B = -18$ K for **1I**. Similarly a smaller S-T energy gap, $2J/k_B = -11$ K, was deduced in **2N**.

Biradical **2I** exhibits an almost linear relation down to 15 K in the intensity *vs* $1/T$ plots. Therefore, imino nitroxide diradical **2I** is most likely to have a singlet ground state of near degeneracy with triplet state. For **1N** and **2I** further proof of their ground-state spin multiplicity was furnished by the magnetic susceptibility measurements for the diluted samples (5%) in poly(vinyl chloride) (PVC) on a SQUID susceptometer/magnetometer in the temperature range 2~300 K. The temperature (T) dependence of the magnetic susceptibilities (χ_p) is shown in Figure 4 in the expression of $[\chi_pT] / [\chi_pT]_{50K}$ versus T plots, where $[\chi_pT] / [\chi_pT]_{50K}$ is χ_pT normalized by the value at 50 K. As the temperature is lowered, the normalized χ_pT value of **1N** decreases, suggesting that in **1N** an antiferromagnetic interaction is predominant at the ground state. The data was analyzed in terms of the S-T model to afford $2J/k_B = -7$ K. On the other hand, **2I** behaves as a paramagnetic species down to 2 K, as shown by the constant $[\chi_pT] / [\chi_pT]_{50K}$ value in Figure 4. Thus, the ground-state of **2I** is degeneracy of singlet and triplet.

The biradicals investigated in this study are not strong couplers besides **1I**. Thus the magnetic exchange interactions decrease in the order **1I** > **2N** > **1N** > **2I**, wherein **2I** has the degenerate singlet-triplet ground state.

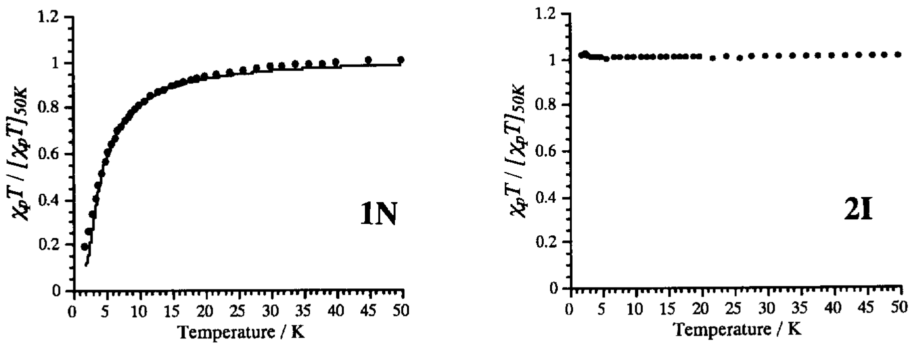
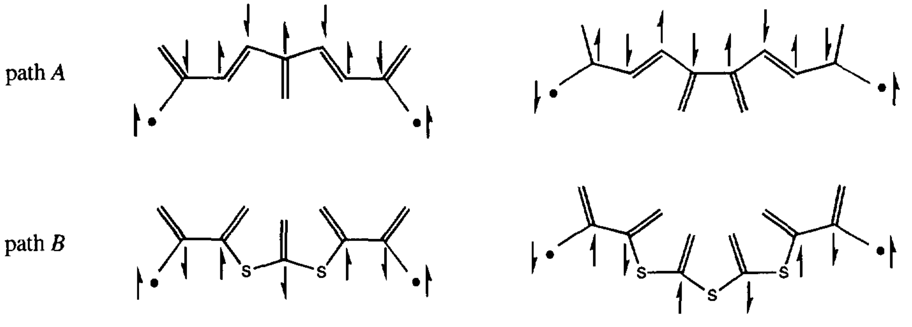


Figure 4. Temperature dependence of magnetic susceptibility (χ_p) in **1N** and **2I**, expressed in $[\chi_pT] / [\chi_pT]_{50K}$ *vs* T plots. The solid line is a simulation curve.

DISCUSSION

The longer the conjugation connecting the two radical units is, the less the exchange interaction should be. Thus, the thiophene-fused thiophenes are not stronger couplers than thiophene ring itself, in which the magnetic interactions have recently been reported to be -218 ~ -50 K depending on the substitution pattern.[6] Furthermore, **1N** and **1I** have smaller antiferromagnetic spin interactions as compared with the spin interactions through thieno[3,2-*b*]thiophene chromophore ($2J/k_B$=-28 K and -23 K) on which we have recently reported.[9] This seems intuitively reasonable, since the π-system of the latter diradicals corresponds to the Kekulé-type conjugation, which could transmit effectively spin polarization via π-conjugation.

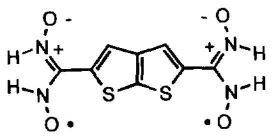
A valence bond theoretical picture of the spin polarization via the carbon π-orbitals may be as in alternant hydrocarbons.[4] Thus, two radical centers will have intermolecular ferro- and antiferromagnetic interaction for the non-Kekulé π-frameworks **1** and **2**, respectively, as depicted in Scheme 1 as path *A*. The spin coupling via the sulfur atoms (path *B*) will be concomitantly operative. This interaction, however, will be in the same fashion as in the path *A* because of the involvement of the super-exchange mechanism at the heteroatom inserted in the planar π-system.[18] Thus, the predictions based on path *A* and *B* are mutually consistent, when a topology/valence bond theory is formally applied.[12]



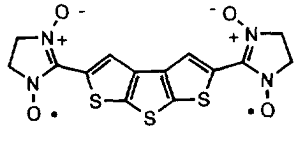
Scheme 1.

Above predictions were also computationally deduced by semi-empirical MOPAC version 6.01 calculations; the heat of the formations of the singlet and triplet states of the diradicals were calculated for the model diradical compounds **1M** and **2M**, bearing the π-conjugated spin couplers of thieno[3,2-*b*]thiophene and thieno[2,3-*b*]thieno[3',2'-*d*]thiophene, respectively. We employed an unrestricted Hartree-Fock (UHF) and the PM3 Hamiltonian. The computed results are summarized in Table 2 and the calculated spin population in the ground states is shown in Figure 5. The latter results indicate that the positive and negative spins alternate along the π-conjugated chromophore, being consistent with the prediction from the spin polarization through π-conjugated chromophore as noted above.[4] There is, however, apparent disagreement in the ground-state spin multiplicity between the present calculation and the experiment in a π-conjugated spin-coupler **1M**: the experimental results of π-framework **1** demonstrated that the singlet is more stable than the triplet.

Diradical species linked by thieno[2,3-*b*]thiophene chromophore is classified as a disjointed system of PMP.[4,10] Therefore, according to the theory of Borden and Davidson based on the localizability of the Hückel nonbonding MOs, the prediction would be a singlet ground state with the small magnitude of the energy gap,[12(c),19] being consistent with the present experimental results.



1M



2M

Table 2. Heat of formations in triplet and singlet states and their difference for **1M** and **2M**. / kcal mol^{-1}

	triplet	singlet	H_s-H_t
1M	151.64	154.02	2.38
2M	135.48	131.36	-4.12

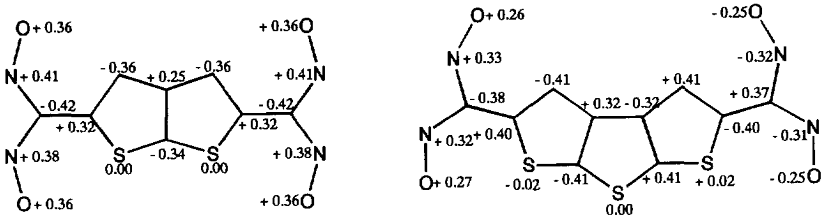


Figure 5. Spin population for diradicals in **1M** and **2M** in the ground state.

The question is why thieno[2,3-*b*]thiophene is actually an antiferromagnetic coupler ? We envisaged that the intramolecular NO---S interaction would be responsible for the ground-spin multiplicity. In related compounds, i.e. mono(nitronyl nitroxide)-substituted thiophene compounds, we have observed the significantly short NO---S contacts of ca 2.73 Å. Thus, the intramolecular S---O distance dependence of triplet and singlet energies was calculated by fixing the angle N-C-N constant at 108.6° and varying the angle C-C-N. The geometry in each structure was not optimized and referred, by assuming $C2v$ symmetry and planar structures, to the X-ray structural parameters observed in related compounds.[13] The results are illustrated in Figure 6. For the angles larger than 125° (S---O; 2.68 Å), the triplet state is the ground state. Upon passing from 120° to the shorter angles, there is a large increase in the triplet energy, while the singlet energy is not effected.

The C-C-N angle in **1N** or **1I** was not be determined because of the difficulty in obtaining appropriate single crystals for X-ray analysis. However, the results shown in Figure 6 clearly indicate that the triplet state becomes highly unstable when the oxygen of the NO radical units is closely arranged to the sulfur atom. Such structural situation could qualitatively hold, judging from the X-ray crystal data of related compounds including **3** and **4**: the observed intramolecular NO---S distances are 2.73, 2.79, 2.76 Å,[13] being extremely shorter than the sum (3.32 Å) of the van der Waals radii of S and O. We have also carried out a calculation for the singlet and triplet energies by assuming the non-planar conformations. In this case the dihedral angle dependence of the energies is small and the reversion of the triplet and singlet energies was not observed.

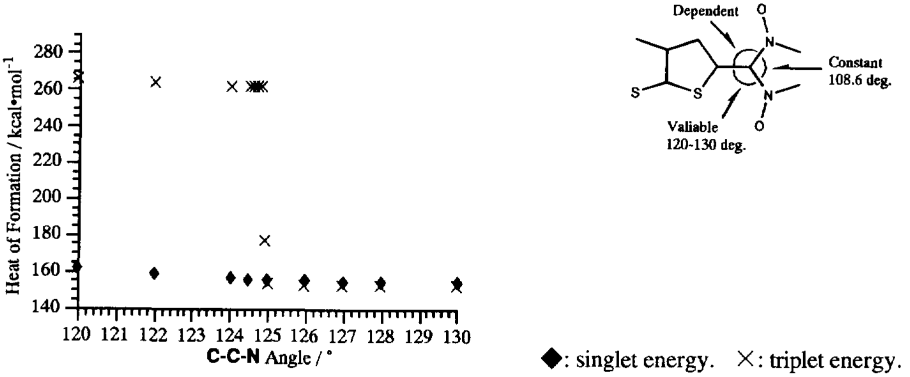


Figure 6. Angle dependence of the heat of formation of **1M** and the definition of the parameters.

The origin of the reversion of the triplet and singlet states caused by the close intramolecular NO---S contact would be ascribed to the spin-spin repulsion on the sulfur and oxygen atoms. When we look closely insight into each α– and β–spin orbital of the triplet state (Figure 7), we find characteristic feature that α–spins are highly populated in the sulfur atoms to constitute an α-HOMO and below this orbital the spin orbitals of the ON-C-NO radical centers are positioned. As a result of the close NO---S contact, the mixing of the α–HOMO (α-48) with the ON-C-NO orbitals (α–47 and 46) results in raising high the latter orbitals owing to the α-spin - α-spin repulsion on the sulfur and NO moieties. Thus the α–spin populations on the NO-C-NO moieties are deformed to unsymmetrical distribution. The β-spin orbitals exhibited no such remarkable effects as observed in the α-spin orbitals upon the NO---S contact.

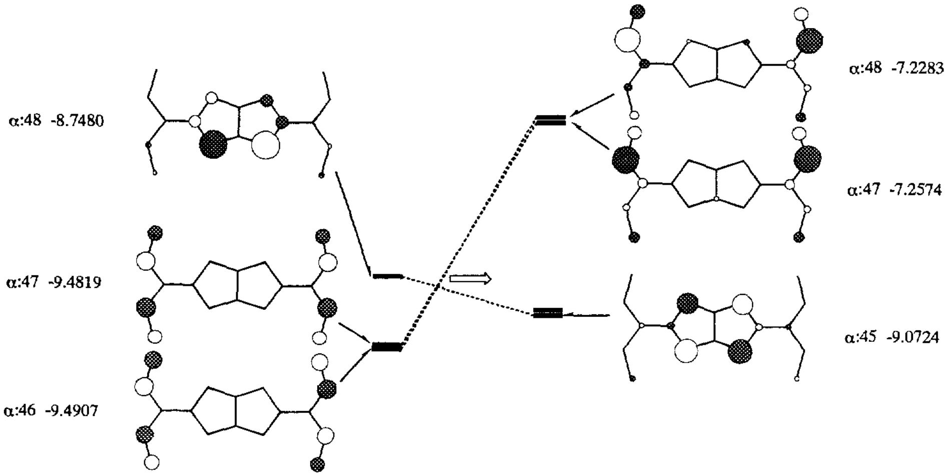


Figure 7. The triplet state α-spin orbitals at 126.9° (left-hand side) and 124.9° (right-hand side), indicating their orbital energies and the interactions.

The question may be arisen; why imino nitroxide diradical **1I** exhibits the exchange interaction more strongly than nitronyl nitroxide diradical **1N** ? These could be interpreted by means of the nodal properties of the SOMO on going from imino nitroxide to nitronyl nitroxide; in nironyl 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 the insufficient spin polarization on the thienothiophene ring moiety. Furthermore, the NO groups situated closely to the sulfur atom can interact strongly to bring about coplanarity of the nitroxide moieties with the thiophene ring, ensuring effectively the spin polarization to the ring.[13] As discussed above, in such situation the stronger intramolecular NO---S interactions is expected for the imino nitroxide than for the nitronyl nitroxide, since the spin density is concentrated in one NO group for imino nitroxide, whereas for nitronyl nitroxide the spin is shared by the two NO groups.

EXPERIMENTAL SECTION

2,5-Bis(4,4,5,5-tetramethyl-1-oxyl-3-oxide-imidazoline-2-yl)thieno[2,3-*b*]thiophene (1N). A mixture of 0.30 g of 2,5-diformylthieno[2,3-*b*]tiophene and 1.35 g of 2,3-bis(hydroxyamino)-2,3-

dimethylbutane was refluxed in 120 ml of benzene for 24 hour under nitrogen. After evaporation of the solvent in *vacuo*, the residue was dissolved in 300 ml of chloroform and treated with 5.0 g of sodium periodate in 300 ml of water for 5 minute. The organic phase was washed twice with water, dried with magnesium sulfate, and then the solvent was evaporated. The residual solids were chromatographed on silica gel with chloroform as an eluent to give blue solids, which were further purified by GPC (gel permeation chromatography) and recrystallization from chloroform-hexane to give 80 mg (15%) of **1N** as green needles. m.p.217 °C (decomp.) ; λ_{max} [CH_2Cl_2/nm (ε)] 729.6 (900), 660.4 (1300), 604.4 (900), 558.4 (400), 385.4 (16000), 319.2 (34000), 301.0 (32000), 241.8 (12000); m/z 450 (M^+). Anal. Calcd for $C_{20}H_{26}N_4O_4S_2$: C, 53.31; H, 5.82; N, 12.43; S, 14.23. Found: C, 53.42; H, 5.82; N, 12.15; S, 14.23.

2,5-Bis(4,4,5,5-tetramethyl-1-oxyl-imidazoline-2-yl)thieno[2,3-*b*]thiophene (**1I**). A solution of 0.50 g of **1N** in 200 ml of chloroform and 0.30 g of sodium nitrite in 200 ml of water was shaken with a drop of acetic acid vigorously for 5 minutes. After a work-up similar as described for **1N**, the red residue was chromatographed on silica gel with chloroform to give 0.39 mg (85%) of **1I** as red needles. The sample for magnetic measurements were further purified by recrystallization from chloroform-hexane. m.p. 224-230 °C; λ_{max} [CH_2Cl_2/nm (ε)] 509.0 (1300), 269.8(43000); m/z 418(M^+). Anal. Calcd for $C_{20}H_{26}N_4O_4S_2$: C, 57.38; H, 6.26; N, 13.39; S, 15.33. Found: C, 57.08; H, 6.23; N, 13.26; S, 15.32.

2,5-Bis(4,4,5,5-tetramethyl-1-oxyl-3-oxide-imidazoline-2-yl)thieno[2,3-*b*]thieno[3',2'-*d*] thiophene (**2N**). A mixture of 0.37 g of 2,5-diformylthieno[2,3-*b*]thieno[3',2'-*d*]tiophene and 2.10 g of 2,3-bis(hydroxyamino)-2,3-dimethylbutane in 100 ml of methanol was refluxed for 15 hour. After cooling the reaction mixture down to room temperature, colorless precipitate was filtered. The filtrate was dissolved in 150 ml of chloroform and reacted with 2.5 g of sodium periodate in 100 ml of water. After a work-up, green residue was chromatographed on silica gel with dichloromethane-chloroform to give 0.19 mg (40%) of **2N** as green needles, which were further recrystallized from chloroform. m.p.179°C (decomp.); λ_{max} [CH_2Cl_2/nm (ε)] 734.8, 664.0 (1100), 607.2 (720), 389.0 (9400), 338.4 (37000), 241.0 (24000); m/z 506 (M^+). Anal. Calcd for $C_{22}H_{26}N_4O_4S_3$: C, 52.15; H, 5.17; N, 11.06; S, 18.99. Found: C, 52.25; H, 5.37; N, 10.98; S, 18.66.

2,5-Bis(4,4,5,5-tetramethyl-1-oxyl-imidazoline-2-yl)thieno[2,3-*b*]thieno[3',2'-*d*]-thiophene (**2I**). **2I** was prepared in an almost quantitative yield from **2N** in a similar procedure as described for **1I**. m.p.179°C (decomp.); λ_{max} [CH_2Cl_2/nm (ε)] 523.2 (750), 303.6 (15000), 291.6 (15000), 238.0 (22000); m/z 474 (M^+). Anal. Calcd for $C_{22}H_{26}N_4O_4S_3$: C, 55.07; H, 5.52; N, 11.80; S, 20.27. Found: C, 55.43; H, 5.65; N, 11.57; S, 19.72.

ESR measurement. The spectra were recorded on JEOL JES-RE2X equipped with Air Products LTR 5500 cryostat, the sample temperature being measured with a Au+Fe-Chromel thermocouple.

Magnetic susceptibility measurement. The data for **1N** and **2I** in PVC films were obtained on a Quantum Design MPMS2 SQUID susceptometer in the temperature range 2~300 K.

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11. For the same reason as noted in reference 10, the π–conjugated system involved in **2 N** and **2I** is regarded as HMB. However, when we consider their spin systems, the framework of HMB corresponds to that of tetramethyleneethane (TME) by taking into account the disjointed and nodal properties of the Hückel nonbonding MO.
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