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Intramolecular Spin-Spin Exchange in Cation Radicals of Tetrathiafulvalene Derivatives Substituted with Imino Pyrolidine- and Piperidine-1-oxyls

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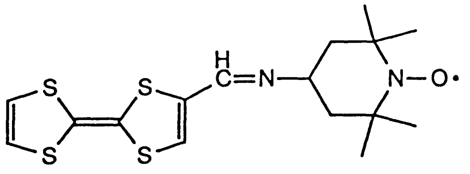
The ESR spectra of tetrathiafulvalene (TTF) derivatives substituted with imino pyrolidine- and piperidine-1-oxyls and their cation radicals were investigated. For the neutral TTF's the unpaired electron is localized at the nitroxide group. While, an intramolecular spin-spin exchange albeit weak occurs between the TTF cation radical and the nitroxide radical in the one-electron oxidized TTF's, and the ground spin state of the biradical is a singlet.

In charge-transfer (CT) complexes and cation (anion) radical salts made of donors (acceptors) bearing a radical substitutent there is a possiblity of aligning spins of the radical substituents by virtue of antiferromagnetic interaction between donor and acceptor spins in an alternate CT stack[1]) and also through interaction with an itinerant electron in a segregated CT stack of donor and acceptor or in a cation (anion) radical stack in a mixed-valence state.[2]) If three-dimensional spin alignment can be attained by the two approaches, then one will realize the dreams of unprecedented organic ferrimagnets and organic ferromagnetic metals. Several attempts have so far been made, but there is no success in purely organic systems.[3]) We were interested in tetrathiafulvalene (TTF) joined through σ-bond with a stable nitroxide compound as a donor with a radical substituent, which has advantages of preserving a comparable donating-ability with that of TTF itself as well as of not interferring a contact with an acceptor in the CT complexes and also with the cation radical. Prior to studying the magnetic properties of the CT complexes and cation radical salts, we need to realize an intramolecular spin-spin exchange between the nitroxide radical and the TTF cation radical. The TTF derivative substituted with 4-imino-2,2,6,6-



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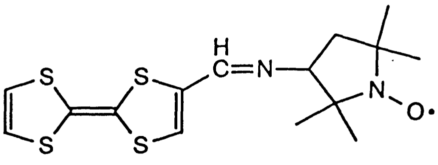

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tetramethylpiperidine-1-oxyl (**1**) has been very recently synthesized by Kinoshita and Sugano.[4] In addition to this a new TTF derivative substituted with 3-imino-2,2,5,5-tetramethylpyrolidine-1-oxyl (**2**) was now obtained, in which the nitroxide center is more close to the TTF core. In this report we show the results on the spin-spin exchange between the two unpaired electrons in cation radicals of **1** and **2** ($\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$), the ground spin state of the biradical, and the magnitude of the exchange integral.

The synthesis of **2** was carried out in a similar manner to that of **1**.[4] Thus, monoformyl-substituted TTF[5] was reacted with 3-amino-2,2,5,5-tetramethylpyrolidine-1-oxyl (3 equiv.) in ethanol containing a small amount of acetic acid (0.8 equiv.) at r.t. to give **2** in 75% yield after separation by basic alumina column chromatography with a CH_2Cl_2 eleuent. On the other hand, **1** was obtained in 66% yield.

The ESR spectra of **1** and **2** were measured in *n*-heptane at r.t. As shown in Fig. 1a,b, three signals with an equal intensity due to hyperfine splitting with the nitrogen-14 atom appear (the constants are 15.53 G for **1** and 14.40 G for **2**), and furthermore each signal is splitted by the methyl carbon-13 atoms. For **1** further splitting due to the methyl hydrogen atoms makes the spectrum more complicated. The computer-simulation of the spectrum of **2** was carried out, and the spectrum obtained by using the following hyperfine splitting constants well reproduced the observed one: $a(^{14}N)=14.40$ G, $a(^{13}C)=2.65$, 1.95 G (1.11% relative intensity), $a(^{15}N)=18.45$ G (the interval between two star marks, 0.36% relative intensity). These results show that the unpaired electron is almost localized at the nitroxide group.

The electron-donating ability of **1** and **2** in comparison with that of TTF itself was estimated using cyclic voltammetry. The cyclic voltammograms of **1** and **2** measured in CH_2Cl_2 containing a supporting electrolyte, $(n\text{-}Bu)_4NBF_4$ at r.t., showed three pairs of reversible waves, and the respective redox potentials were +0.57, +0.88 and +0.92 V vs. SCE for **1**, and +0.56, +0.90 and +0.92 V vs. SCE for **2**. The redox process with a most positive value (+0.92 V) can be reasonably ascribed to that of the nitroxide group from comparison with those of simple nitroxide compounds. Accordingly, the remaining two redox processes are due to that of the TTF moiety. The redox potentials are slightly more positive than those of TTF (+0.49 and +0.82 V vs. SCE), suggesting that **1** and **2** possess almost comparable electron-donating ability to that of TTF.

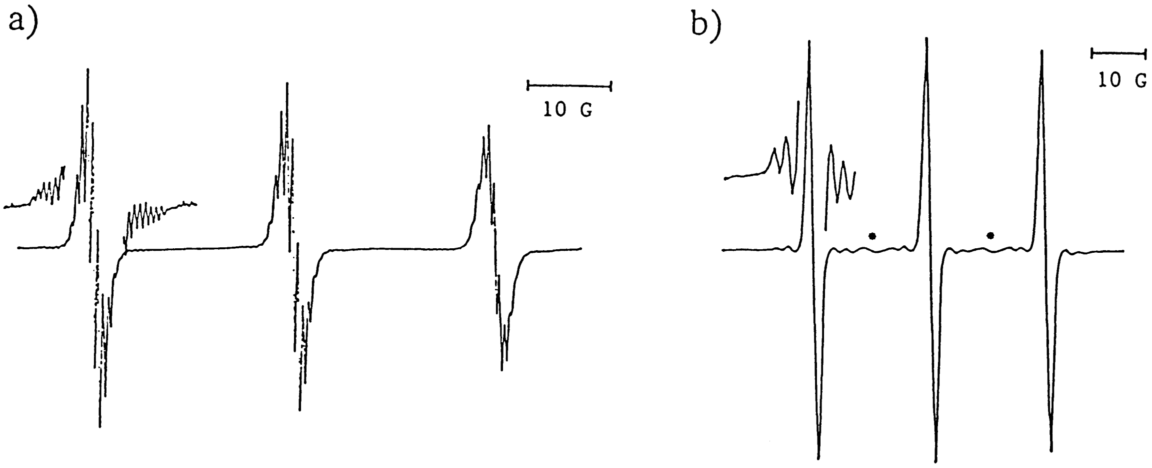

Fig. 1. The ESR spectra of (a) **1** and (b) **2** measured in *n*-heptane at r.t. The g values are 2.0071 and 2.0067, respectively.

As is obvious from the above redox results, the oxidation of **1** and **2** first of all occurs at the TTF moiety. Indeed, **1** and **2** were treated with an excess of iodine, a weak oxidizing agent in chlorobenzene, and the corresponding radical cations were isolated as iodide salts ($\mathbf{1}^{+\cdot}\cdot I_3^-$ and $\mathbf{2}^{+\cdot}\cdot I_3^-$).[6] The ESR spectra measured in highly dilute CH_3CN solutions at r.t. are shown in Fig. 2a,b. In each case only three signals with an equal intensity were observed (the other weak three signals shown by arrow marks are due to **1** and **2** produced by the reaction with some reducing compound involved in CH_3CN). The hyperfine splitting constants of $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ are 7.84 and 7.25 G, respectively, almost a half of the values of **1** and **2** (15.53 and 14.40 G), indicating the presence of an intramolecular spin-spin exchange between the TTF cation radical and the nitroxide radical. The

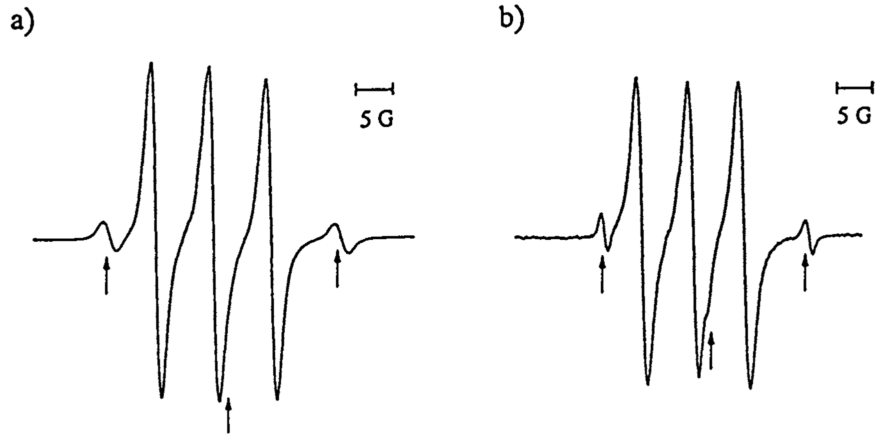

Fig. 2. The ESR spectra of (a) $\mathbf{1}^{+\cdot}\cdot I_3^-$ and (b) $\mathbf{2}^{+\cdot}\cdot I_3^-$ measured in CH_3CN at r.t. The g values are 2.0078 and 2.0079, respectively.

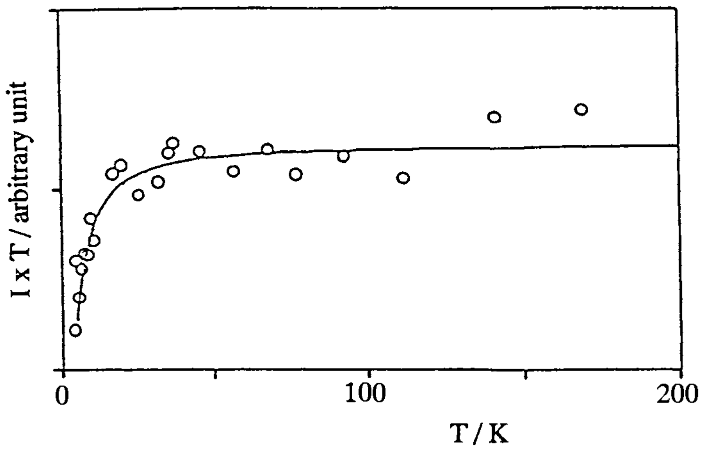

Fig. 3. The temperature (T) dependence of the ESR signal intensity (I) x T in the range of 4 to 180 K for $\mathbf{1}^{+\cdot}\cdot I_3^-$. The line shows a theoretical I x T vs. T behavior obtained with a value of 30 cal/mol as a singlet-triplet energy difference in a Bleaney-Bowers equation.

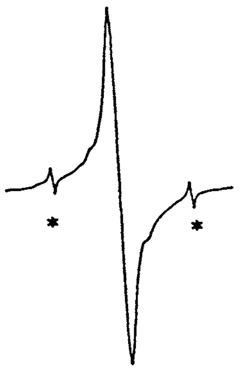

Fig. 4. The ESR spectrum of a frozen CH_3CN solution of $\mathbf{1}^{+\cdot}\cdot I_3^-$ measured at 180 K. The star marks show signals due to an external reference of Mn^{2+} near the sample signal.

similar phenomena were also recognized in the mixed galvinoxyl/nitroxide systems.7) Such a spectral pattern can be attained when the relative magnitude of the spin-spin exchange integral is exceedingly large as compared to the hyperfine interaction. In addition, for instance the highly dilute CH_3CN solution of $\mathbf{1}^{+\cdot}\cdot I_3^-$ was frozen and the temperature (T) dependence of the signal intensity (I)8) was investigated between 4 and 180 K. The analysis of the I x T vs.T behavior (see Fig. 3) by using a Bleaney-Bowers equation9) showed that the ground state is a singlet and its thermally-accessible triplet lies by ca. 30 cal/mol at higher energy.10) On the way of measurement two weak signals appeared at both shoulders of the central signal (see Fig. 4), and the intensity increased as raising the temperature. The interval between the signals, 32.4 G, corresponds to 2D, where D is a zero-field splitting parameter defining a fine structure of the biradical. By assuming a point dipole approximation the distance between the two interacting spins was estimated to be ca. 12 A, being very close to that between the TTF moiety and nitroxide group.

Eventually, **1** and **2** are expected as a suitable donor for the formation of alternate-stack CT complexes with spin alignment of the radical substituents, if an appropriate acceptor is chosen so as to maintain an intramolecular spin-spin exchange between the TTF cation radical and the nitroxide radical. Their segregated-stack CT complexes and cation radical salts in a mixed valence state might also serve as a suitable model in studying an interaction between an itinerant electron and a local spin.

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