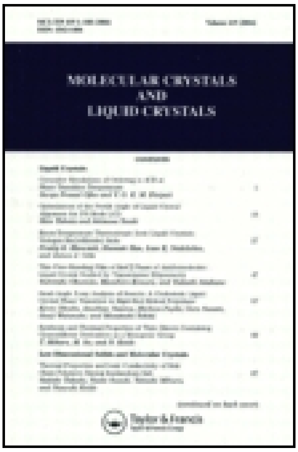

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Ferromagnetic Interaction in Organic Radical Ion Salts

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FERROMAGNETIC INTERACTION IN ORGANIC RADICAL ION SALTS

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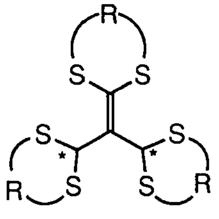
Abstract The *N*-methylated and/or *N*-ethylated I^- and BF_4^- salts of 2-(3-pyridyl)- (**2**(*m*)) and 2-(4-pyridyl)-4,4,5,5-tetramethylnitronylnitroxides (**2**(*p*)), and 2-(4-pyridyl)-4,4,5,5-tetramethylimidazolin-1-oxyl (**3**(*p*)), and also the radical cation/radical anion salts obtained by the exchange reaction of I^- and BF_4^- in the above radical cation salts with radical anions of TCNQ, $TCNQF_4$ and HCBD were synthesized, and their paramagnetic susceptibilities (χ_{para}'s) were measured in the temperature range of 2 (or 5) - 300 K. As shown from the $\chi_{para}\cdot T$ vs. T plots, among the radical cation and radical cation/radical anion salts **2**(*m*)-$Me^{+}\cdot(TCNQ_2)^{-\cdot}$, **2**(*m*)-$Me^{+}\cdot TCNQF_4^{-\cdot}$, **3**(*p*)-$Me^{+}\cdot TCNQF_4^{-\cdot}$ and **3**(*p*)-$Me^{+}\cdot HCBD^{-\cdot}$ exhibited ferromagnetic interaction. The $\chi_{para}\cdot T$ value almost equal to S=1/2 at r.t. and the production of the thermally-accessible triplet suggest that the ferromagnetic interaction comes from that between the radical cations as a result of dimer formation of the radical anions. Nevertheless, the radical anion also plays a crucial role as a partner in the tight contact and/or the ferromagnetic interaction between the radical cations.

INTRODUCTION

Ferromagnetism in organic system remains to be not sufficiently elucidated, and continues to become a challenging subject for a number of chemists in several fields.[1] Many theoretical models have been proposed for obtaining ferromagnetically interacting spins in organic solids. Especially, two models proposed by McConnell, "spin polarization"[2] and "charge-transfer (CT) configurational admixing"[3] mechanisms, serve as a practical guiding principle for the production of molecular/organic ferromagnets. Very recently, with guidance from the first McConnell's mechanism a first purely organic s/p orbital-based ferromagnet has been accomplished in the β-phase crystals of a stable organic radical, 2-(4-nitrophenyl)-4,4,5,5-tetramethylnitronylnitroxide.[4] The extensive experimental efforts based on the second McConnell's mechanism have been also pursued in purely organic CT complexes,[5,6] but it is so far without avail. Nevertheless, several organometallic CT complexes exhibiting ferromagnetic behavior have been reported recently, which involve decamethylferrocenium tetracyanoethanide and its related manganese and chromium derivatives.[7-10] For the CT complexes the molecular arrangement of alternating donors and acceptors in a stack as well as the orbital pattern for a donor - acceptor pair provide prerequisites for the application of this mechanism. A critical discussion of the role of CT processes for the ferromagnetic interaction in these CT complexes has been however presented,[11] and even a different model based on the first McConnell's mechanism has been suggested.[10,12-14]

We have very recently recognized the ferromagnetic behavior in the CT complexes of hexathio-substituted trimethylenemethane dication (1^{2+})[15] with tetrafluoro-substituted TCNQ (TCNQF4) and hexacyano-trimethylene cyclopropane dianions.[16] This provides the second example

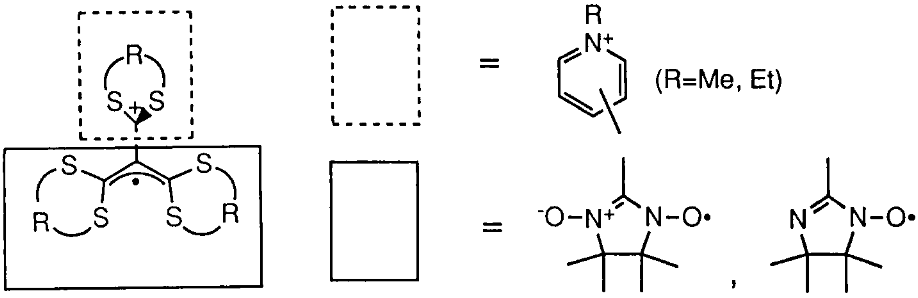


1^{2+} : *=+, +

$1^{+\bullet}$: *=+, •

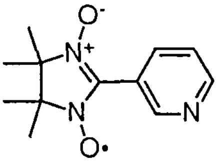
R=ethylene, benzo

following the CT complex between C_{60} and tetrakis(dimethylamino)-ethylene.[17] Based on the molecular structure of the tris(1,2-benzodithio)-substituted $\mathbf{1}^{2+}$, where the (1,3-benzodithiol-2-ylidene)-1,3-benzodithiolium moiety takes almost a plane and one more 1,3-benzodithiolium group is largely twisted from the plane, we suggested that the first McConnell's mechanism might operate on the ferromagnetic interaction. In order to confirm this possiblity and also to search another ferromagnetic CT complex, we were interested in two new radical cations, pyridinium-substituted nitronylnitroxide and imidazolin-1-oxyl, which have a resemblance to the trimethylenemethane radical cation ($\mathbf{1}^{+\cdot}$) in the electronic structure, but are very stable compared with $\mathbf{1}^{+\cdot}$. In this study we report the synthesis of the radical cation and radical cation/radical anion salts and their magnetic properties.

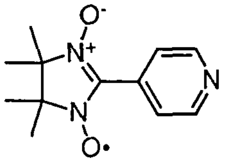


SYNTHESIS OF 2-(3- OR 4-PYRIDYL)-4,,4,5,5-TETRAMETHYLNITRONYLNITROXIDE AND -IMIDAZOLIN-1-OXYL AND THEIR *N*-ALKYLATED SALTS

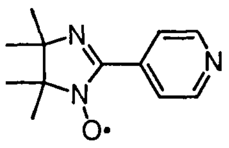
The three radicals, 2-(3-pyridyl)- and 2-(4-pyridyl)-4,4,5,5-tetramethylnitronylnitroxides ($\mathbf{2}(m)$ and $\mathbf{2}(p)$), and 2-(4-pyridyl)-4,4,5,5-tetramethylimidazolin-1-oxyl ($\mathbf{3}(p)$) were synthesized according to literatures,[18,19] and after recrystallization the pure crystals were obtained. *N*-Methylation of $\mathbf{2}(m)$ and $\mathbf{2}(p)$ was readily completed by the reaction with methyl iodide ($\mathbf{2}(m)$-$\mathrm{Me}^{+}\cdot\mathrm{I}^{-}$ and $\mathbf{2}(p)$-$\mathrm{Me}^{+}\cdot\mathrm{I}^{-}$). In spite of two possible alkylation sites for $\mathbf{3}(p)$, nitrogen atoms of imidazolin-1-oxyl and pyridine rings, methylation and ethylation with use of methyl and



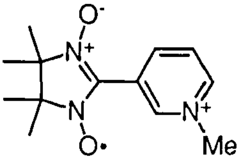
2(*m*)



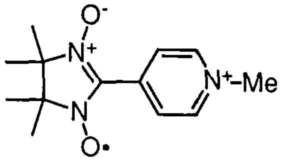
2(*p*)



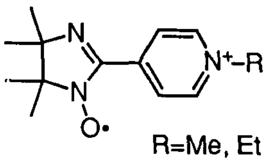
3(*p*)



2(*m*)-Me$^+$

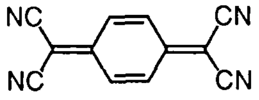


2(*p*)-Me$^+$

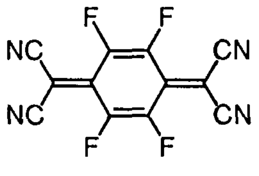


3(*p*)-R$^+$

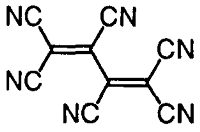
ethyl iodides and also trimethyloxonium tetrafluoroborate took place selectively at the latter nitrogen atom (**3**(*p*)-Me$^+$·I$^-$, **3**(*p*)-Et$^+$·I$^-$ and **3**(*p*)-Me$^+$·BF$_4^-$). The exchange reaction of I$^-$ and BF$_4^-$ with radical anions of TCNQ, TCNQF$_4$ and hexacyanobutadiene (HCBD) (TCNQ$^{-\cdot}$, TCNQF$_4^{-\cdot}$ and HCBD$^{-\cdot}$) was accomplished by mixing respective solutions of **2**(*m*)-Me$^+$·I-, **2**(*p*)-Me$^+$·I$^-$, **3**(*p*)-Me$^+$·I$^-$ or **3**(*p*)-Et$^+$·I$^-$ and a lithium salt of TCNQ$^{-\cdot}$, TCNQF$_4^{-\cdot}$ or HCBD$^{-\cdot}$ in equal concentrations and the corresponding radical cation/radical anion salts were obtained. The elemental analyses showed that the TCNQ$^{-\cdot}$ salts have a composition of 2:1 with **2**(*m*)-Me$^+$, **2**(*p*)-Me$^+$ and **3**(*p*)-Me$^+$, i.e., **2**(*m*)-Me$^+$ (**2**(*p*)-Me$^+$ or **3**(*p*)-Me$^+$)· (TCNQ$_2$)$^{-\cdot}$, while for all the TCNQF$_4^{-\cdot}$ and HCBD$^{-\cdot}$ salts the composition is 1:1, i.e., **2**(*m*)-Me$^+$ (**2**(*p*)-Me$^+$ or **3**(*p*)-Me$^+$)·TCNQF$_4^{-\cdot}$ and **2**(*m*)-Me$^+$ (**2**(*p*)-Me$^+$ or **3**(*p*)-Me$^+$)·HCBD$^{-\cdot}$. For the TCNQ$^{-\cdot}$ salts two different CN stretching frequencies appeared, which



TCNQ



TCNQF$_4$



HCBD

correspond to those of TCNQ and $TCNQ^{-}\cdot$, respectively. On the other hand, for each of the $TCNQF_4^{-}\cdot$ and $HCBD^{-}\cdot$ salts only one CN stretching due to $TCNQF_4^{-}\cdot$ or $HCBD^{-}\cdot$ was observed.

X-RAY STRUCTURE OF **3**(*p*)-$Me^{+}\cdot BF_4^{-}$

The recrystallization of I^{-}, BF_4^{-} of **3**(*p*)-Me^{+} and of the radical anion salts of **2**(*m*)-Me^{+}, **2**(*p*)-Me^{+} and **3**(*p*)-Me^{+} from several solvents was attempted, whose single crystals are subjected to X-ray structure analysis in order to elucidate not only the molecular structures of the radical cations, but also the respective contacts between the radical cations and between the radical cation and radical anion. As a result of a number of attempts only single crystals of **3**(*p*)-$Me^{+}\cdot BF_4^{-}$ were till now obtained. obtained. The molecular structure and packing structure are depicted in Figures 1 and 2, respectively. The *N*-methylpyridinium ring is twisted by 20° from the imidazolin-1-oxyl ring. The dihedral angle is comparable to those of 2-(4-nitrophenyl)-4,4,5,5-tetramethylnitronylnitroxide in the α– and γ-phase crystals,[20,21] indicating a close resemblance in the molecular structure as well as in the electronic structure between **3**(*p*)-Me^{+} and the neutral radical. As is seen from Figure 2, there is no contact between the neighboring **3**(*p*)-Me^{+}'s. Even the shortest contact has a long distance of 4.88 Å. The magnetic properties of the crystals are expected to be paramagnetic, and in fact it was just so, as mentioned later. On the other

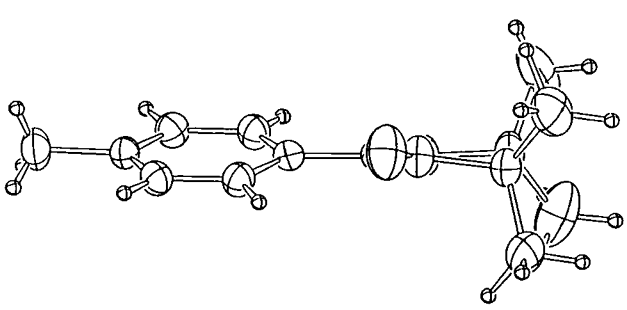


FIGURE 1 The molecular structure of **3**(*p*)-$Me^{+}\cdot BF_4^{-}$ (the anion is omitted).

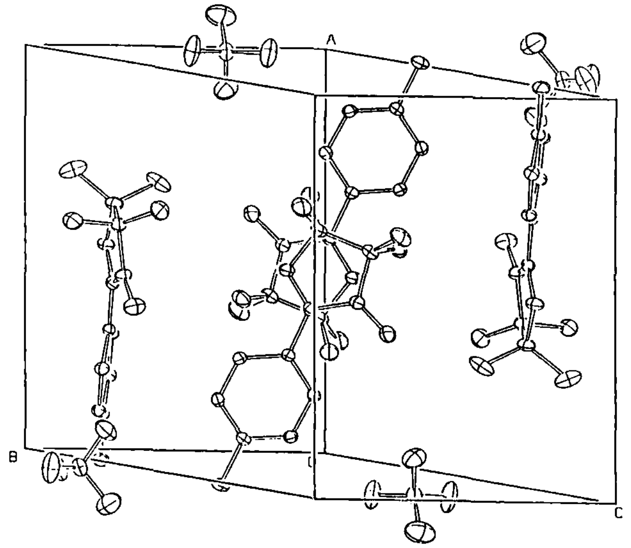


FIGURE 2 The packing structure of 3(p)-Me$^+$·BF$_4^-$.

hand, 3(p)-Me$^+$ is in comparatively tight contact with BF$_4^-$ (the shortest distance is 2.91 Å). If the anion could be replaced by an appropriate radical anion without changing the crystal structure, it might be possible to observe significant spin interaction between 3(p)-Me$^+$ and the radical anion.

ESR AND ENDOR SPECTRA OF 3(p) and 3(p)-Me$^+$·I$^-$

The ESR and ENDOR spectra of 3(p) and 3(p)-Me$^+$·I$^-$ were measured and the unpaired-electron density distribution on the molecules was determined based on the observed hyperfine coupling constants (hfcc's) due to hydrogen and nitrogen atoms. Figure 3a shows the ESR spectrum of 3(p) in n-heptane at r.t., and seven signals appear, whose hfcc's due to two different nitrogen atoms are 8.69 G and 4.30 G, respectively. The quite similar spectrum was also observed for 3(p)-Me$^+$·I$^-$ in CH$_2$Cl$_2$ at r.t. (see Figure 3b): the hfcc's are 8.89 G and 4.20 G, respectively, suggesting attachment of methyl group to the pyridyl nitrogen atom. The

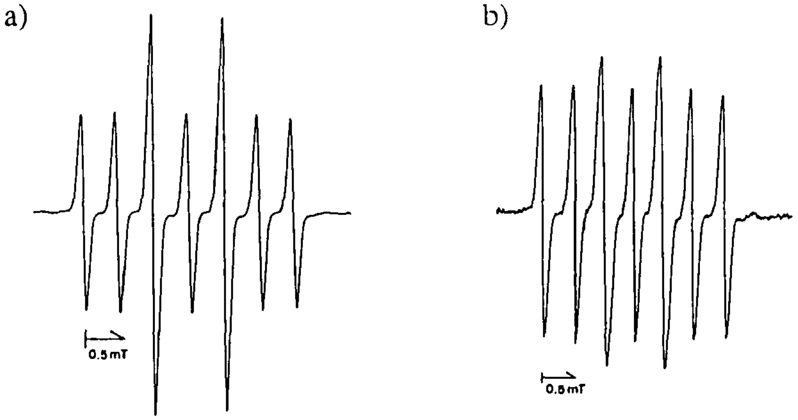


FIGURE 3 The ESR spectra of (a) **3**(*p*) in *n*-heptane at r.t. and (b) **3**(*p*)-$Me^+ \cdot I^-$ in CH_2Cl_2 at r.t..

more accurate values of hfcc's were determined by the ENDOR measurement. The spectra of **3**(*p*) in *n*-heptane at -85 °C and of **3**(*p*)-$Me^+ \cdot I^-$ in methanol at -50 °C, respectively, are shown in Figures 4a and 4b. In addition to the hfcc's due to nitrogen atoms, 8.65 G and 4.46 G for **3**(*p*), and 8.56 G and 4.68 G for **3**(*p*)-$Me^+ \cdot I^-$, respectively, the hfcc's due to hydrogen atoms of methyl groups were also obtained: 0.20 G for **3**(*p*) and 0.18 G for **3**(*p*)-$Me^+ \cdot I^-$, respectively. By using a McConnell's

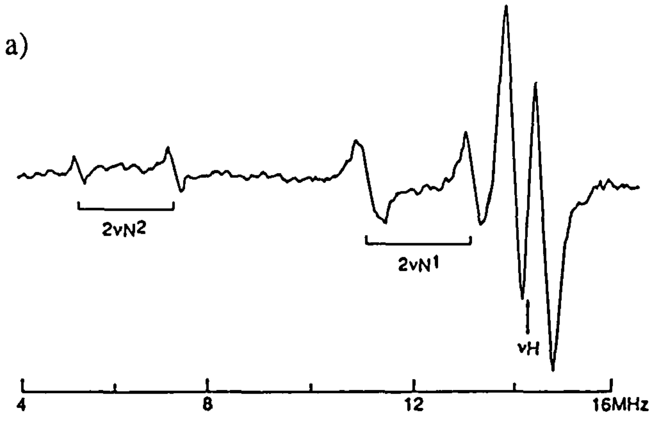


FIGURE 4a The ENDOR spectrum of **3**(*p*) in *n*-heptane at -85 °C.

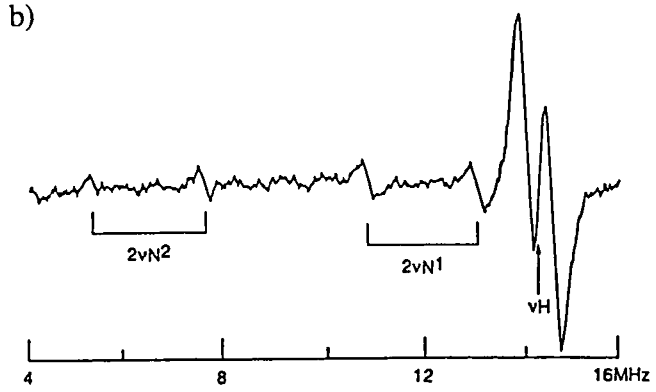


FIGURE 4b The ENDOR spectrum of **3**(*p*)-$Me^+ \cdot I^-$ in methanol at -50°C.

equation, hfcc=Q·ρ, where Q is 33.1 G for a nitrogen atom[22] and ρ is the unpaired-electron density, the ρ values on the nitrogen atoms were calculated to be 0.261 and 0.292 for **3**(*p*), and 0.259 and 0.306 for **3**(*p*)-$Me^+ \cdot I^-$. The values are close to those obtained for the already known phenyl analogue, 0.276 and 0.278. The McLachlan calculations well reproduce the experimental result[23] and also indicate the presence of a negative spin density on the carbon between the two nitrogen atoms albeit in a very small amount compared with that of the corresponding nitronylnitroxide.

MAGNETIC PROPERTIES OF 3(*p*) AND 3(*p*)-$R^+ \cdot X^-$ (R=Me, Et; X=I, BF_4)

The magnetic properties of crystals of **2**(*m*), **2**(*p*), **2**(*m*)-$Me^+ \cdot I^-$ and **2**(*p*)-$Me^+ \cdot I^-$ have been already investigated by Awaga et al..[24] The ferromagnetic interaction was recognized for **2**(*p*) and **2**(*m*)-$Me^+ \cdot I^-$. Accordingly, we now investigated the magnetic properties of the crystals of **3**(*p*), **3**(*p*)-$Me^+ \cdot I^-$, **3**(*p*)-$Me^+ \cdot BF_4^-$ and **3**(*p*)-$Et^+ \cdot I^-$. The magnetic susceptibility (χ_{obs}) was measured in the temperature range of 5 (or 2) - 300 K by use of SQUID method. The paramagnetic susceptibility ($\chi_{para} = \chi_{obs} - \chi_{dia}$) was obtained by substracting the diamagnetic contribution

(χ_{dia}) estimated from Pascal's atomic susceptibility values from χ_{obs}. Figures 5 and 6 show the temperature (T) dependence of the product of χ_{para} and T (χ_{para}·T) for **3**(*p*), **3**(*p*)-$Me^+ \cdot I^-$ and **3**(*p*)-$Me^+ \cdot BF_4^-$, and

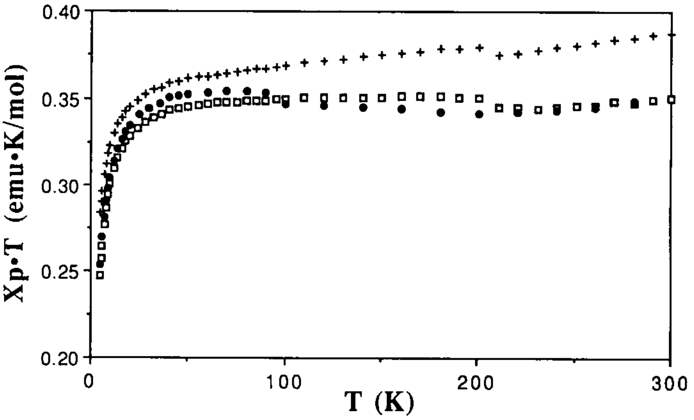


FIGURE 5 The χ_{para}·T vs. T plots for **3**(*p*) (●), **3**(*p*)-$Me^+ \cdot I^-$ (+) and **3**(*p*)-$Me^+ \cdot BF_4^-$ (□).

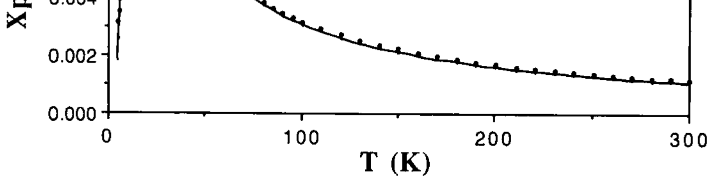


FIGURE 6 The χ_{para} vs. T plot for **3**(*p*)-$Et^+ \cdot I^-$.

the χ_{para} - T plot for **3**(*p*)-$Et^{+}\cdot I^{-}$, respectively. For all the former three salts weak antiferromagnetic interaction preferentially occurs below 10 K. The Weiss constants (θ's) are -2.5 K, -2.7 K and -1.6 K, respectively. This magnetic result can be readily understood from the packing structure of **3**(*p*)-$Me^{+}\cdot BF_4^{-}$ (see Figure 2), where there is no close contact between any parts of the neighboring molecules (even the distance of nearest contact is 4.88 Å).

On the other hand, the latter **3**(*p*)-$Et^{+}\cdot I^{-}$ salt revealed a bell-shaped curve with a maximum at ca. 20 K in the χ_{para} - T plot. This is a typical χ_{para} - T behavior of a ground-state singlet in equilibrium with its thermally-accessible triplet. Now, when in a Bleaney - Bowers equation,[25,26] $\chi_{para} = N_d g^2 \mu_B{}^2 \cdot 1(1+1)/\{3kT(1+1/3\exp(\Delta E/kT))\}$, N_d (the amount of a dimer) and ΔE (the energy gap between a ground-state singlet and its thermally-accessible triplet) are put 2.9 x 10^{23} molecules/mol (96% purity) and 49.2 cal/mol, respectively, the calculated χ_{para} - T curve is reasonably consistent with the observed one (see Figure 6). From this result it is presumed that the two neighboring **3**(*p*)-Et^{+}'s are located so close by each other as to bring about interaction between the spins, albeit antiferromagnetically on the contrary to expectation. The detail must be awaited until elucidation of the crystal structure. Nevertheless, it is evident that the packing of **3**(*p*)-R^{+}'s in the crystal can be controlled by choosing a kind of alkyl group (R) on the pyridyl nitrogen atom.

MAGNETIC PROPERTIES OF RADICAL ANION SALTS OF 2(*m*)-Me^{+}, 2(*p*)-Me^{+} and 3(*p*)-R^{+} (R=Me, Et)

The powdered samples of $TCNQ^{-\cdot}$, $TCNQF_4^{-\cdot}$ or $HCBD^{-\cdot}$ salts of **2**(*m*)-Me^{+}, **2**(*p*)-Me^{+} or **3**(*p*)-R^{+} (R=Me, Et), whose single crystals are not yet obtained in all cases, were subjected to magnetic susceptibility measurement by use of SQUID method. Figures 7 - 10 show the plots of $\chi_{para}\cdot T$ vs. T for **2**(*m*)-$Me^{+}\cdot(TCNQ_2)^{-\cdot}$, **2**(*m*)-$Me^{+}\cdot TCNQF_4^{-\cdot}$, **2**(*p*)-$Me^{+}\cdot(TCNQ_2)^{-\cdot}$ and **2**(p)-$Me^{+}\cdot TCNQF_4^{-\cdot}$, respectively. The three main characteristics can emerge from these results. First, the $\chi_{para}\cdot T$ decreases as lowering the temperature, indicating preferential antiferromagnetic interaction, in particular remarkably for **2**(*p*)-$Me^{+}\cdot TCNQF_4^{-\cdot}$. Second, the $\chi_{para}\cdot T$ at r.t. amounts to about a half of the value (0.750 emu·K/mol) calculated on the basis of two S=1/2 spins

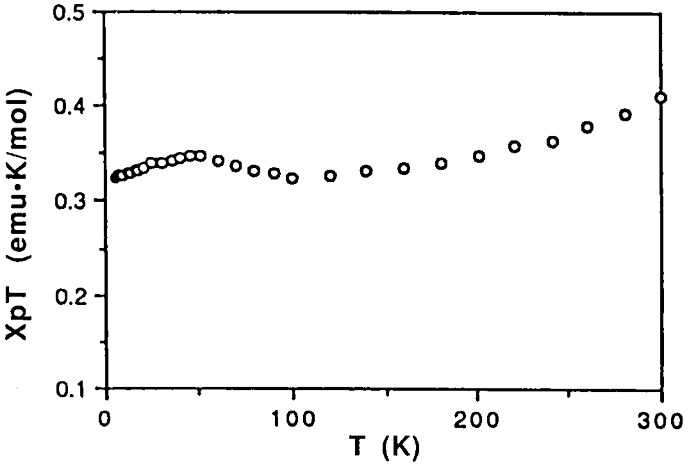


FIGURE 7 The $\chi_{para}\cdot T$ vs. T plot for **2**(*m*)-$Me^{+}\cdot(TCNQ_2)^{-\cdot}$.

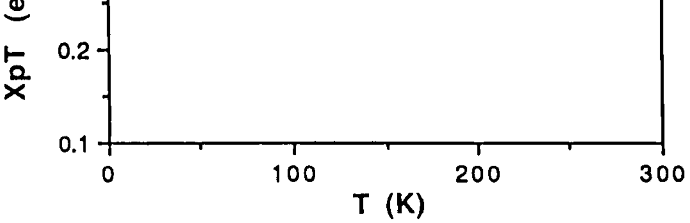


FIGURE 8 The $\chi_{para}\cdot T$ vs. T plot for **2**(*m*)-$Me^{+}\cdot TCNQF_4^{-\cdot}$.

per one molecule of the salt. This can be readily understood by considering that the spin of either the radical cation or radical anion apparently disappears as a result of strong antiferromagnetic interaction

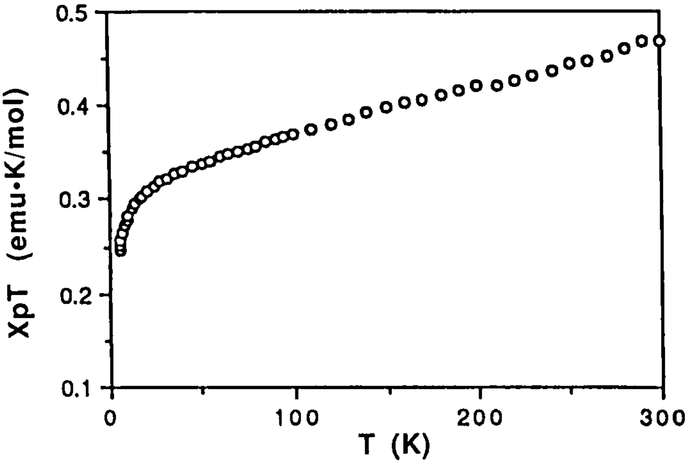


FIGURE 9 The $\chi_{para} \cdot T$ vs. T plot for 2(*p*)-Me$^+ \cdot$(TCNQ2)$^{-\cdot}$.

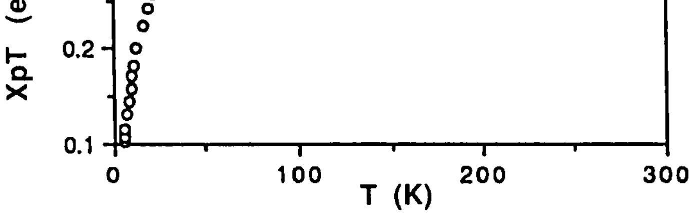


FIGURE 10 The $\chi_{para} \cdot T$ vs. T plot for 2(*p*)-Me$^+ \cdot$TCNQF4$^{-\cdot}$.

with the neighboring spin. In fact, as raising the temperature the χ_{para}·T tends to increase by the production of the thermally-accessible triplet. It is probable that the radical anions prefer to form a dimer in view that there is no observation for the I^- and BF_4^- salts of **2**(*m*)-Me^+ and **2**(*p*)-Me^+ at all. Third, for the $TCNQ^{-\cdot}$ and $TCNQF_4^{-\cdot}$ salts of **2**(*m*)-Me^+ an anomaly was seen in the χ_{para}·T vs. T below ca. 100 K, where there was an increase in the χ_{para}·T till 70 K, but again a gradual decrease as further lowering the temperature from 70 K. It might be likely that the ferromagnetic interaction occurs preferentially in the narrow temperature range between 70 and 100 K.

In a similar manner the magnetic properties of **3**(*p*)-Me^+·$(TCNQ_2)^{-\cdot}$, **3**(*p*)-Me^+·$TCNQF_4^{-\cdot}$, **3**(*p*)-Me^+·$HCBD^{-\cdot}$ and **3**(*p*)-Et^+·$TCNQF_4^{-\cdot}$ were investigated. The χ_{para}·T vs. T plots are shown in Figures 11 - 14, respectively. For **3**(*p*)-Me^+·$(TCNQ_2)^{-\cdot}$ and **3**(*p*)-Et^+·$TCNQF_4^{-\cdot}$ the first two characteristics as mentioned above are also included, i.e., weak antiferromagnetic interaction between the radical anions and production of a thermally-accessible triplet of the ground-state singlet radical anion dimer. The latter phenomenon was also recognized for **3**(*p*)-

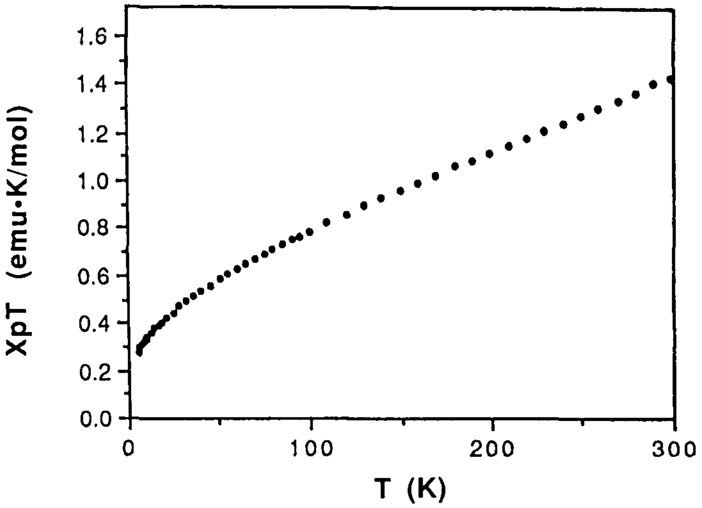


FIGURE 11 The χ_{para}·T vs. T plot for **3**(*p*)-Me^+·$(TCNQ_2)^{-\cdot}$.

$Me^+ \cdot TCNQF4^- \cdot$ and **3**(*p*)-$Me^+ \cdot HCBD^- \cdot$. In particular, for **3**(*p*)-$Me^+ \cdot HCBD^- \cdot$ there is almost no production of the thermally-accessible triplet in the temperature range of 10 - 300 K because of a tight dimer formation between the $HCBD^- \cdot$'s. To be noted, the two radical ion salts indeed exhibited such a ferromagnetic interaction as expected. Thus,

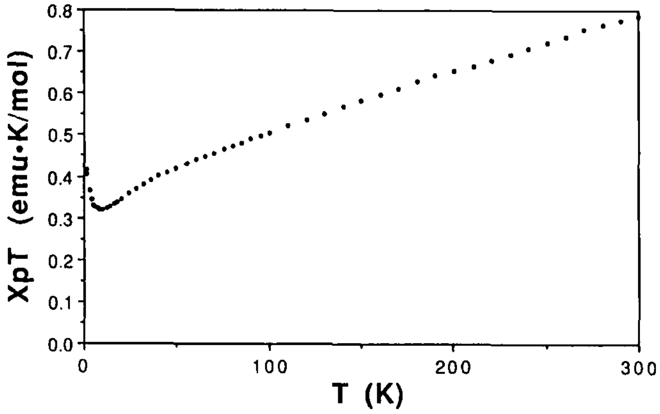


FIGURE 12 The $\chi_{para} \cdot T$ vs. T plot for **3**(*p*)-$Me^+ \cdot TCNQF4^- \cdot$.

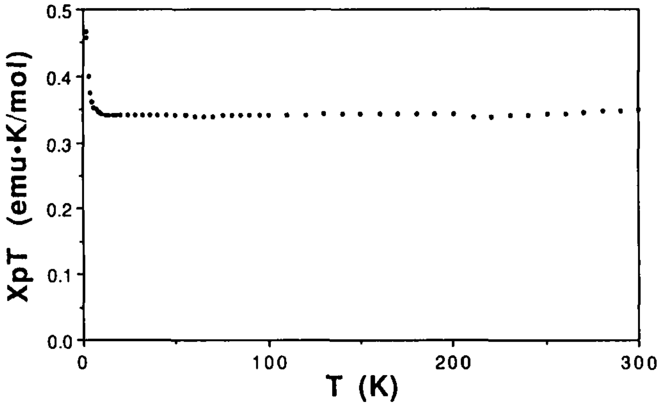


FIGURE 13 The $\chi_{para} \cdot T$ vs. T plot for **3**(*p*)-$Me^+ \cdot HCBD^- \cdot$.

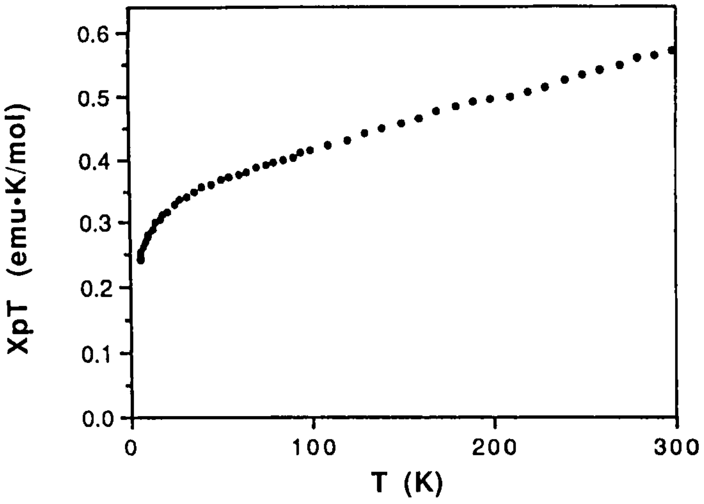


FIGURE 14 The $\chi_{para} \cdot T$ vs. T plot for 3(*p*)-Et^{+}·TCNQF4^{-}·.

below 10 K the $\chi_{para} \cdot T$ increased sharply, as also demonstrated by a positive sign in the θ value: +0.53 K for 3(*p*)-Me^{+}·TCNQF4^{-}· and +0.59 K for 3(*p*)-Me^{+}·HCBD^{-}·, respectively. The field (H) dependence of the magnetization (M) was measured at 2.0, 5.0 and 10.0 K, respectively, for 3(*p*)-Me^{+}·HCBD^{-}·. Figure 15 shows the plots of M/Ms (saturation M) vs. H/T. Obviously, M/Ms approaches to saturation more rapidly with a decrease of T between 2 and 5 K, indicating that the magnitude of the ferro- magnetic interaction is comparable to the thermal fluctuation energy in this temperature range. The M/Ms vs. H/T result shows further evidence of the ferromagnetic interaction for this radical cation/radical anion salt.

There are two possibilities of the ferromagnetic interaction in these radical cation/radical anion salts. One is based on the direct ferromagnetic interaction between 3(*p*)-Me^{+}'s, and for the other the neighboring radical anion pair participates the interaction. As demonstrated by the ESR and ENDOR results the unpaired-electron in 3(*p*)-Me^{+} resides preferentially at the two nitrogen atoms, but also at both the intervened carbon atom and the pyridyl ring albeit in a very

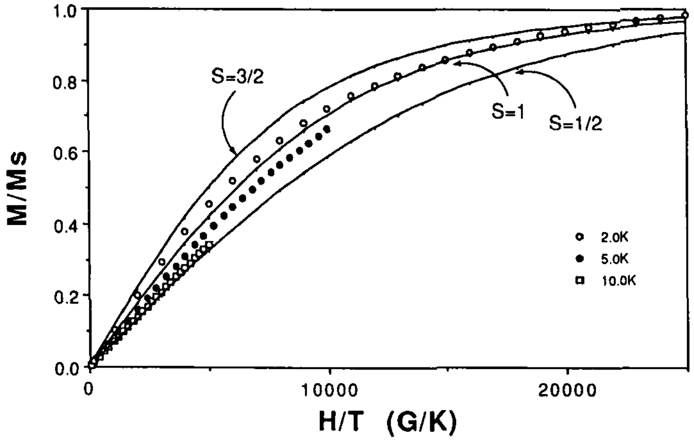


FIGURE 15 The field (H) dependence of the magnetization (M)/the saturation one (Ms) at 2.0, 5.0 and 10.0 K, respectively, for 3(*p*)-$Me^+ \cdot HCBD^{-\cdot}$. The solid curves correspond to the theoretical ones for the S = 1/2, 1 and 3/2 paramagnetic spin entities.

small contribution. The negative spin density involved in the latter unpaired-electron distribution should play a crucial role in ferromagnetic interaction between 3(*p*)-Me^+'s, irrespectively of participation by the radical anion pair or not. The details of the interactions between 3(*p*)-Me^+'s as well as between 3(*p*)-Me^+ and the radical anion must be elucidated in taking account of the crystal structure of these radical ion salts, in particular, 3(*p*)-$Me^+ \cdot HCBD^{-\cdot}$.

CONCLUSION

Our purpose is directed to the preparation of organic radical ion salts exhibiting ferromagnetic interaction between the radical cation and radical anion in one-dimension and furthermore in two- or three-dimension if possible. Unfortunately, for all the $TCNQ^{-\cdot}$, $TCNQF_4^{-\cdot}$ and $HCBD^{-\cdot}$ salts of 2(*m*)-Me^+, 2(*p*)-Me^+, 3(*p*)-Me^+ and 3(*p*)-Et^+ prepared in this work, the significant magnetic properties come from the interaction between the radical cations as a result of dimer formation of the radical anions. Nevertheless, the radical anion might contribute as a crucial partner to the tight contact as well as the ferromagnetic interaction between the radical cations. As a matter of course the dimer formation of the radical anions should strongly depend on the kind of the radical cation used as a partner. For the radical cations of **2**-Me$^+$ and **3**-R$^+$ a positive charge is preferentially located at the nitrogen atom of the pyridinium ring , so that the Coulomb interaction between the pyridinium ion and the radical anion is presumably very weak. Accordingly, the interaction between the radical cation and radical anion rather than between the radical anions (and also the radical cations) might be expected by use of much more potential cationic groups than a pyridinium ion. Now, we are investigating the synthesis of 4,4,5,5-tetramethyl-nitronylnitroxide and -imidazolin-1-oxyl substituted with a 1,3-benzodithiolium ion as a new radical cation still endowed with the characteristics of separate location of an unpaired electron and a positive charge like **2**-Me$^+$ and **3**-R$^+$, and the magnetic properties of their radical cation/radical anion salts.

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