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Temperature Dependence of Crystal Structures, and Electrical Conducting and Magnetic Properties in Plate Crystals of 1:2 Tetrafluorotetracyanoquinodimethane/Tetrafluorotetracyanoquinodimethanide Mixed Tetramethyl-Ammonium and -Phosphonium Salts

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TEMPERATURE DEPENDENCE OF CRYSTAL STRUCTURES, AND ELECTRICAL CONDUCTING AND MAGNETIC PROPERTIES IN PLATE CRYSTALS OF 1:2 TETRAFLUOROTETRACYANOQUINODIMETHANE / TETRAFLUOROTETRACYANOQUINODIMETHANIDE MIXED TETRAMETHYL-AMMONIUM AND -PHOSPHONIUM SALTS

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Abstract The structure of a plate crystal of (($PMe_4^+ \cdot TCNQF_4^{-\cdot}$)·1/2TCNQF4) was analyzed and very similar to that of the corresponding

NMe_4^+ salt. However, significant difference was recognized between the two crystals in the structures of $TCNQF_4$ and $TCNQF_4^{-\cdot}$ molecules, and especially in the contacts between the two $TCNQF_4^{-\cdot}$ molecules in dimerization and between the $TCNQF_4$ and $TCNQF_4^{-\cdot}$ molecules. The change in both molecular structure and contact as above was also observed at a lowering temperature. The magnitude in change was larger in the NMe_4^+ salt than in the PMe_4^+ salt. However, the change exerted no special influence on the elctrical conducting and magnetic properties.

INTRODUCTION

Very recently we have succeeded in the preparation of a new type of tetramethyammonium (NMe_4^+) salt of tetrafluorotetracyanoquinodimethane ($TCNQF_4$) and its radical anion ($TCNQF_4^{-\cdot}$) in 1:2 molar ratio, $(NMe_4^+\cdot TCNQF_4^{-\cdot})\cdot 1/2TCNQF_4$.[1] This mixed salt has two different crystal forms of plates (**I**) and needles (**I'**), of which **I'** very interestingly exhibited ferromagnetic behavior at room temperature. The crystal structure of **I** has already been disclosed by X-ray structure analysis,[2] while the single crystal of **I'** suitable for the analysis is still not available. The crystal structure of **I** was shown to be very unique at room temperature. Thus, the crystal is composed of alternating $TCNQF_4$/ $TCNQF_4^{-\cdot}$ and NMe_4^+ ion layers, and in each $TCNQF_4$/ $TCNQF_4^{-\cdot}$ layer the two neighboring $TCNQF_4^{-\cdot}$ molecules form a tight dimer and each dimer is arranged in a completely perpendicular manner to each of $TCNQF_4$ molecules. We now had interest in the change of this unique crystal structure with a lowering temperature as well as with other gegencations (tetramethyphosphonium ion, PMe_4^+ was used in this study) than NMe_4^+, and furthermore in the electrical conducting and magnetic properties of **I** and the corresponding PMe_4^+ salt ($(PMe_4^+\cdot TCNQF_4^{-\cdot})\cdot 1/2TCNQF_4$, **II**).

EXPERIMENTAL

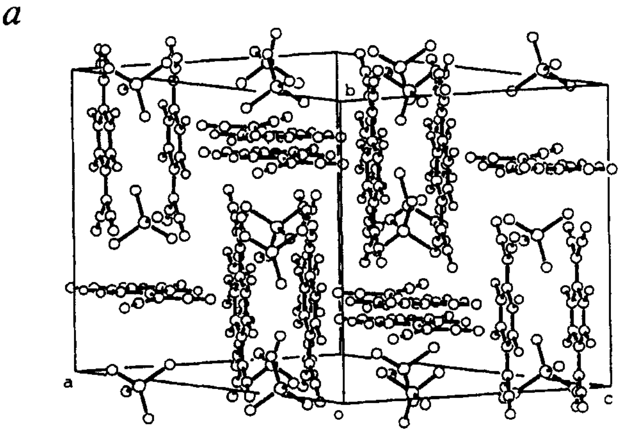
The $NMe_4^+\cdot TCNQF_4^{-\cdot}$ and $PMe_4^+\cdot TCNQF_4^{-\cdot}$ salts were prepared by treatment of $Li^+\cdot TCNQF_4^{-\cdot}$, obtained by the reaction of $TCNQF_4$ with an excess of LiI in hot acetonitrile,[3] with an excess of $NMe_4^+\cdot Cl^-$ or $PMe_4^+\cdot Cl^-$ in water, respectively. The salts were purified by recrystallization from acetonitrile/ether. When the $NMe_4^+\cdot$

$TCNQF_4^{\cdot -}$ or $PMe_4^+ \cdot TCNQF_4^{\cdot -}$ crystal was again recrystallized in the presence of an excess of $TCNQF_4$ from acetonitrile/ether, $(NMe_4^+ \cdot TCNQF_4^{\cdot -}) \cdot 1/2TCNQF_4$ (**I**) (mp 254-255 °C) and $(PMe_4^+ \cdot TCNQF_4^{\cdot -}) \cdot 1/2TCNQF_4$ (**II**) crystals (mp 228-229 °C) were isolated as plates. The X-ray crystal analysis of **II** at 300 K was performed on a Rigaku AFC7R diffractometer with graphite monochromated Cu - Kα radiation and 12 kW rotating anode generator on a purple prism (0.50 x 0.50 x 0.50 mm^3) mounted on a glass capillary by the ω - 2θ scan method. Of total 3605 collected reflections, 3500 were observed. Cell constants and an orientation matrix for data collection were determined from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 56.18° < 2θ < 56.88°. The X ray crystal analyses of **I** at 250, 200, 150 and 100 K, and of **II** for 200 and 100 K were also performed on Rigaku RAXIS II imaging plate area detector with graphite monochromated MoKα radiation. Indexing was performed from 1873716430 stills which were exposed for 30.0 minutes. The crystal-to-detector distance was 300.0 mm. The detector swing angle was 0.00°. The crystal data were as follows. For **II** at 300 K: $C_{22}H_{12}N_6PF_6$, M = 505.34, monoclinic, space group $C2/c$, a = 22.24, b = 14.65, c = 13.90 Å, β = 96.4 °V = 4497.9 Å^3, Z = 8, ρ_{calcd} = 1.87 g·cm^{-3}, λ = 1.54 Å, μ(CuKα) = 22.0 cm^{-1}; at 200 K: monoclinic, space group $C2/c$, a = 22.13, b = 14.59, c = 13.81 Å, β = 96.2°, V = 4434.3 Å^3, Z = 8, ρ_{calcd} = 1.51 g·cm^{-3}; at 100 K: monoclinic, $C2/c$, a = 22.03, b = 14.58, c = 13.72 Å, β = 96.2° V = 4379.5 Å^3 Z = 8, ρ_{calcd} = 1.53 g·cm^{-3}. For **I** at 250 K: $C_{22}H_{12}N_7F_6$, M = 488.37, monoclinic, $C2/c$, a = 21.80, b = 14.62, c = 13.76 Å, β = 97.6°, V = 4345.6 Å^3, Z = 8, ρ_{calcd} = 1.49 g·cm^{-3}; at 200 K: monoclinic, $C2/c$, a = 22.13, b =14.60, c = 13.81 Å, β = 96.3°, V = 4434.3 Å^3 Z = 8, ρ_{calcd} = 1.53 g·cm^{-3}; at 150 K: monoclinic, $P2_1/n$, a = 13.47, b = 14.58, c = 21.92 Å, β = 98.2°, V = 4262.0 Å^3, Z = 8, ρ_{calcd} = 1.52 g·cm^{-3}; at 100 K: monoclinic, space group $P2_1/n$, a = 13.41. b = 14.57, c = 21.89 Å, β = 98.1°, V = 4233.7 Å^3, Z = 8, ρ_{calcd} = 1.53 g·cm^{-3}. The structure was solved by a direct method (SHELX-86)[4] and expanded using Fourier technique (DIRDIF94).[5] The data were corrected for absorption, Lorentz and polarization effects. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Refinement by full-matrix least-squares calculations converged at R = 0.078 and Rw = 0.116 at 300 K, R = 0.039 and Rw = 0.075 at 200 K, and R = 0.035 and Rw = 0.078 at 100 K for **II**; R = 0.072 and Rw = 0.131 at 250 K, R = 0.078 and Rw = 0.116 at 200 K, R = 0.048 and Rw = 0.090 at 150 K, and R = 0.042 and Rw = 0.078 at 100 K for **I**. The ORTEP drawings, and full tables of fractional atomic coordinates, bond distances, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. The electrical conductivity was measured by using a two-probe method at room temperature. The electrical contact was achieved with gold paste. The magnetic susceptibility measurement was carried out in the temperature range of 5 to 300 K under an applied field of 500 Oe by a SQUID magnetometer (Quantum Design, MPMSR2). The paramagnetic susceptibility (χ_p) was obtained by subtracting a diamagnetic contribution calculated by a Pascal method from the observed value.

RESULTS AND DISCUSSION

CRYSTAL STRUCTURE OF II AT ROOM TEMPERATURE

The ($\mathrm{NMe_4^+ \cdot TCNQF_4^{-\cdot}}$)$\cdot$1/2$\mathrm{TCNQF_4}$ was obtained as two crystal forms of plates (**I**) and needles by recrystallization of $\mathrm{NMe_4^+ \cdot TCNQF_4^{-\cdot}}$ in the presence of an excess of $\mathrm{TCNQF_4}$ from acetonitrile/ether. On the other hand, when $\mathrm{PMe_4^+ \cdot TCNQF_4^{-\cdot}}$ was used in place of $\mathrm{NMe_4^+ \cdot TCNQF_4^{-\cdot}}$, only plate-form crystals (**II**) were crystallized out. The crystal structure of **II** at 300 K is shown in Fig. 1a, which is very similar to that of **I**. Thus, the crystal is composed of alternating $\mathrm{TCNQF_4/TCNQF_4^{-\cdot}}$ and $\mathrm{PMe_4^+}$ layers along the *a* axis. The $\mathrm{TCNQF_4/TCNQF_4^{-\cdot}}$ layer adopts a unique packing structure, in which each pair of $\mathrm{TCNQF_4^{-\cdot}}$ molecules is arranged in a completely perpendicular manner to each $\mathrm{TCNQF_4}$ molecule (see Fig. 1b). The C-C bond distances of $\mathrm{TCNQF_4}$ and $\mathrm{TCNQF_4^{-\cdot}}$ molecules are quite similar to those of **I**, as shown in Fig. 2a,b. The



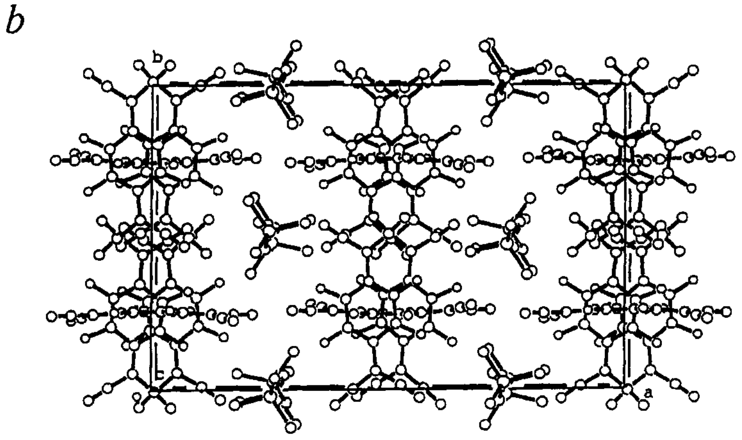


FIGURE 1. The crystal structures of **II** at 300 K: (*a*) the whole view and (*b*) the stacking projected down *c* axis.

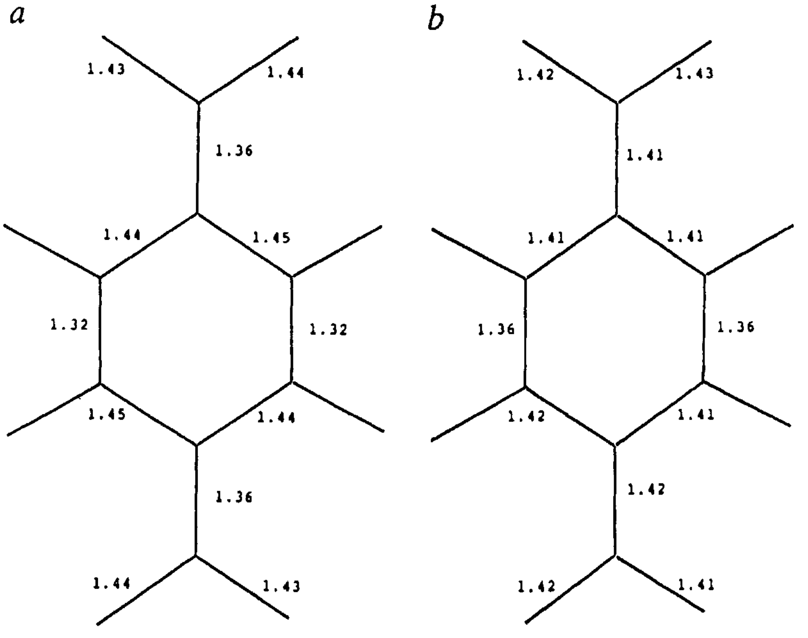


FIGURE 2. The C-C bond distances (Å) of (*a*) TCNQF4 and (*b*) TCNQF4$^{-\cdot}$ molecules.

TCNQF4$^{\cdot-}$ molecule in **I** has smaller deviation from the plane (0.007 Å) as compared with that of **II** (0.020 Å). Conversely, for the TCNQF4 molecule the deviation from the plane is seen in **II** (0.030 Å), while there is no such deviation in **I**. The two neighboring TCNQF4$^{\cdot-}$ molecules essentially form a tight dimer, judging from the very short contact distance (3.12 Å). This contact is slightly different from that in **I**. The contact distance is somewhat larger by 0.1 Å, and the torsional angle between the long axes of TCNQF4$^{\cdot-}$ molecules is 0.3° in contrast with zero in **I** (see Fig. 3a). The dimer has two different contacts with the neighboring TCNQF4 molecules, as shown in Fig. 3a,b. One is the contact between one TCNQF4$^{\cdot-}$ molecule in dimerization and one TCNQF4 molecule. The dihedral angle between the

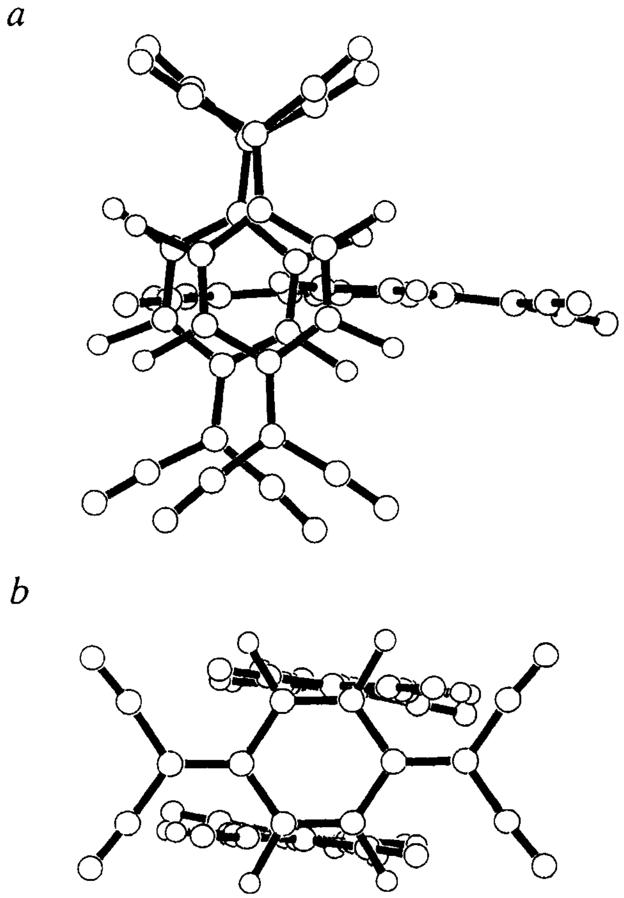


FIGURE 3. The contacts between TCNQF4 and TCNQF4$^{\cdot-}$ molecules projected down (*a*) *a* and (*b*) *b* axes.

two molecules is 89.75°. The other contact occurs between one TCNQF4 molecule and two TCNQF4$^{-\cdot}$ molecules in dimerization with the dihedral angle of 90.25°. These dihedral angles are slightly larger by 0.1° than those in **I**. The contact between the neighboring TCNQF4/TCNQF4$^{-\cdot}$ layers in **II** increases by 0.24 Å as compared with in **I**. This is considered as a result of accommodation of larger PMe4^{+} ions in volume in place of NMe4^{+} ions between the layers.

TEMPERATURE DEPENDENCES OF CRYSTAL STRUCTURES OF I and II

The plate crystals of **I** and **II** possess very unique molecular arrangement of each pair of TCNQF4$^{-\cdot}$ molecules in a perpendicular manner to each TCNQF4 molecule. To our knowledge such a molecular arrangement can not be often found among a lot of crystals of organic compounds. Judging from the informations obtained so far, this molecular arrangement seems to be thermodynamically not so stable. By external stimuli such as temperature, pressure and so on, a remarkable change in molecular arrangement is expected to occur. Now we investigated the temperature dependence of molecular arrangement in **I** and **II**, in particular, the stacking structure of the TCNQF4$^{-\cdot}$ dimer, the molecular structure of the TCNQF4 molecule, and the contact between the TCNQF4$^{-\cdot}$ dimer and the TCNQF4 molecule in a perpendicular orientation. The Fig. 4 shows the structures of a unit of one TCNQF4$^{-\cdot}$ dimer and one TCNQF4 molecule in **I** at 300, 250, 200, 150 and 100 K. The temperature dependence of the same unit structure in **II** was also investigated. The results measured at 300, 200 and 100 K are given in Fig. 5. As is obvious from the Figures, for **I** the TCNQF4$^{-\cdot}$ molecule is gradually less deviated from the plane with a lowering temperature. In contrast to this, an increasing deviation with lowering temperature is seen for the TCNQF4 molecule. Thedeviation magnitudes amount to 0.030 Å for the TCNQF4 molecule and 0.014 Å for the TCNQF4$^{-\cdot}$ molecule between 300 and 100 K. The contact distance between the two TCNQF4$^{-\cdot}$ molecules in dimerization decreases with a lowering temperature from 300 K (3.105 Å) to 100 K (3.045 Å). At the same time the deviation between the molecules also begins to appear with lowering temperature. The torsional angle is zero at room temperature, but becomes 0.96° at 100 K. Both contacts between one TCNQF4$^{-\cdot}$ molecule or two TCNQF4$^{-\cdot}$ molecules in dimerization and one TCNQF4 molecule get out of a perpendicular manner with lowering temperature. Thus, the dihedral angles of the two

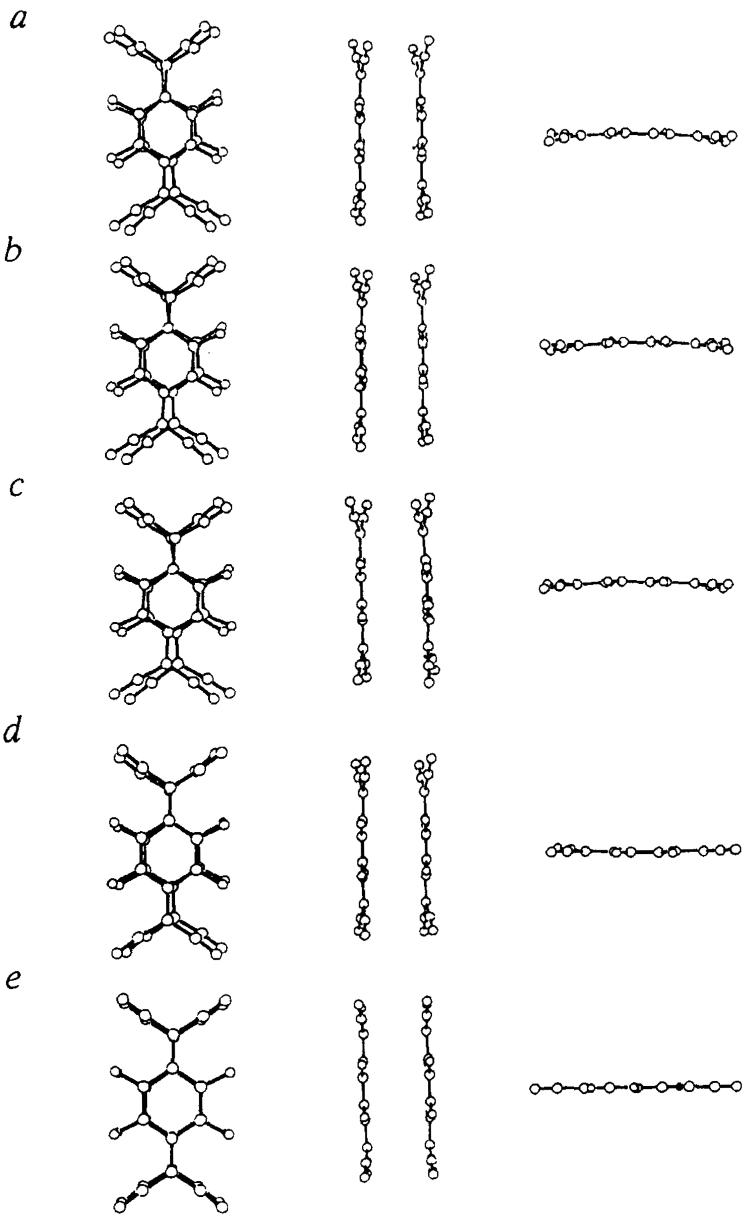


FIGURE 4. The molecular structures of TCNQF4$^{-\cdot}$ molecules in a dimer and of a TCNQF4 molecule in **I** at different temperatures: (*a*) 100, (*b*) 150, (*c*) 200, (*d*) 250 and (*e*) 300 K.

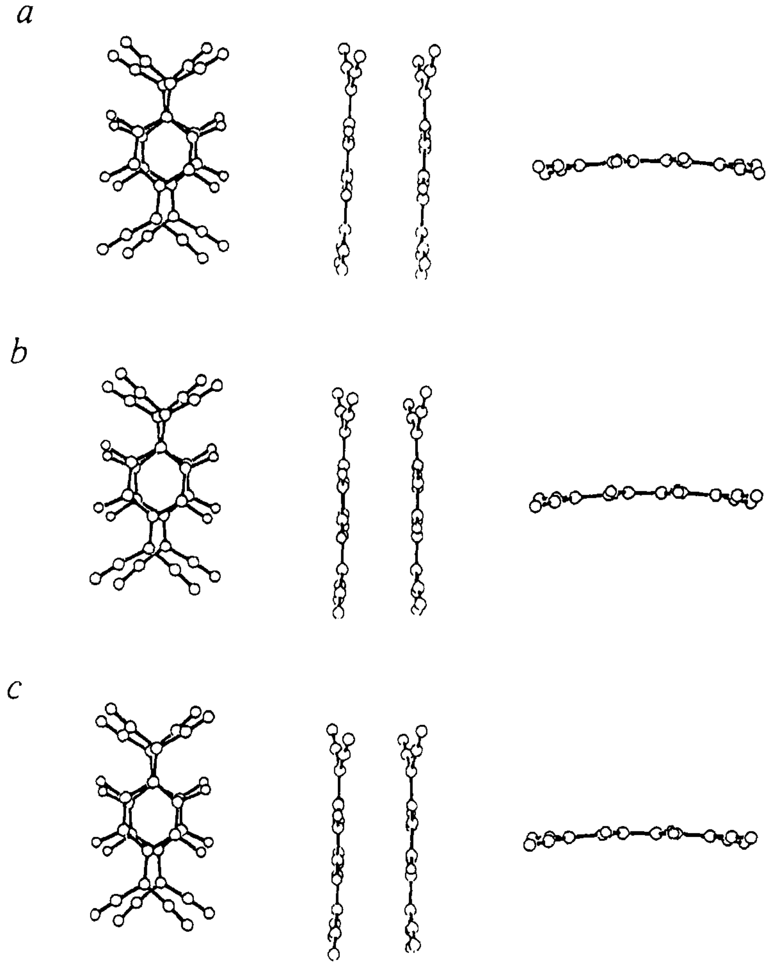


FIGURE 5. The molecular structures of a TCNQF4$^{-\cdot}$ dimer and a TCNQF4 molecule in **II** at different temperatures: (*a*) 100, (*b*) 200 and (*c*) 300 K.

contacts are both 90.08° at room temperature, and become 89.36° at 100 K. The distance between the neighboring TCNQF4/TCNQF4$^{-\cdot}$ layers changes from 10.981 Å at 300 K to 10.671 Å at 100 K. Similar tendencies can be also recognized for (1) the plane deviation of the TCNQF4$^{-\cdot}$ and TCNQF4 molecules, (2) the contact distance and distortion between the two TCNQF4$^{-\cdot}$ molecules, (3) the dihedral angles of two contacts between one TCNQF4$^{-\cdot}$ dimer and one TCNQF4 molecule, and (4) the distance between the neighboring TCNQF4/TCNQF4$^{-\cdot}$ layers in **II**. However, their magnitudes in change are smaller as compared with those of **I**: (1) 0.001 and 0.006 Å; (2) 0.060 Å and 0.14°; (3) 0.31 and 0.19°; (4) 0.099 Å. This might be related to the fact that deviation of TCNQF4 and TCNQF4$^{-\cdot}$ molecules from a plane, decreased contact between the TCNQF4$^{-\cdot}$ molecules in dimerization and decreased perpendicular contact between one TCNQF4 molecule and one TCNQF4$^{-\cdot}$ dimer already occur at room temperature.

ELECTRICAL CONDUCTING AND MAGNETIC PROPERTIES OF I and II

The electrical conductivities of **I** and **II** were 6 x 10^{-9} and 1 x 10^{-8} S·cm^{-1}, respectively. This result clearly shows that **I** and **II** are essentially insulators. Some change in this insulator-like electrical conductivity might be observed with lowering temperature, since the crystal structure changes albeit in small degree, as already discussed. Unfortunately, the temperature dependence of electrical conductivity was in fact impossible to investigate, because of much more decrease in electrical conductivity with lowering temperature from room temperature. The temperature dependence of χ_p was also investigated in the temperature range of 5 to 300 K under an applied field of 500 Oe for **I** and **II**. The result is shown in Fig. 6. The χ_p values are almost zero

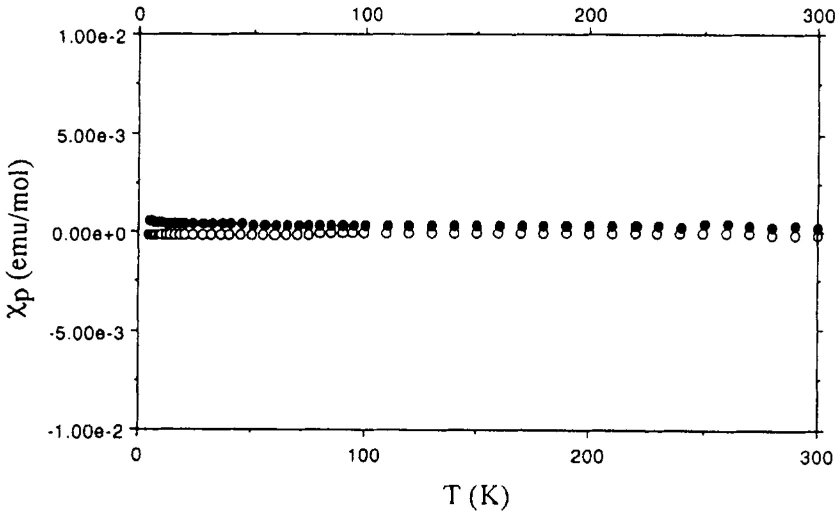


FIGURE 6. The temperature dependences of χ_p in **I** (●) and **II** (o).

throughout all temperature range, suggesting strong antiferromagnetic interaction between the $TCNQF4^{-\cdot}$ spins. Furthermore, at any temperature no unusual change in χ_p was recognized. This means that even if the crystal structure changes with a lowering temperature, it exerts almost no significant influence on the interaction between the $TCNQF4^{-\cdot}$ spins. The magnetic property of **I** has marked a contrast to that of **I'**. Thus, for **I'** the χ_p value at room temperature is ca. 0.012 emu/mol, which is larger by ca. 10 times than that assumed by a non-interacting $S=1/2$ spin entity per formula unit of this salt. In addition, there is entirely no change in χ_p in the temperature range of 5 to 300 K. This abnormal observation suggests appearance of ferromagnetic behavior even at room temperature. Indeed, it was the case. The mechanism on the room-temperature ferromagnetic behavior remains unsolved, because the crystal structure is still unknown.

DEDICATION

It is our pleasure to dedicate this paper to Professors Yusei Maruyama and Fumio Ogura on the occasion of their retirement from Institute for Molecular Science and Hiroshima University, respectively.

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