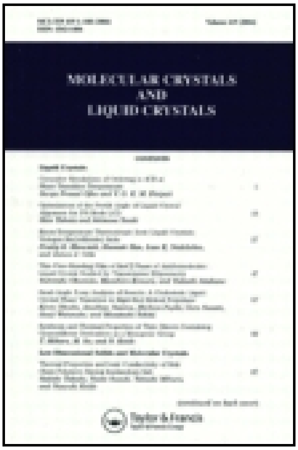

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CHEMICAL CONTROL OF THE ELECTRONIC STATES IN THE pπ-d SYSTEM

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Abstract Substituent effects in the pπ-d system $(DCNQI)_2Cu$ are described. Electrical and magnetic properties of $(R_1,R_2\text{-}DCNQI)_2Cu$ are quite sensitive to the substituents R_1 and R_2. Especially, when $R_1 = R_2 = CH_3$, the system at low temperature changes from a metal to an insulator according to the isotope substitution. A variety of substituent effects would be generally understood in terms of the amount of charge transfer from Cu to DCNQI which is sensitive to the N–Cu–N coordination angle.

INTRODUCTION

Molecular conductors form one of the most attractive categories of materials. They have clear and simple electronic structures which can be well described by the simple tight-binding band calculation. They form a treasury of exotic phenomena associated with low dimensionality (Charge Density Wave (CDW), Spin Density Wave (SDW), Spin Peierls transition, Field Induced Spin Density Wave (FISDW), Angle-Dependent MagnetoResistance Oscillations (ADMRO), ···etc). One of the most fascinating characters of molecular conductors is its "designability", that is, we can control solid state properties with chemical modifications of the molecule.

Almost all the successful materials, for example TMTSF and BEDT-TTF salts, were based on organic pπ electrons. An introduction of metal d electrons to the pπ-electron system would promise a variety of new phenomena. A series of π-acceptor molecules R_1,R_2-DCNQI (DCNQI=*N*,*N*'-dicyanoquinonediimine; R_1, R_2 = CH_3, CH_3O, Cl, Br, I) form 2:1 salts with various metal (Cu, Ag, Li, Na, K, NH_4, Rb, and Tl).[1] Amongst them, the Cu salts is located at the special position. In this system, an interaction between the one-dimensional pπ band of DCNQI and 3d orbital of Cu has provided unique electronic states.[2] In contrast to other salts, the electronic properties of the Cu salts are very sensitive to the choice of R_1 and R_2. We show that the electronic state of this pπ-d system can be finely controlled by a choice of the substituents (including isotope substitution) and discuss a mechanism of the substituent effect.

RESULTS AND DISCUSSION

Electronic Structure of $(DCNQI)_2Cu$

—Coexistence of one- and three-dimensional Fermi surfaces—

All the Cu salts of R_1,R_2-DCNQI (R_1,R_2=CH_3, CH_3O, I, Br, Cl) are isomorphous and have a tetragonal unit cell.[2] Planar DCNQI molecules stack to form one-dimensional columns along the tetragonal *c* axis. These DCNQI columns are interconnected to each other through tetrahedrally coordinated Cu ions with local symmetry of D_{2d} (Fig. 1). Therefore, there exists three-dimensional metal–π-molecule network. The Cu ions are separated far from each other and there is no direct Cu···Cu interaction.

In the metallic state, the mixed valence state of the Cu ion is established by XPS and IR measurements.[3] The formal charge of Cu is close to +4/3 ($Cu^+ : Cu^{2+} = 2 : 1$). This implies an interaction between the organic pπ electron and the d electron near the Fermi level. The metal-insulator (M-I) transition of the Cu salt is accompanied by the formation of CDW with three-fold periodicity, while an isostructural Ag salt exhibits a four-fold superstructure.[4]

All these features indicates very unique electronic structure of the Cu salt. We have calculated the band structure using the simple tight-binding approximation.[5] The primitive unit cell contains two Cu ions and four DCNQI molecules. We consider the LUMO of DCNQI and the highest-lying d_{xy} orbital of Cu as frontier orbitals. Figure 2 shows calculated Fermi surface of $(DMe\text{-}DCNQI)_2Cu$. The Fermi surface (FS) is composed of two types of sheets (FS1 and FS2) and a connected "arm" with three-dimensional character (FS3). FS1 comes from two-fold degenerated LUMO (pπ) bands with a purely one-dimensional character. Although FS2 is also associated with the pπ band, a mixing of the 3d character makes the FS2 distorted sheet. FS3 originates from mainly the 3d band and has a three-dimensional character. FS2 and FS3 touch at the point Q. Our results explains angular dependence of the dHvA frequencies quite well.[6] Recently, first-principles calculations based on the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA) on the density function theory have been performed for the $(DCNQI)_2Cu$ system.[7] The results strongly support our calculations.

Temperature-dependent Resistivity of $(DCNQI)_2Cu$

—Pressure and Substituent Effects—

The Cu salts are classified into three groups according to their transport properties. The type I salts (R_1 and R_2 = CH_3, CH_3O, I···etc.) are metallic down to the lowest temperature under ambient pressure, while the type II salts (R_1 and R_2 = Br, Cl···etc.) exhibit a sharp first-order M-I transition at rather high transition temperature $T_{M\text{-}I}$ (80–200 K). This M-I transition is accompanied by a CDW formation and a static charge

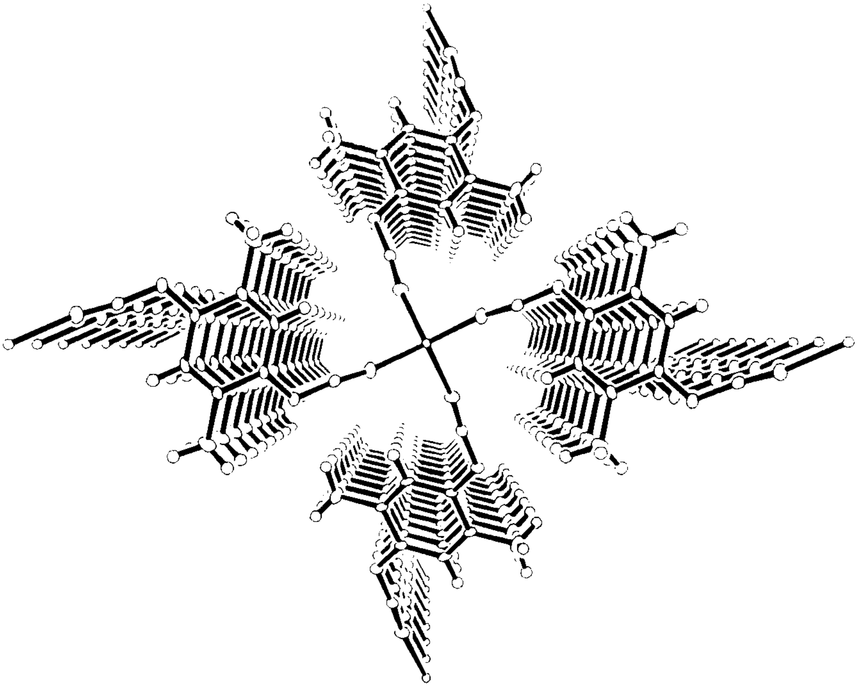
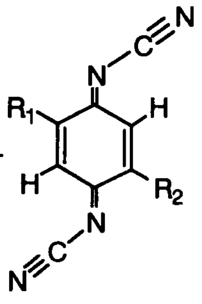


FIGURE 1 Crystal structure of $(\text{DMe-DCNQI})_2\text{Cu}$.

TABLE 1 Physical and structural data for $(\text{R}_1,\text{R}_2\text{-DCNQI})_2\text{Cu}$.

	R_1	R_2	$T_{\text{M-I}}$ / K	P_c / kbar	α / deg. (∠N–Cu–N)
Type I	I	I	metal	15.3	122.3
	I	Br	metal	3	123.1
	I	CH_3	metal	4	123.6
	CH_3	CH_3	metal	0.1	124.7
Type II	CH_3	Br	152	—	125.3
	Br	Br	161	—	125.3
	CH_3	Cl	210	—	126.2
	Br	Cl	213	—	126.1
	Cl	Cl	230	—	127.1



R_1,R_2-DCNQI

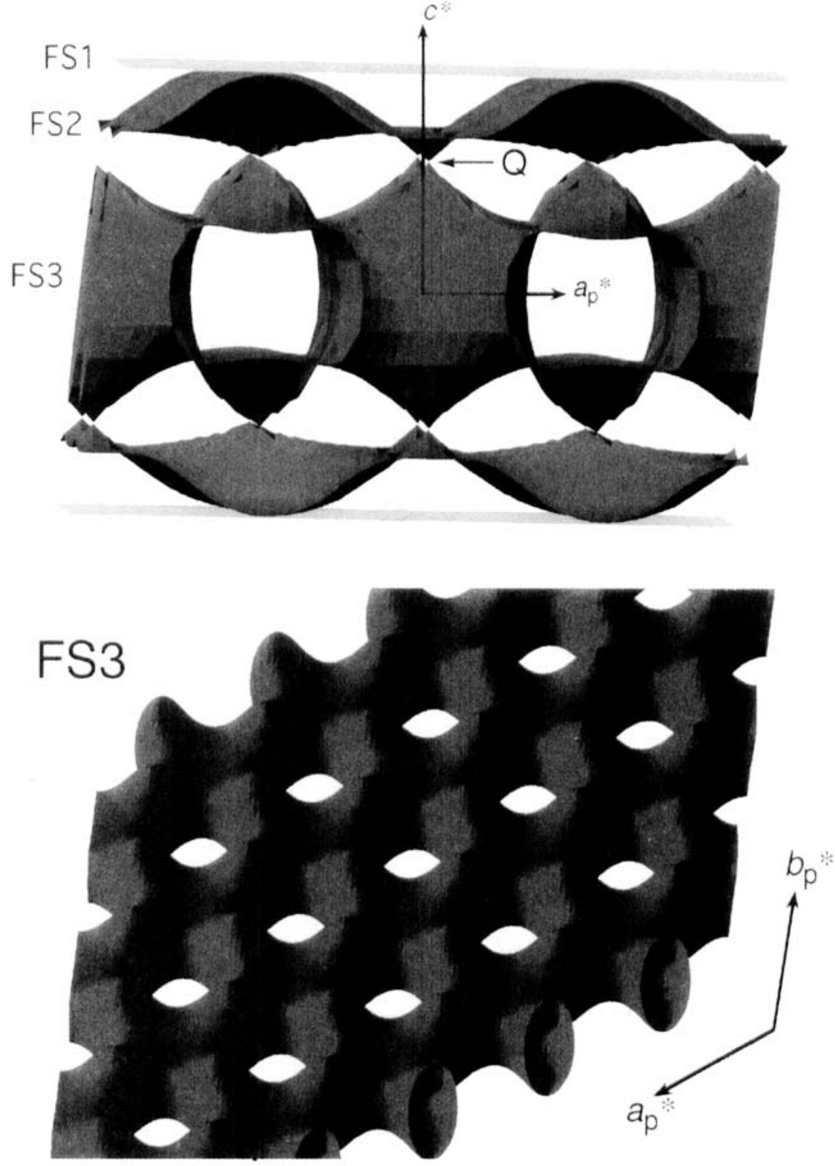


FIGURE 2 Calculated Fermi surface (FS) of $(\text{DMe-DCNQI})_2\text{Cu}$. In this calculation, the body-centered unit cell (**a**, **b**, **c**) is reduced to the primitive cell ($\mathbf{a}_p, \mathbf{b}_p, \mathbf{c}_p$) as $\mathbf{a}_p = \mathbf{a}$, $\mathbf{b}_p = (\mathbf{a}+\mathbf{b}+\mathbf{c})/2$, $\mathbf{c}_p = \mathbf{c}$. See Color Plate I.

ordering at the Cu sites ($\cdots Cu^{+}Cu^{+}Cu^{2+}\cdots$).[2] An application of pressure transforms the group I salt into the group II salt.[8] In the vicinity of the critical pressure (P_c), the system exhibits a unique reentrant behavior of successive phase transitions (metal→ insulator → metal) with lowering temperature. We call Cu salts in this region type III.

Above-mentioned classification of the Cu salts is correlated to the size of substituents R_1 and R_2 (Table 1). The smaller substituents provoke the M-I transition. We consider that **these pressure and substituent effects have the same origin** (*vide infra*).

Selectively Deuterated $(DMe\text{-}DCNQI)_2Cu$ System

—Fine chemical control of the electronic state—

Among the Cu salts, $(DMe\text{-}DCNQI)_2Cu$ shows very low critical pressure (<100 bar) and is located on the verge of the M-I transition. In addition, only this salt provides single crystals of a large size and good quality for physical measurements. In 1992, Hünig et al. reported that the replacement of CH_3 by CD_3 causes the M-I transition.[9] This remarkable isotope effect implies that the deuteration works as the application of pressure and suggested to us that the effective pressure can be finely controlled by the number and position of deuterium atoms.

The DMe-DCNQI molecule contains eight hydrogen atoms and there are 35 patterns of deuteration. We have developed synthetic methods for all the deuteration patterns and established the way for accurate control of 'pressure' by organic synthesis.[10] The low-pressure region of the phase diagram is now chemically reproduced. Figures 3 shows typical temperature dependence of electrical resistivity for each type (I, II, and III). Hereafter, we use a notation $\text{-d}_n[a_1,a_2;b]$, where a_1 and a_2 are numbers of deuterium atoms in each methyl group and b is that in the six-membered ring, for the simplified expression of the selectively deuterated molecule. Non- and fully-deuterated molecules are represented as -h and -d_8, respectively. We compared transition temperatures with those in the -h salt under pressure, and found that the effect of deuteration can be converted into pressure. This "effective pressure" P_{eff}(bar) is approximately expressed as a linear function of a_1, a_2, and b,

$$P_{\text{eff}} \approx 80\{(a_1+a_2)+0.2b\}.$$

This formula indicates that (1) the methyl deuteration is more effective than the ring deuteration, and (2) the deuteration pattern within the methyl groups is not significant (for example, the $\text{-d}_2[1,1;0]$ and $\text{-d}_2[2,0;0]$ salts show very similar behavior).

The most plausible origin of the deuterium isotope effect on $(DMe\text{-}DCNQI)_2Cu$ is the steric isotope effect.[10] Figure 4 clearly shows the unit cell contraction by the deuteration. A C–D bond is slightly shorter than a C–H bond as a result of the lower zero-point energy. In the crystal, the bulky methyl groups contact to each other along the stacking axis. The deuteration makes the methyl group a bit less bulky and leads to the

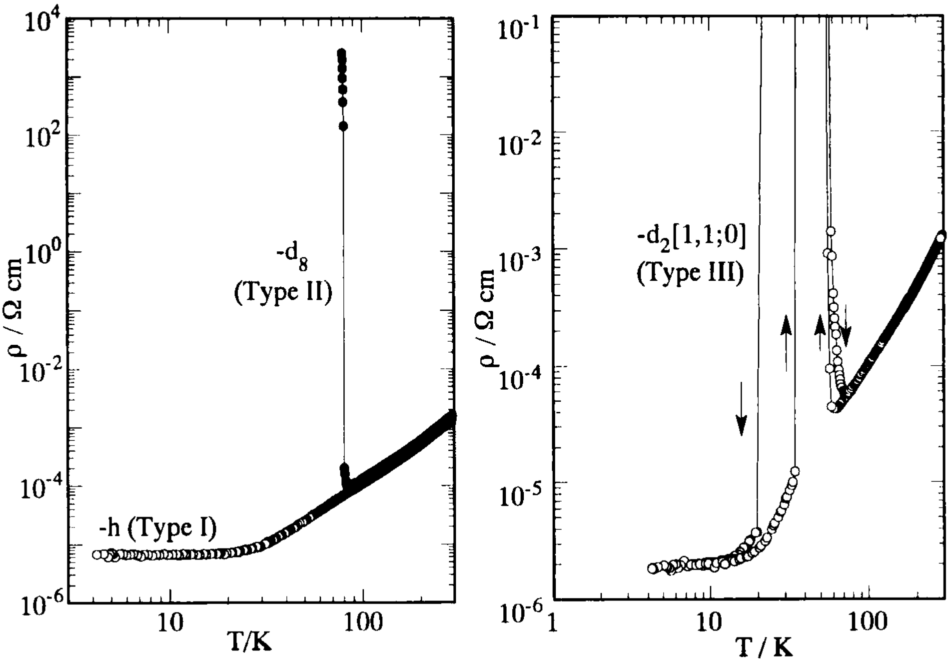


FIGURE 3 Resistivity of pristine (type I), fully deuterated (type II), and selectively deuterated $(DMe\text{-}DCNQI)_2Cu$.

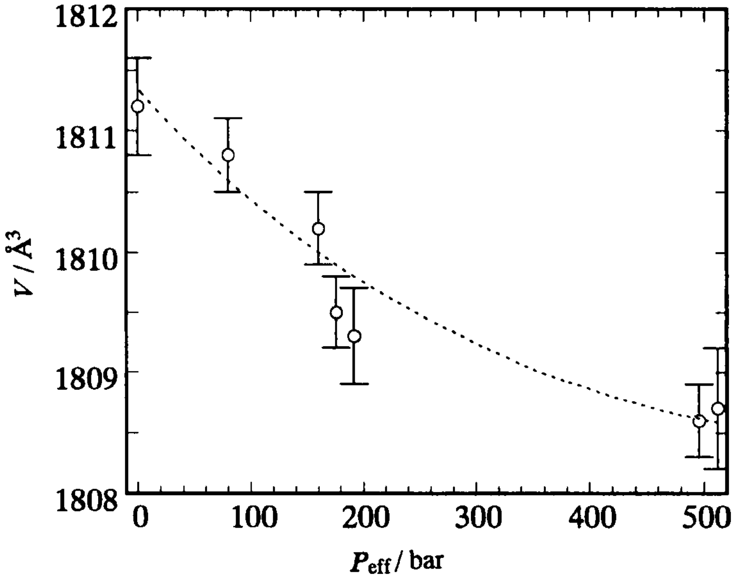


FIGURE 4 Cell volume (*V*) of selectively deuterated $(DMe\text{-}DCNQI)_2Cu$ systems at room temperature vs. effective pressure (P_{eff}).

contraction along the *c* axis direction. In this sense, the deuteration at the methyl group is equivalent to the application of pressure. The ring deuteration exhibits a smaller, but significant effect. This can be explained from the rather short distance (2.7 Å) between the ring hydrogen and the terminal cyano nitrogen of the neighboring molecule.

How are Phase Transitions Connected with the Chemical Modifications?

—An importance of the amount of charge transfer—

The substitution effect including the deuterium effect is equivalent to the pressure effect and they are summarized in the same phase diagram (Fig. 5). Both effects should be related to a subtle change in the crystal structure. Table 1 shows that the M-I transition temperature $T_{\text{M-I}}$ for the type II salts and the critical pressure P_c for the type I salts are highly correlated to the N–Cu–N coordination angle α. The phase transitions in the (DCNQI)$_2$Cu system are accompanied by a discontinuous change of the coordination angle α.[2] We have performed crystal structure determinations for selectively deuterated (DMe-DCNQI)$_2$Cu systems (type I, II, and III) from room temperature down to 7 K using the Weissenberg-type imaging plate system equipped with a closed-cycle helium refrigerator.[11] Figure 6 shows temperature dependence of the coordination angle α. The coordination angle α increases gradually in the metallic phase with lowering temperature, but shows a jump at the M-I transition. Across the I-M transition in the type III salt, the α value drops into the same value that the type I salt reaches. All these facts indicate that the electronic states of this system are interrelated to the distortion of the coordination tetrahedron around the Cu ion.

The lattice distortion in the insulating state always exhibits the 3*c* periodicity. This is associated with the CDW formation on the DCNQI column and the static charge ordering at the Cu sites ($\cdots Cu^{+}Cu^{+}Cu^{2+}\cdots$). It has been theoretically indicated that an interplay of the three-fold periodic potential and the strong correlation leads to the first-order M-I transition followed by the large hysteresis and the localized spin.[12] It should be noticed that the 3*c* periodicity is a special point where both the CDW and the charge ordering possess the same period.[13] Such a situation yields a large energy gain due to the commensurability between the pπ- and d-systems. Therefore, a deviation of the valence of Cu (DCNQI) from +4/3 (-2/3) should require the redistribution of the charge for the M-I transition and lower the transition temperature $T_{\text{M-I}}$. This can be substantiated by the Li^{+} doping at the Cu site (Fig. 5).[14]

The next step is to consider an interrelation between the distortion of the coordination tetrahedron and the charge transfer amount (therefore the valence of Cu). In the tetrahedral coordination geometry with T_d symmetry, the 3d levels are split into t_{2g} (d_{xy}, d_{yz}, d_{zx}) and e_g (d_{z^2}, $d_{x^2-y^2}$) subgroups. A distortion toward D_{4h} symmetry raises the d_{xy} level in the t_{2g} set and lowers the d_{yz} and d_{zx} levels. The highest-lying d_{xy} level is located near the Fermi level and interacts with the pπ band. Therefore, the distortion

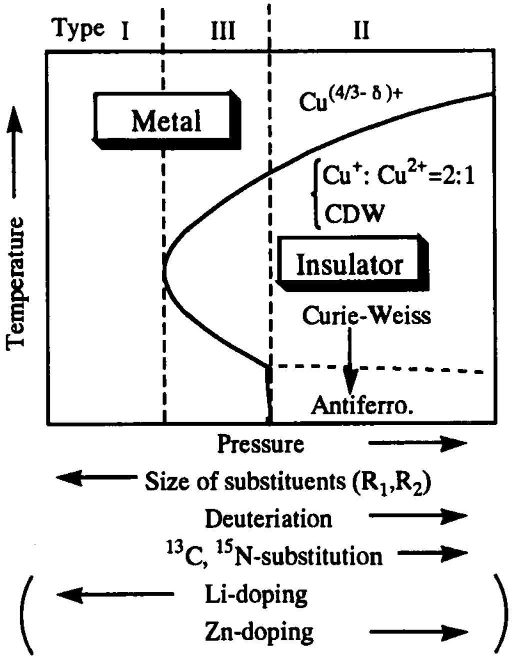


FIGURE 5 Generalized phase diagram for the $(DCNQI)_2Cu$ system.

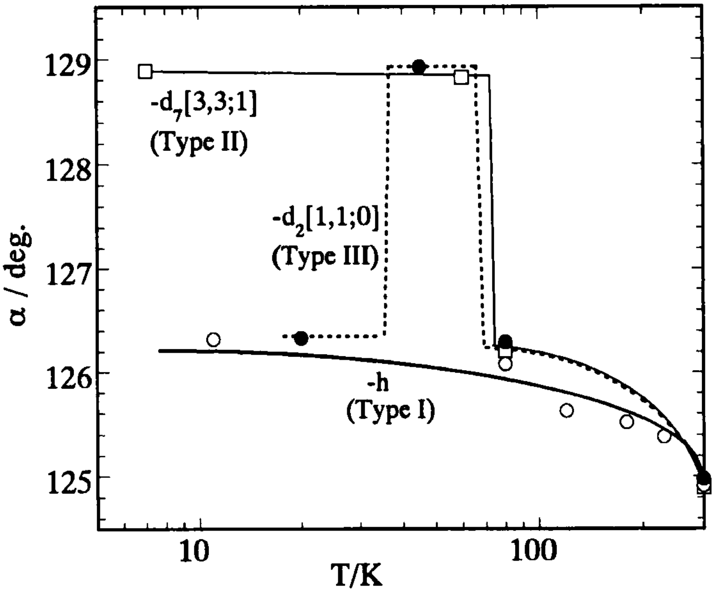


FIGURE 6 Temperature dependence of the coordination angle α for selectively deuterated $(DMe\text{-}DCNQI)_2Cu$ systems (warming process).

associated with the pressure or size effect induces small extra electron transfer from Cu to DCNQI and increases the formal charge of Cu.

Let us now consider the valence state of Cu in the metallic state. In the -d7[3,3;1] salt (type II), the Zn^{2+} doping at the Cu site slightly raises $T_{M\text{-}I}$, while the Li^+ doping lowers it. In the -h salt (type I), the Zn^{2+} doping induces the weak reentrant behavior.[14] On the other hand, the Li^+ doping does not affect the metallic state except for the increase in the residual resistance. These results suggest that the valence of Cu in the pure Cu salt is negatively shifted from +4/3. Recently, Takahashi et al. have measured Cu 2p core-level photoemission spectra for *in situ* prepared $(DMe\text{-}DCNQI\text{-}h)_2Cu$ (type I) and $(MeBr\text{-}DCNQI)_2Cu$ (type II; $R_1=CH_3$, $R_2=Br$) at room temperature.[15] The line-shape analyses have revealed that the Cu^{2+} configurations are about 27 % ($Cu^+ : Cu^{2+} = 2 : 0.76$) for $(DMe\text{-}DCNQI\text{-}h)_2Cu$ and about 32 % for $(MeBr\text{-}DCNQI)_2Cu$ ($Cu^+ : Cu^{2+} = 2 : 0.93$). This implies that the formal charge of Cu in the metallic phase is slightly smaller than +4/3 and the amount of charge transfer from Cu to DCNQI in the type II salt is larger than that in the type I salt. Takahashi et al. also reported temperature dependence of the photoemission spectra for $(DMe\text{-}DCNQI\text{-}d_2[1,1;0])_2Cu$ (type III), and claimed that even in the metallic phase the amount of the charge transfer from Cu to DCNQI increases on lowering temperature.[16] This corresponds with the temperature dependence of the coordination angle α in the metallic phase (Fig. 6).

To sum up, our interpretation of the pressure and substitution effects in the $(DCNQI)_2Cu$ system is as follows;[14]

(1) The valence of Cu in the metallic state is slightly smaller than +4/3. This shift of the valence from +4/3 stabilizes the metallic state.

(2) The application of pressure or the smaller substituent enhances the distortion of the coordination tetrahedron.

(3) The distortion raises the highest-lying d_{xy} level and induces extra charge transfer from Cu to DCNQI.

(4) The valence state of Cu closer to +4/3 provokes the first-order M-I transition triggered by the CDW in the presence of the strong correlation.

The point is that the amount of charge transfer is an essential factor which governs the stability of the metallic state.

Other Isotope Effects

—^{13}C and ^{15}N isotope effects—

We have introduced ^{13}C atoms into two cyano groups in the non-deuterated (-h) and selectively deuterated ($\text{-}d_1[1,0;0]$, $\text{-}d_2[1,1;0]$, and $\text{-}d_8$) DMe-DCNQI molecules. Resistivity measurements for each Cu salt have revealed that the ^{13}C–substitution causes reproducible and systematic shifts of transition temperatures.[17] That is, the ^{13}C–substitution increases "effective pressure" by ca. 100 bar (Fig. 7). Furthermore, we have replaced all four N atoms in the -h and -d_4[1,1;2] DMe-DCNQI molecules with ^{15}N atoms, and have observed the same isotope effect (Fig. 7).[18] In this case, an increase in the effective pressure (ca. 90 bar) is slightly smaller than that in the ^{13}C-substitution.

An origin of these unexpected isotope effects remains an open question. It would be possible that the coordination angle α is affected by the introduction of ^{13}C or ^{15}N atoms. Such a structural change, however, should be extremely small and difficult to detect with the X-ray diffraction method. Nevertheless, the cyano group in direct contact with the coordination tetrahedron would have more influence on the pπ–d interaction and the electron-molecular vibration coupling (e–mv coupling) associated with the DCNQI—Cu linkage than the methyl group. This is supported by the fact that the methyl ^{13}C-isotope effect is very small.[18] In any case, the anomalous cyano ^{13}C- and ^{15}N-isotope effects have demonstrated that the electronic state of the $(DCNQI)_2Cu$ system is quite sensitive to perturbations in the coordination around Cu.

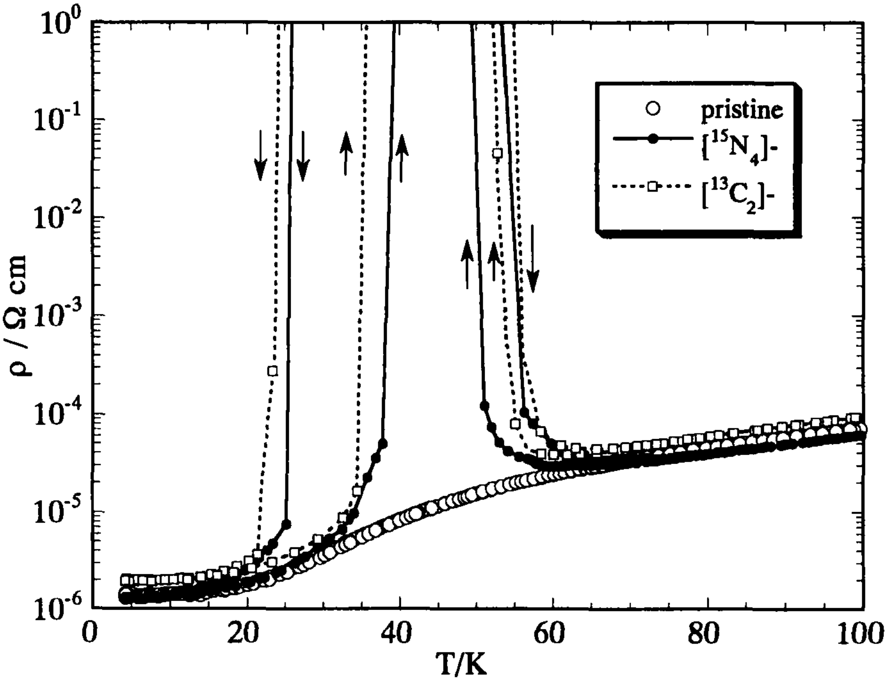


FIGURE 7 Resistivity of pristine, cyano [$^{13}C_2$]-, and [$^{15}N_4$]-substituted (DMe-DCNQI-h)$_2$Cu.

CONCLUSION

We have described the fine tuning of the electronic states in the $(DCNQI)_2Cu$ system with the chemical method. The remarkable substitution effect is based on the pπ-d interaction which provides the exotic electronic structure. The story described in this paper is only a part of fertile solid state science of the $(DCNQI)_2Cu$ system. We must add that in the Cu salts containing iodine atom(s) the high-pressure region of the pressure–temperature phase diagram is qualitatively modified.[19] And the metallic state of these salts under ambient pressure shows a novel magnetism which suggests the exchange enhanced paramagnetism of the itinerant electrons.[20] One of important factors should be a direct inter-chain interaction which was neglected in other $(DCNQI)_2Cu$ systems. These new interesting stories will be reported elsewhere.

ACKNOWLEDGMENT

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