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Giant Metal–Insulator–Metal Transition Induced by Selective Deuteration of the Molecular Conductor, $(\text{DMe-DCNQI})_2\text{Cu}$ (DMe-DCNQI = 2,5-dimethyl-*N*,*N*'-dicyanoquinonediimine)

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The Cu salts of selectively deuterated DMe-DCNQI's were prepared, and the electrical conductivities were examined. By deuteration of two hydrogens of the methyl groups, a drastic metal–insulator–metal transition was induced for the first time in a non-alloy system at ambient pressure. On the other hand, deuteration of two ring hydrogens or one methyl hydrogen did not affect the stability of a metallic state down to 4.2 K. These phenomena are discussed in terms of the "chemical pressure" effect.

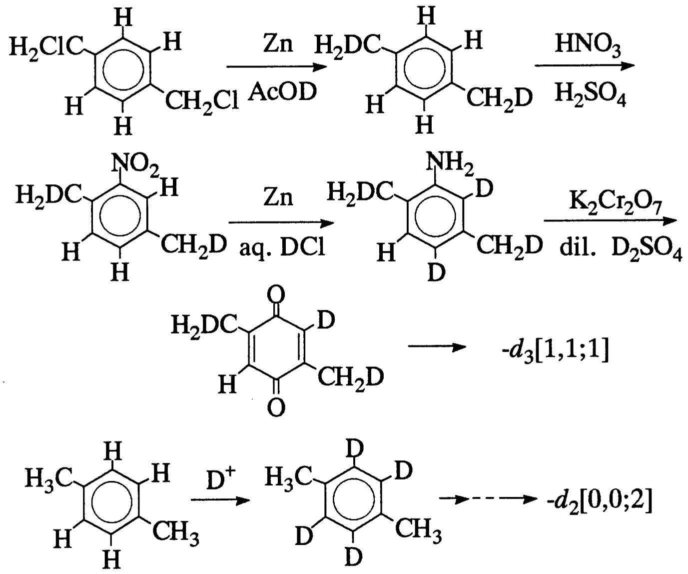
The Cu salts of R^1,R^2-DCNQI's (2,5-disubstituted-*N*,*N*'-dicyanoquinonediimines)1) provide various unique characters due to the interaction between the conducting pπ electrons on the DCNQI columns and the 3d electrons of the Cu atoms. Among the Cu salts, $(\text{DMe-DCNQI})_2\text{Cu}$ is of special interest. It indicates a metal–insulator (M–I) transition at pressures above 100 bar, whereas it is metallic down to the lowest temperatures at ambient pressure. In the very low pressure region, the reentrant behavior (a metal–non-metal–metal transition) is observed.2) The reentrant state has attracted much interest because it suggests the possibility of the heavy electron system. This experiment can be achieved only by a helium-gas-pressure method, which is technically difficult. The reentrant state is produced also in the alloy systems of $((\text{DMe})_{1-x}(\text{MeBr})_x\text{-DCNQI})_2\text{Cu}$3) and $(\text{DBr-DCNQI})_2\text{Cu}_{1-x}\text{Li}_x$.4) Though the practical difficulty can be avoided in these systems, there exists a severe effect of disorder.

Recently, Hünig *et. al* reported a M–I transition induced by the introduction of deuterium atoms (^{2}D).5) This phenomenon has been explained on the basis of the "chemical pressure" due to a steric isotope effect.5,6) Quite recently, we found the giant reentrant behavior in the (-*h*)–(-d_8) alloy system, $((\text{DMe-DCNQI-}h)_{1-x}(\text{DMe-DCNQI-}d_8)_x)_2\text{Cu}$.7) In this paper, we attempted to produce the ambient-pressure reentrant state in a non-alloy system by selective deuteration of DMe-DCNQI, where the experimental difficulty or the severe disorder is excluded. Using the x–T phase diagram for the (-*h*)–(-d_8) alloy system as a guiding principle, we aimed at the preparations of $n \leq 4$ entries among thirty-five deuterated species of the DMe-DCNQI-d_n family.

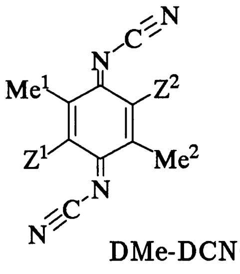
In order to readily recognize the substitution pattern, which is found to be an essential factor (*vide infra*), the expression is simplified in this paper as -$d_n[a_1, a_2; b]$, where a_1 and a_2 are numbers of ^{2}D's in each methyl group, and b is that in the six-membered ring. The deuterides synthesized herein are

-d_1[0, 0; 1], -d_2[0, 0; 2], -d_1[1, 0; 0], -d_2[1, 0; 1], -d_2[1, 1; 0], -d_3[1, 1; 1] and -d_4[1, 1; 2].

The methyl ^{2}D's were introduced by the reduction of the corresponding α-chlorinated *p*-xylenes by Zn powder in CH_3CO_2D.[8] Deuterations of the ring hydrogens were performed by applying $^1H/^2D$ exchange reactions in acidic media of xylidines[6] or of xylenes. Representative routes were shown in Scheme 1. Deuteration selectivity was checked by ^{1}H-NMR (peak areas and ^1H–^2D coupling patterns) and mass spectra. Isotopic purities of the methyl ^{2}D's would be ≥ 91% at least, and those of the ring ones would be ≥ 97%. Details will be published elsewhere.



Scheme 1.



DMe-DCNQI-d_n

→2-Methyl-d_{a_1}-5-methyl-d_{a_2}-DCNQI-d_b

Me^1	Me^2	Z^1	Z^2	-$d_n[a_1, a_2; b]$
CH_3	CH_3	H	H	-d_0[0, 0; 0] ≡ -*h*
CH_3	CH_3	D	H	-d_1[0, 0; 1]
CH_3	CH_3	D	D	-d_2[0, 0; 2]
CH_2D	CH_3	H	H	-d_1[1, 0; 0]
CH_2D	CH_3	D/H		-d_2[1, 0; 1]
CH_2D	CH_2D	H	H	-d_2[1, 1; 0]
CH_2D	CH_2D	D	H	-d_3[1, 1; 1]
CH_2D	CH_2D	D	D	-d_4[1, 1; 2]

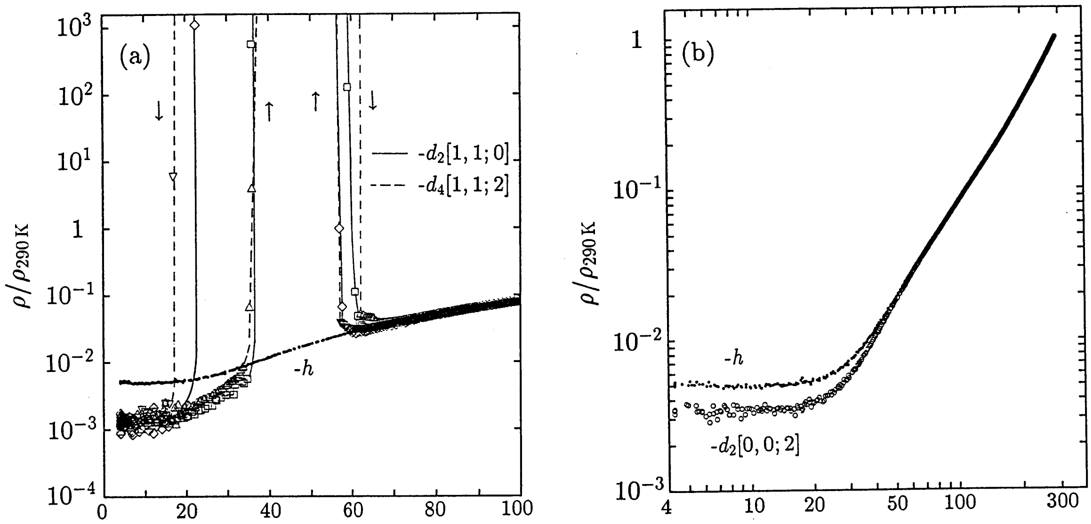


Fig. 1. Temperature dependence of the normalized resistance of the DMe-DCNQI-d_n salts. (a) -d_2[1, 1; 0] (◇ on cooling, □ on warming) and -d_4[1, 1; 2] (▽ on cooling, △ on warming) (b) -d_2[0, 0; 2] (○). The full circles (●) are for the -*h* salt.

Table 1. Electrical Conductivity and the Ratio $r = \rho_{4.2\ \mathrm{K}}/\rho_{290\ \mathrm{K}}$ of (DMe-DCNQI-d_n)$_2$Cu

$a_1 + a_2 =$	0	1	2	3	...	6
$b = 0$	Metallic $r = 5 \times 10^{-3}$	Metallic$^{a)}$ $r = 3 \times 10^{-3}$	Reentrant$^{c)}$ $r = 1 \times 10^{-3}$	M–I $T_{\mathrm{M\text{-}I}} = 58$ K$^{d)}$		M–I $T_{\mathrm{M\text{-}I}} = 73$ K$^{d)}$
1	Metallic$^{a)}$ $r = 2 \times 10^{-3}$	Metallic$^{a,b)}$ $r = 2 \times 10^{-3}$	Reentrant$^{c)}$ $r = 2 \times 10^{-3}$			M–I $T_{\mathrm{M\text{-}I}} = 83$ K$^{e)}$
2	Metallic$^{a)}$ $r = 2 \times 10^{-3}$	in progress	Reentrant$^{c)}$ $r = 1 \times 10^{-3}$			M–I $T_{\mathrm{M\text{-}I}} = 82,^{d)}$ 84 K$^{f)}$

a) With slight shoulder around 50 K. b) Mixture of two positional isomers.
c) Giant metal–insulator–metal transition. d) Ref. 5. e) Ref. 6. f) Ref. 7.

The Cu salt crystals were prepared by the slow chemical reduction of DMe-DCNQI-d_n in the presence of $(\mathrm{Et_4N})_2[\mathrm{CuBr_4}]$ and $(n\text{-Bu})_4\mathrm{NI}$ in acetonitrile.$^{7)}$ Electrical resistivity (ρ) was measured along the crystallographic c axis (needle axis) by the standard dc four-probe method down to 4.2 K. Electrical contacts were made with conductive gold paste using 10-μm gold wires.

The giant "reentrant" behavior was observed in the -d_2[1, 1; 0], -d_3[1, 1; 1] and -d_4[1, 1; 2] salts. As shown in Fig. 1(a), there occurs an extremely drastic M–I transition around 60 K in the cooling process. This insulating state continues down to ca. 20 K. Then, a metallic state appears again after a sudden drop in resistivity of at least 10^7 order. There exists a certain hysteresis. In the warming process, this reentrant metallic ($\mathrm{M_R}$) state transforms to the insulating state at ca. 35 K. The high-temperature metallic state appears again at ca. 60 K. In addition, the $\rho_{4.2\ \mathrm{K}}/\rho_{290\ \mathrm{K}}$ ratio (r) of the reentrant samples are less than half of that of the DMe-DCNQI-h salt (Table 1).

The -d_1[0, 0; 1], -d_2[0, 0; 2], -d_1[1, 0; 0] and -d_2[1, 0; 1] salts are all metallic down to 4.2 K. Compared with the -h salt, the enhancement of conductivity was also observed at the lowest temperature (Table 1). Very slight shoulder was observed around 50 K (Fig. 1(b)). These suggest the possibility that the above-mentioned $\mathrm{M_R}$ state is going to appear in the low-temperature region of these salts.

It would be of interest to evaluate the effect of a ^{2}D-substitution pattern. The -d_2[1, 1; 0] salt shows the reentrant behavior, whereas the -d_1[1, 0; 0] salt is metallic. This marked difference arises from only one ^{2}D on the methyl group. On the other hand, the -d_2[1, 0; 1] and -d_2[0, 0; 2] salts are metallic. Thus, the methyl ^{2}D works more effective than the ring one. This situation can be understood from the crystal structure. These salts are all isostructural with a space group of $I4_1/a$. The chemical pressure arises from the contraction of the DCNQI column along the c axis due to the size relationship of C–D < C–H.$^{5,6)}$ The space-filling drawing of the DCNQI column (Fig. 2) indicates that the major inter-planar interaction comes from the van der Waals repulsion between the neighboring methyl groups.

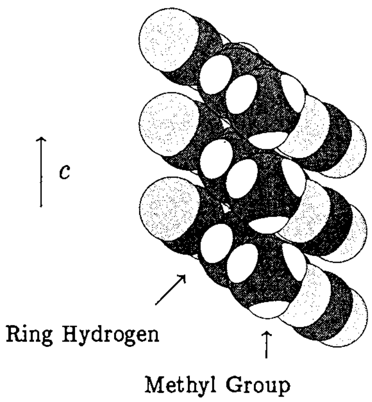


Fig. 2. Space filling drawing of the DCNQI column for (DMe-DCNQI)$_2$Cu.

Due to high cost for the preparation of the deuterides, it is important to make a good choice of a target compound. Quantitative estimation of the deuteration effect will be useful as a guiding principle for a future synthetic study. The effective chemical pressure ($P_{\rm eff}$) would be expressed as a function of a_1, a_2 and b. From comparison of the transition temperatures with those in the P–T phase diagram of Tomić *et. al*,[2] we can estimate the $P_{\rm eff}$ of the -$d_8[3,3;2]$ salt as ca. 500 bar, and that of the -$d_2[1,1;0]$ salt as ca. 150 bar. In addition, the ring ^{2}D works far less effectively than the methyl ^{2}D. Based on these considerations, we tentatively assumed that $P_{\rm eff}/{\rm bar} \approx 75\,\{(a_1 + a_2) + 0.2b\}$. Figure 3 indicates a $P_{\rm eff}$–T phase diagram obtained by using this equation.

In conclusion, the selective deuteration of (DMe-DCNQI)$_2$Cu has enabled us to control the chemical pressure. Application of this technique, together with the empirical $P_{\rm eff}$ value, easily produces the reentrant state in a non-alloy system at ambient pressure without any practical difficulty. Further studies on the physical properties of the M_R state are in progress.[9]

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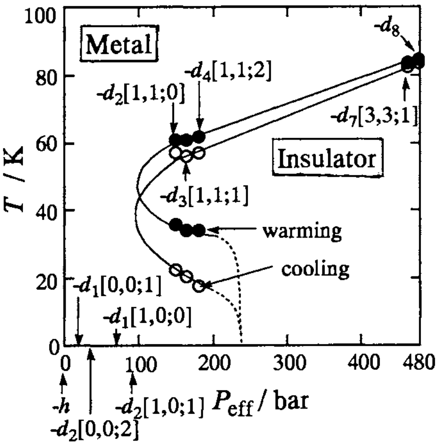

Fig. 3. $P_{\rm eff}$–T phase diagram for (DMe-DCNQI-d_n)$_2$Cu.

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8) The method for $C_6H_5CD_3$ was applied, see R. Renaud and L. C. Leitch, *Can. J. Chem.*, **34**, 98(1956).

9) Similar to the case of the (-h)-(-d_8) alloy system (Ref. 7), the Pauli-like suspectibility in the M_R state of the -$d_2[1,1;0]$ salts is enhanced compared with the one in the high-temperature metallic state.

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