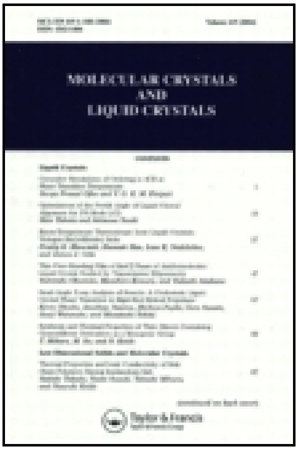

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ANOMALOUS $^{13}C/^{15}N$ ISOTOPE EFFECT IN THE π–d SYSTEM $(DMe\text{-}DCNQI)_2Cu$ STUDIED BY SELECTIVE ISOTOPE SUBSTITUTION

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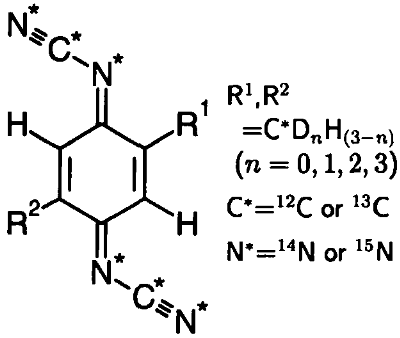
Abstract D, ^{13}C and ^{15}N isotopes were selectively introduced to the pπ–d system $(DMe\text{-}DCNQI)_2Cu$. Anomalously remarkable isotope effect was found in ^{13}C or ^{15}N substitutions of the terminal cyanoimino groups as well as deuteration of the methyl groups.

INTRODUCTION

DMe-DCNQI (2,5-dimethyl-*N,N'*-dicyano-*p*-quinonediimine) is a π-acceptor molecule first synthesized by Aumülar and Hünig,[1] and several conductive salts had been prepared with various inorganic metals.[2] Among them, the copper salt $(DMe\text{-}DCNQI)_2Cu$ shows very unique electrical and magnetic behaviors. In this system, DMe-DCNQI molecules stack to form one-dimensional columns. These columns are linked to each other by tetrahedraly coordinated Cu atoms. Through these linkages, the organic pπ band and the Cu d electrons are interacted with each other near the Fermi level.[3] The Cu ion is in the mixed valence state in the metallic state,[4] with the valence slightly smaller than 4/3+. This shift of the valence, which is very sensitive to the coordination angle of the Cu tetrahedron, stabilizes the metallic state.[5]



DMe-DCNQI

The metallic state of $(DMe\text{-}DCNQI)_2Cu$ is destabilized by applying a slight pressure of ca. 100 bar, and metal–insulator–metal (reentrant) transition occurs around the critical pressure.[6] Similar destabilization of the metallic state is triggered by deuteration,[7] and the actual pressure can be chemically controlled by selective

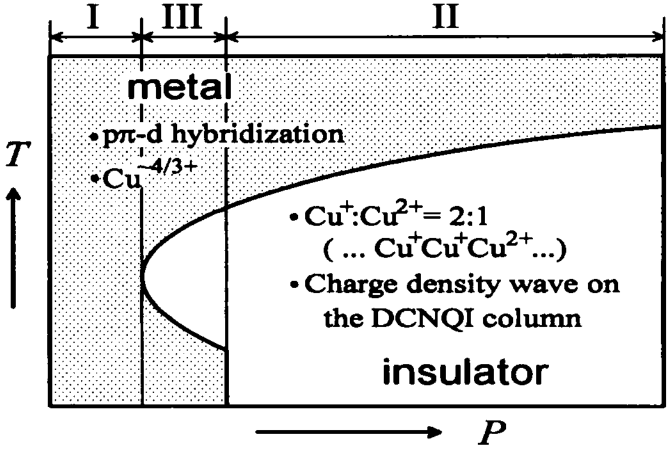


FIGURE 1 Schematic pressure (P)–temperature (T) phase diagram of (R^1,R^2-DCNQI)$_2$Cu system. P includes 'chemical pressure' brought in by substituents or alloying effects.

deuterations of a DMe-DCNQI molecule.[8] A schematic pressure–temperature phase diagram is shown in Fig. 1.

Using a_1 and a_2 as numbers of deuterium atoms in each methyl group and b as that of those directly attached to the six-membered ring, the effective pressure (P_{eff}) is formulated as a linear function of these parameters:

$$P_{\text{eff}}/\text{bar} = 80(a_1 + a_2 + 0.2b) \tag{1}$$

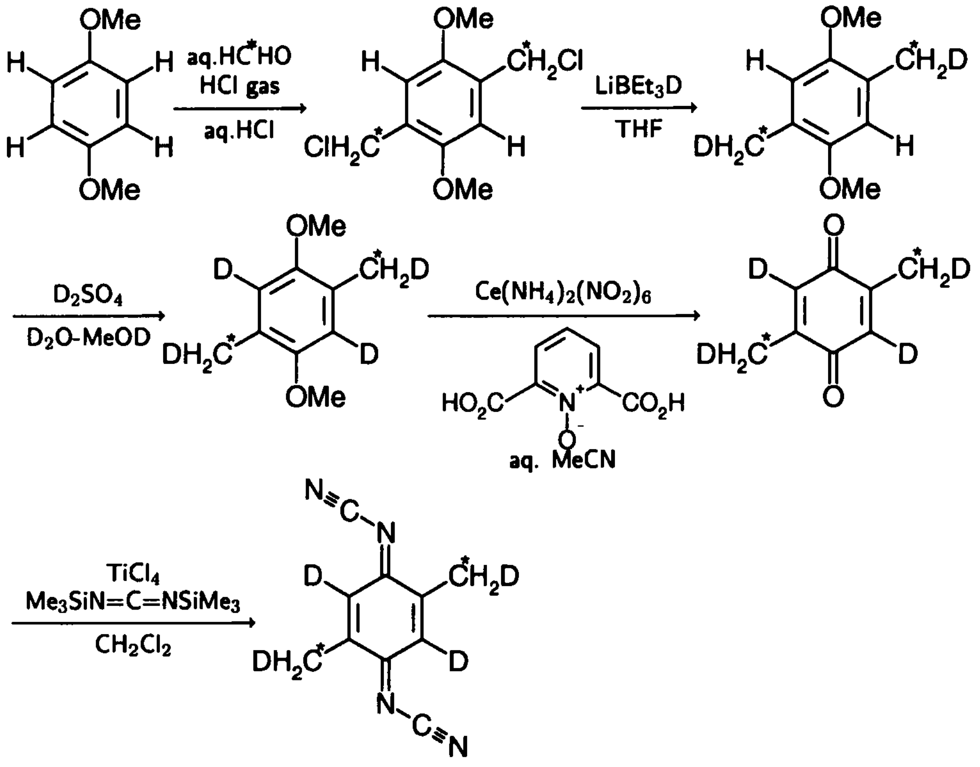
Hereafter the deuterated positions for the selective deuterides are symbolically indicated in the form of -$d_n[a_1, a_2; b]$ for convenience.

These drastic deuterium effects are assigned to steric origins. The slightly smaller deuterium atoms enhance the distortion of the coordination tetrahedron around Cu atoms. This induces extra charge transfer from Cu to DCNQI, and thus destabilizes the metallic state.[5] Introductions of ^{13}C and ^{15}N isotopes to terminal cyanoimino groups of DCNQI molecule are of another interest because these groups are directly coordinated to Cu atoms. In the following sections, these isotopes are marked as $C^*$and N^*, respectively.

RESULTS AND DISCUSSION

Isotope Labeling

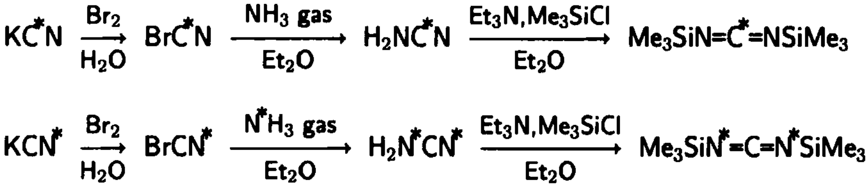
We introduced C^* to the methyl groups by stepwise reactions starting from the formylation of *p*-dimethoxybenzene with HC^*HO followed by *in situ* chlorination



SCHEME 1

with gaseous hydrogen chloride (Scheme 1).

Terminal cyanoimino (=N–C≡N) groups were isotopically labeled by use of $Me_3SiN{=}C^*{=}NSiMe_3$[9] or $Me_3SiN^*{=}C{=}N^*SiMe_3$ as dicyanoimination reagent (Scheme 2).

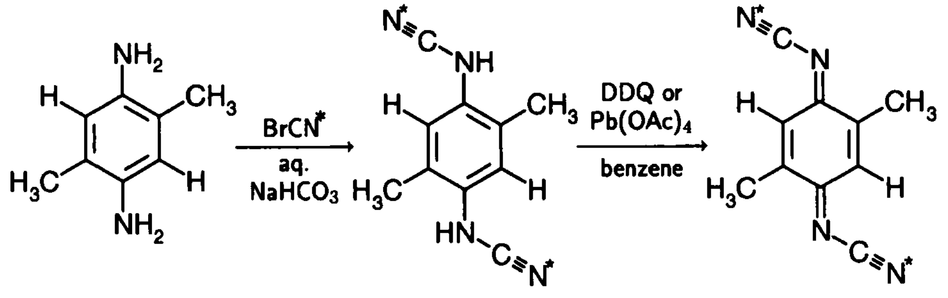


$$KC^*N \xrightarrow[H_2O]{Br_2} BrC^*N \xrightarrow[Et_2O]{NH_3\ gas} H_2NC^*N \xrightarrow[Et_2O]{Et_3N,Me_3SiCl} Me_3SiN{=}C^*{=}NSiMe_3$$

$$KCN^* \xrightarrow[H_2O]{Br_2} BrCN^* \xrightarrow[Et_2O]{N^*H_3\ gas} H_2N^*CN^* \xrightarrow[Et_2O]{Et_3N,Me_3SiCl} Me_3SiN^*{=}C{=}N^*SiMe_3$$

SCHEME 2

Cyano-N* was introduced according to the literature[1] except that BrCN*was used instead (Scheme 3). At the final oxidation step, the reaction by $Pb(OAc)_4$ proceeded more clean, and the yield was much higher than that by DDQ. However, DMe-DCN*QI or unlabeled reference obtained by the $Pb(OAc)_4$ route should be repeatedly purified with care by chromatography (SiO_2/CH_2Cl_2) and recrystallization



SCHEME 3

(acetonitrile). Otherwise residual resistance of the Cu salt was higher than those prepared by the usual dicyanoimination route.

Resistivity Measurements

Preparation of the copper salt and electrical resistivity measurement were carefully performed because this system is quite sensitive to various experimental conditions.[8] The representative results of resistivity measurement are summarized in Table I.

In sharp contrast to the methyl-deuteration effect,[8] an isotope effect in methyl-C^* seems faint (Fig. 2). These results agree with their mass ratio ($D/H \gg C^*/C$).

As for the isotope effect in the terminal cyanoimino groups (Fig. 3), the anomalously large effect was found in the case of $=N-C^*\equiv N$, which is equivalent to $P_{\rm eff}$ of ca. 100 bar. Also drastic isotope effect was observed for the case of $=N^*-C\equiv N^*$, though $P_{\rm eff}$ is slightly less than that for the C^* substitution (~ 90 bar). When the ratios of $D/H \gg C^*/C \gtrsim N^*/N$ are taking into account, these C^* and N^* effects are anomalously drastic. These have demonstrated that the electronic state of the $(DMe\text{-}DCNQI)_2Cu$ system is quite sensitive to any perturbation to the coordination around Cu. Whereas, the methyl-isotope effect indirectly affects the coordination through repulsion between bulky methyl groups along the DCNQI column.[8]

TABLE I Transition Temperatures (K) of $(DMe\text{-}DCNQI)_2Cu$

DMe-DCNQI	on cooling T_1	on cooling T_2	on warming T_1	on warming T_2
-*h*	—^{a}	—^{a}	—^{a}	—^{a}
$=N-C\equiv N^*$	—^{a}	—^{a}	—^{a}	—^{a}
$=N^*-C\equiv N^*$	48	27	41	54
$=N-C^*\equiv N$	52	24	35	55
-d_2[1,1;0]	55	21	35	56
$=N-C^*\equiv N$	68	—^{a}	—^{a}	71
-d_4[1,1;2]	61	13	30	63
methyl-C^*	62	9	26	65
$=N^*-C\equiv N^*$	68	—^{a}	—^{a}	72

[a] Transition is not observed.

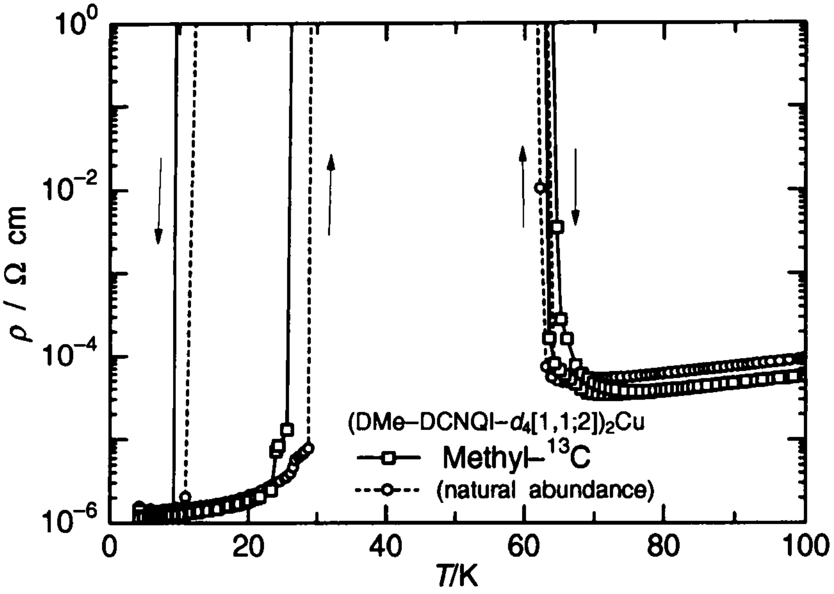


FIGURE 2 Resistivity of $[^{13}C_2]$methyl-labeled and unlabeled (DMe-DCNQI-d_4[1,1;2])$_2$Cu.

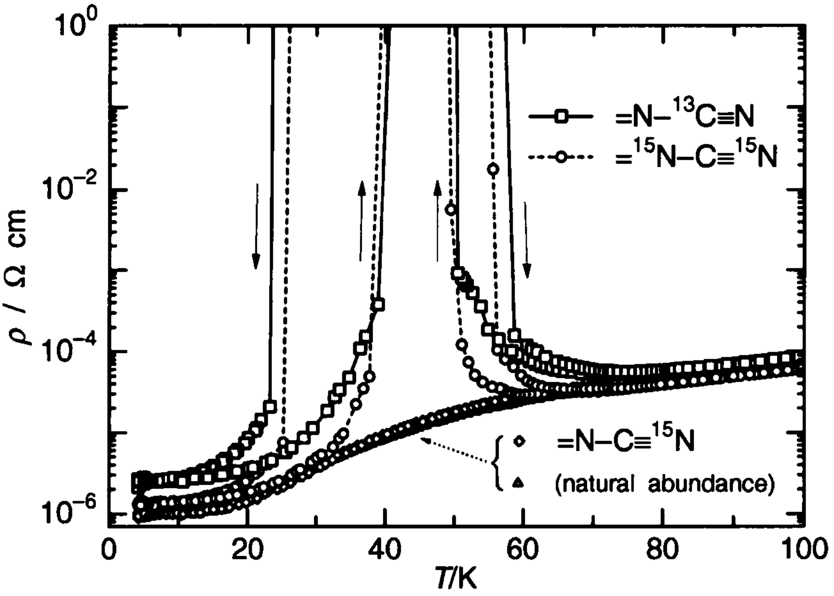


FIGURE 3 Resistivity of $[^{13}C_2]$cyanoimino-, $[^{15}N_2]$cyano$[^{15}N_2]$imino- and $[^{15}N_2]$cyanoimino-labeled (DMe-DCNQI-*h*)$_2$Cu.

Terminal cyano-N* labeling ($=\text{N}-\text{C}\equiv\text{N}^*$) induced no clear transition ($P_{\text{eff}} \lesssim$ 80 bar). It is not clear at present why the effect in $=\text{N}-\text{C}\equiv\text{N}^*$ is less than that in $=\text{N}-\text{C}^*\equiv\text{N}$, in spite of the direct contact with Cu.

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