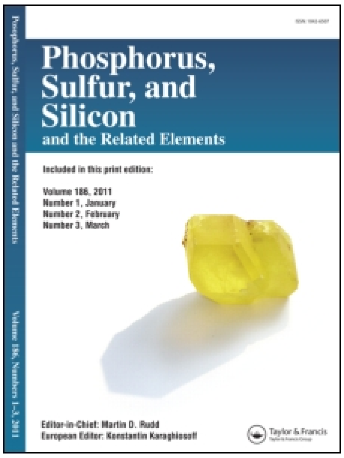


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Isotope Effect on Physical Properties of BEDT-TTF Based Organic Superconductors

Tokutaro Komatsu[a]; Nozomu Matsukawa[a]; Toshikazu Nakamura[a]; Hideki Yamochi[a]; Gunzi Saito[a]; Hiroshi Ito[b]; Takehiko Ishiguro[b]
[a] Dep. Chem., Fac. Sci., Kyoto Univ., Kyoto, Japan [b] Dep. Phys., Fac. Sci., Kyoto Univ., Kyoto, Japan

To cite this Article Komatsu, Tokutaro , Matsukawa, Nozomu , Nakamura, Toshikazu , Yamochi, Hideki , Saito, Gunzi , Ito, Hiroshi and Ishiguro, Takehiko(1992) 'Isotope Effect on Physical Properties of BEDT-TTF Based Organic Superconductors', Phosphorus, Sulfur, and Silicon and the Related Elements, 67: 1, 295 — 300

To link to this Article: DOI: 10.1080/10426509208045850

URL: http://dx.doi.org/10.1080/10426509208045850

Phosphorus, Sulfur, and Silicon, 1992, Vol. 67, pp. 295–300

Printed in the United Kingdom

ISOTOPE EFFECT ON PHYSICAL PROPERTIES OF BEDT-TTF BASED ORGANIC SUPERCONDUCTORS

TOKUTARO KOMATSU, NOZOMU MATSUKAWA, TOSHIKAZU NAKAMURA,
HIDEKI YAMOCHI, and GUNZI SAITO
Dep. Chem., Fac. Sci., Kyoto Univ., Sakyo-ku, Kyoto, Japan
HIROSHI ITO, and TAKEHIKO ISHIGURO
Dep. Phys., Fac. Sci., Kyoto Univ., Sakyo-ku, Kyoto, Japan

Abstract The isotope shifts of the superconducting transition temperature for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br were evaluated from the resistivity and dc magnetization measurements. The deuteration of the terminal ethylene groups of the donor molecule lowered T_c by 0.4 to 0.5K, whereas the ^{13}C substitution on the same fragments gave no isotope shifts within the experimental accuracy.

INTRODUCTION

Since the discovery of the superconductivity in (TMTSF)$_2$PF$_6$, about 40 organic superconductors have been synthesized and the superconducting transition temperatures (T_c) of them have exceeded 12K. Some of them exhibit peculiar properties which can not be explained by the simple BCS theory, including the isotope shift of T_c. For example, unexpectedly large positive isotope shift has been observed in the deuterated (TMTSF)$_2$ClO$_4$[1]. On the other hand, inverse isotope shifts have been detected in both the deuterated and the ^{13}C substituted κ-(BEDT-TTF)$_2$Cu(NCS)$_2$[2].

Recently, new organic superconductors, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X (X=Br, Cl), with the highest T_c among the TTF related organic superconductors were discovered[3]. In this paper, the results of the resistivity and dc magnetization measurements on the Cu[N(CN)$_2$]Br salts of hydrogenated, deuterated, and ^{13}C substituted BEDT-TTF (for short, h$_8$-,

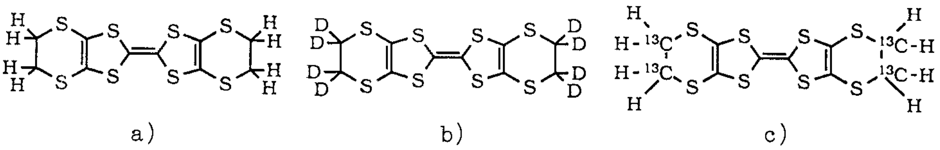

a) b) c)

FIGURE 1 a) h$_8$-BEDT-TTF, b) d$_8$-BEDT-TTF, c) ^{13}C-BEDT-TTF

d_8-, and ^{13}C-salt, respectively) are reported.

EXPERIMENTAL

The h_8-, d_8- and ^{13}C-salts were prepared by the electrocrystallization of corresponding BEDT-TTF in the presence of CuBr, NaN(CN)$_2$ and 18-crown-6 ether from THF containing 10 vol. % of ethanol. The dc magnetization was measured with Quantum Design Magnetic Property Measurement System. About 1 to 2 mg of small crystals were wrapped with a polyethylene film and held in a polyvinylidenechloride tube. Resistivities were measured by dc four-probe method on the h_8- and d_8-salt. Gold wires were attached to the single crystal with gold paste.

RESULTS AND DISCUSSION

All the single crystals of h_8-, d_8- and ^{13}C-salts on which the X-ray diffraction experiments were carried out gave the unit cell parameters similar to each other within experimental error and these values were in good agreement with that reported for the h_8-salt[3]. This indicates that the isotope substituted salts are isostructural to the original one at least at room temperature in which the donor molecules form the conducting sheets in the ac plain.

From the temperature dependences of the resistivities, the h_8- and d_8-salts are categorized in four groups. The four typical behaviors are depicted in Figure 2.

Some d_8- and most of the h_8-salts showed the temperature dependences of the resistivity in the ac plain as the curve [1] in Figure 2. This curve has the broad resistivity maximum at around 110K to 90K and the shoulder at around 70K. The samples in this group have relatively small residual resistivities, and the highest T_c among the four groups. The T_c's of both salts in this group are shown in Table 1.

The behavior indicated by the curve [2] was sometimes observed in both salts, in the parallel and the perpendicular direction to the ac plain. The crystals in this group showed the resistivity maximum at around 50K, and the residual resistivities are comparable to their own resistivities at room temperature.

A few crystals of the d_8-salt exhibited the most pronounced semiconducting behavior and the sharpest semiconductor-metal transition at

40K (curve [3]). These behaviors were observed independently of the measured direction. The samples that belong to this group showed the increment of the resistivity below about 20K and had rather broad superconducting transition.

Curve [4] was observed only for one d_8-salt in one batch and for the measurement along the b direction so far. On cooling the sample, the faint semiconductive behavior was observed down to ca. 50K including the plateau at around 100 to 90K. Then the metallic region was found at lower temperatures, however the metal-insulator transition took place at 24K and the superconductivity was not observed down to

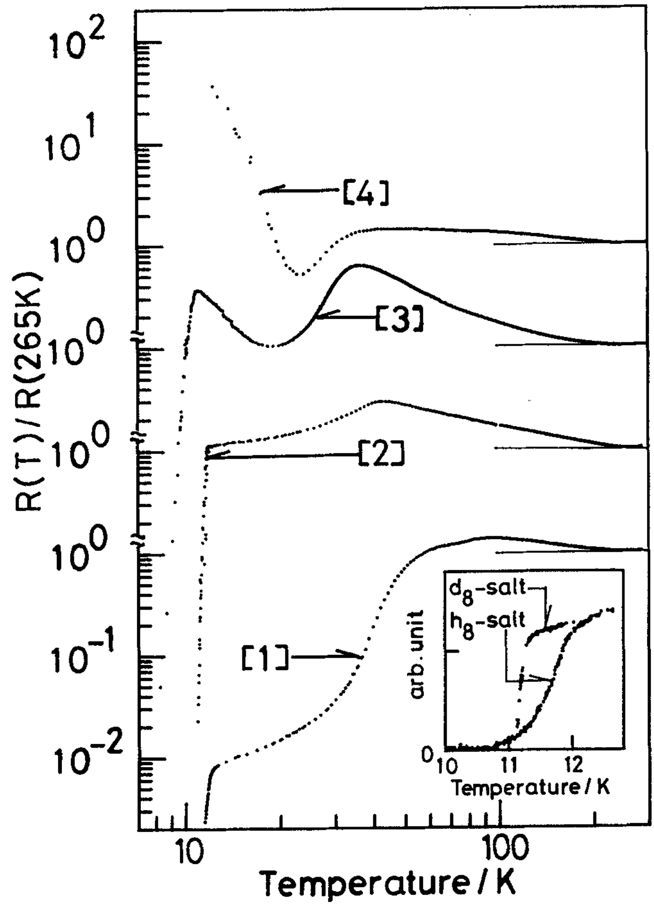
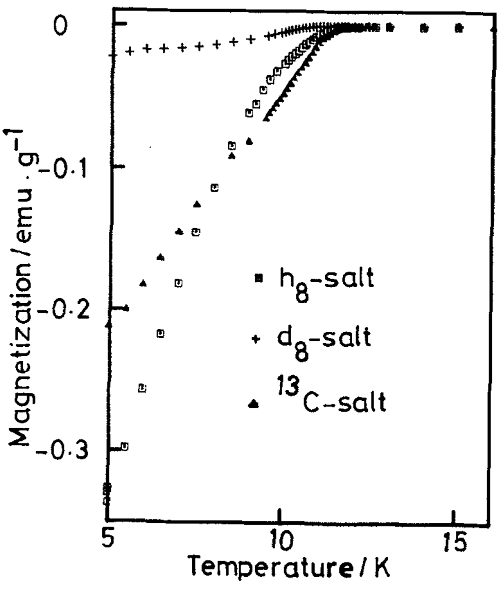


FIGURE 2 Four typical temperature dependences of the normalized resistivities of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. About the four groups, see text. The inset shows the superconducting transition of the h_8- and d_8-salts those belong to the group [1].

1.5K. All the crystals of this batch had needle-like appearances, which differ from thick rhombus-platelet of the ordinal h_8- and d_8-salts. In spite of their unusual properties, the lattice constants of the needles were in fair agreement with the reported values for the h_8-salt[3] within the experimental error. Therefore the sample exhibited the metal-insulator transition does not belong to the entirely different modification. This anomalous behavior could be attributed to the slight modification of crystal structure, to the strain caused by the electrode, and/or to the concentration of the defects in the crystal.

Summarizing the results, the following tendencies for the cooling processes emerge. (a) The semiconductive behavior persisted from about 260K down to a certain temperature T_{max} for all samples. (b) Below T_{max}, the metallic regimes were observed. (c) The increment of T_{max} suppressed the metal-insulator transition and increased T_c.

These various properties may indicate that this compound is on the boundary between insulator and superconductor, similar to the Cl-



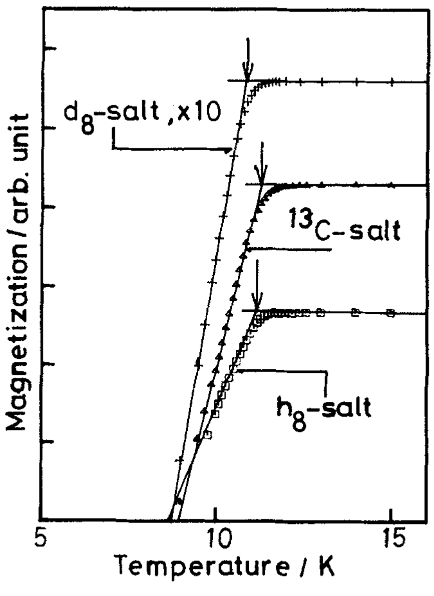


FIGURE 3a(left) The temperature dependences of the magnetization of the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. Squares, crosses and triangles denote the h_8-, d_8- and ^{13}C-salt, respectively.

FIGURE 3b(right) The same results as Figure 3b shown by arbitrary unit. The T_c's are indicated by the arrows.

analog, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl.

Figures 3a and 3b show the temperature dependences of the magnetizations in the magnetic field of 500 Oe after zero-field cooling.

All the d_8-salts measured to date gave the diamagnetic signal at 5K with about one order smaller intensity than other isotope analogs. These anomalously small values coincide in magnitude with those reported previously[5]. The dimensions of the crystals of the d_8-salt used for this experiment did not differ so much from the h_8- and ^{13}C-salts. So this result indicates that the superconducting volume fraction of the d_8-salts is rather small compared with other isotope analogs.

Table 1 summarizes the T_c's evaluated from the resistivity and the magnetization measurements. For the magnetization values, T_c's were defined by the intersection of the linear extrapolations of the paramagnetic and the abrupt changing region, as indicated by the arrows in Figure 3b.

TABLE 1 T_c's evaluated for three isotope analogs

	resistivity			magneti-
	onset	midpoint	offset	zation
h_8-salt	11.9K	11.7K	10.8K	11.3K
d_8-salt	11.3K	11.2K	10.8K	10.9K
^{13}C-salt	----	----	----	11.3K

For the d_8-salt, T_c was 0.4K-0.5K lower than the h_8-salt. This shift is larger than that predicted by the simple BCS theory. The magnitude of this shift is about the same as the value evaluated from the rf penetration experiment(0.5K)[4], and about half compared with that given by previously reported magnetization measurement(0.9K)[5], but is still enormous. For the ^{13}C-salt, the magnetization measurement gave almost the same T_c as that of the h_8-salt within the experimental error.

The single crystal measurements of magnetization on the h_8- and d_8 salt were also carried out and analyzed in terms of the renormalized theory of superconductivity fluctuation[6]. The results gave the same Ginzburg-Landau coherence length for the d_8-salt as for the h_8-salt. This single crystal of the d_8-salt was also used for the resistivity measurement, and revealed to be the group [3]. The details will be reported elsewhere.

Summarizing our results, the substitution of the four outer carbon atoms of BEDT-TTF with ^{13}C has no detectable isotope effects on the superconductivity of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, however, the deuteration of the donor molecule lowers the T_c anomalously.

CONCLUSION

We observed larger isotope shift than that predicted from the simple BCS theory only for d_8-salt. On the other hand, the ^{13}C-salt gave no observable shift. The latter is not opposite to the BCS theory. This result is contrary to the case of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, where inversed isotope shifts were observed by both ^{13}C and deuterium substitutions of the terminal ethylene groups.

ACKNOWLEDGMENT

We would acknowledge Dr. N. Hosoito, Mr. M. Watanabe and Dr. Y. Nogami for their support in SQUID measurements, and Dr. M. Kusunoki, Mr. K. Sakaguchi, and Dr. T. Mori for the X-ray measurements. This work was partly supported by the Grant-in-Aid for Scientific Research from Ministry of Education, Science and Culture, Japan.

REFERENCES

1. H. Schwenk, E. Hess, K. Andres, F. Wudl and E. Aharon-Shalom, Phys. Lett., 102A, 57 (1984)
2. G. Saito, H. Yamochi, T. Nakamura, T. Komatsu, M. Nakashima, H. Mori and K. Oshima, Physica B, 169, 372 (1991)
3. A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams W. K. Kwok, K. G. Vandervoort, J. E. Thompson and D. L. Stupka, Inorg. Chem., 29, 2555 (1990) ; J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. Strieby Crouch, W. K. Kwok, J. E. Schirber and D. L. Overmyer, Inorg. Chem., 29, 3272 (1990)
4. H. H. Wang, K. D. Carlson, U. Geiser, A. M. Kini, A. J. Schultz, J. M. Williams, L. K. Montgomery, W. K. Kwok, U. Welp, K. G. Vandervoort, S. J. Boryschuk, A. V. Strieby Crouch, J. M. Kommers, D. M. Watkins, J. E. Schirber, D. L. Overmyer, D. Jung, J.J. Novoa and M. H. Whangbo, Synth. Met., 42, 1983 (1991) (Proceedings of ICSM'90, Tübingen, Aug., 1990)
5. M. Tokumoto, N. Kinoshita, Y. Tanaka and H. Anzai, J. Phys. Soc. Jpn., 60, 1426 (1991)
6. R. Ikeda and T. Tsuneto, J. Phys. Soc. Jpn., 60, 1337 (1991)