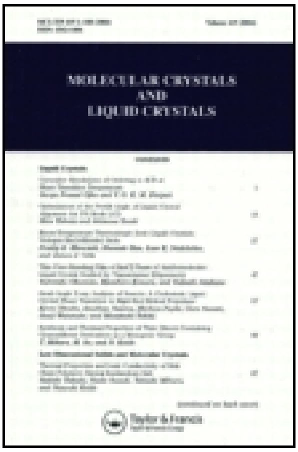

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Superconductivity in BEDT-TTF Based Organic Metals: Role of Uniaxial Pressure and Inverse Isotope Effect

M. Tokumoto [a] , K. Murata [a] , N. Kinoshita [a] , K. Yamaji [a] , H. Anzai [a] , Y. Tanaka [b] , Y. Hayakawa [b d] , K. Nagasaka [b] & Y. Sugawara [c]

[a] Electrotechnical Laboratory, Tsukuba, Ibaraki, Japan

[b] Department of Physics, Science University of Tokyo, Tokyo, Japan

[c] Riken Institute, Wako, Saitama, Japan

[d] Hitachi, Ltd., Tokyo, Japan

Version of record first published: 22 Sep 2006.

To cite this article: M. Tokumoto , K. Murata , N. Kinoshita , K. Yamaji , H. Anzai , Y. Tanaka , Y. Hayakawa , K. Nagasaka & Y. Sugawara (1990): Superconductivity in BEDT-TTF Based Organic Metals: Role of Uniaxial Pressure and Inverse Isotope Effect, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 181:1, 295-304

To link to this article: http://dx.doi.org/10.1080/00268949008036013

Mol. Cryst. Liq. Cryst., 1990, vol. 181, pp. 295–304
Reprints available directly from the publisher
Photocopying permitted by license only

SUPERCONDUCTIVITY IN BEDT-TTF BASED ORGANIC METALS: ROLE OF UNIAXIAL PRESSURE AND INVERSE ISOTOPE EFFECT

M. TOKUMOTO, K. MURATA, N. KINOSHITA, K. YAMAJI, H. ANZAI
Electrotechnical Laboratory, Tsukuba, Ibaraki, Japan.
Y. TANAKA, Y. HAYAKAWA*, K. NAGASAKA
Department of Physics, Science University of Tokyo, Tokyo, Japan
Y. SUGAWARA
Riken Institute, Wako, Saitama, Japan

Abstract The superconducting properties characteristic to the two most extensively studied BEDT-TTF based organic metals are compared. A whole family of β-$(BEDT\text{-}TTF)_2X$ salts, including its mixed-anion crystals, with T_c varying from 8 K to below 1 K enables us to study various factors governing T_c in a systematic way. A new member, κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$, with the highest Tc among organic superconductors, obviously constitutes another case. One of the important feature common to both β-$(BEDT\text{-}TTF)_2X$ and κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ is seen in the effect of hydrostatic pressure on Tc. In order to clarify its origin, the role of uniaxial pressure is discussed with some recent experimental results. Finally, an estimation of the isotope effect on the superconductivity in TTF-analog based organic metals is made, which leads us to an inverse isotope effect.

INTRODUCTION

In the history of organic superconductors, "*Pressure*" has been playing an essential role. The first observation of superconductivity in organic material was made in $(TMTSF)_2PF_6$ by application of pressure in 1980.[1] The effect of pressure in the TMTSF based quasi-one-dimensional organic metals is understood basically to increase the dimensionality and stabilize metallic state at low temperatures. In contrast to the case of TMTSF salts, quasi-two-dimensional nature of BEDT-TTF based

* Present address: Hitachi, Ltd., Tokyo , Japan.

organic metals have provided us a plenty of superconductors at ambient pressure.[2] It turned out, however, the application of pressure does not favor the superconductivity in most of the BEDT-TTF based ambient-pressure superconductors. In other words, Tc decreases rapidly by application of pressure. The origin of this large pressure dependence of Tc is not quite understood.

It is now well known that the superconductivity in BEDT-TTF based organic metals are very sensitive to (1) disorder, defects and impurities,[2,3] as well as (2) pressure. A most outstanding example of the former characteristic is seen in the mixed anion crystals of β-(BEDT-TTF)$_2$ trihalides, including the effect of anion disorder in I_2Br salt, in which the correlation between Tc and residual resistivity and the requirement of *minimum conductivity* (6000S/cm) for superconductivity were established.[4,5] Another well-known example of the former characteristic is seen in the difference between the low-Tc state (β_L phase) and the high-Tc state (β_H phase) in β-(BEDT-TTF)$_2$I$_3$. Namely, the β_L phase has additional *disorder* due to the incommensurate lattice modulation[6] accompanied by the disordered ethylene group as designated as A-type vs. B-type,[7] or staggered vs. eclipsed,[8] at one end of the BEDT-TTF molecules. In this case, we also see a good correlation between Tc and residual resistivity, i.e. β_H phase has much lower resistivity than β_L phase at low temperatures.[9]

Recently, annealing at about 110K was found to result in a change of the incommensurate lattice modulation in β-(BEDT-TTF)$_2$I$_3$.[10] It was further found that annealing results in a decrease in resistance up to almost 10% and appearance of a new superconducting state with Tc=2K.[11] This 2K state with lower resistance is metastable and goes back to the low-Tc state when warmed above 120K. Here, a correlation between Tc and resistivity seems to hold at least around 100K. However, the difference in the resistance between the 2K state and the low-Tc state was found to disappear at low temperatures.[3,12] The origin of the difference in Tc has not been clarified, and needs further study.

In this paper, we review the effect of hydrostatic pressure on both the lattice parameter and superconductivity. We also discuss the usefulness of application of uniaxial pressure on the superconductivity with some preliminary experimental results. Finally, an estimation of the isotope effect on the basis of intramolecular-vibration-mediated superconductivity in TTF-analog based organic metals are presented.

EFFECT OF HYDROSTATIC PRESSURE

Figure 1 shows the effect of hydrostatic pressure on Tc in β-(BEDT-TTF)$_2$X for X=I_3,[13,14] IBr_2,[15] and AuI_2[16] and in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.[17] Somewhat similar but not quite the same results were reported for β-(BEDT-TTF)$_2$X (X=I_3,[18] and IBr_2[16]) and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.[19] The difference comes from either the calibration of pressure, definition of Tc or samples. It can be said safely from Fig. 1 that the superconductivity in organic metals (BEDT-TTF)$_2$X is very sensitive to pressure. The largest pressure effect on Tc is seen in the κ-Cu(NCS)$_2$ salt and is about -2K/kbar,[17] (or -1.3K/kbar[19]), while that in the β-(BEDT-TTF)$_2$X salts is about -1K/kbar or less. The rate of the decrease in Tc seems to be larger for superconductors with higher Tc.

This large pressure dependence is very important since it could give us a clue to understand the mechanism of superconductivity in

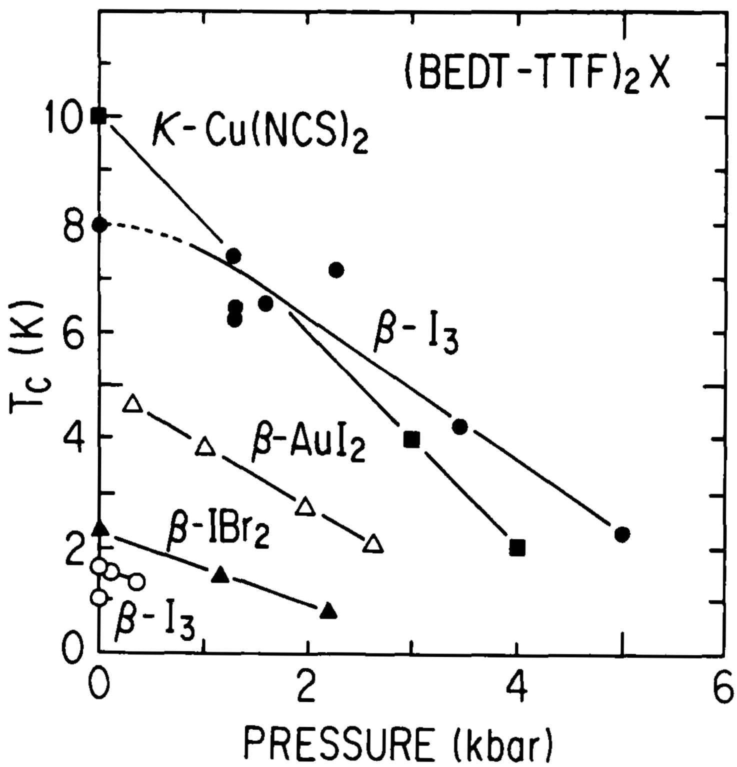

FIGURE 1 Effect of hydrostatic pressure on Tc in β-(BEDT-TTF)$_2$X (X=I_3,[13,14] IBr_2,[15] and AuI_2[16]) and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.[17]

these organic materials. Origins of these pressure dependence of Tc is, however, not clarified yet, although some models to explain it are proposed.[20,21] Here we classify them into three categories as follows.

1. Density of states $N(E_F)$ within the plane *<Intraplane Interaction>*
2. Interaction between the conducting planes *<Interplane Interaction>*
3. Electron-molecular vibration model[21] *<intramolecular vibration>*

The first one is to relate it to the change of the density of state of 2-D electron system. Since the pressure generally reduces the intermolecular distance, it is expected to increase the transfer integrals and consequently the bandwidth, which in turn reduces the density of state at the Fermi level in a simple tight-binding picture of 2-D electron system. And a simple formalism based on the BCS theory tells us that the Tc decrease with decreasing density of state. This explanation is qualitatively consistent with the observed decrease in Tc, but has a difficulty in quantitative agreement. For example, the effect of pressure on the density of states (~-3%/kbar) estimated from spin susceptibility[22] or from ^{1}H-NMR measurement under pressure[23] seems to be too small to explain the large change in Tc. Nowak et al.[20] discussed this possibility in greater detail.

The possibility of second origin is interesting. Since a pure 2-D electronic system is not expected to show superconductivity, we need to introduce interaction between conducting layers, which possibly governs the Tc in organic superconductors with layered structure. In order to understand the effect of pressure, we must know the change of lattice parameters in each case. However, only a few compressibility studies have been reported so far.

Figure 2 shows the effect of hydrostatic pressure on the lattice parameters in β-(BEDT-TTF)$_2$I$_3$,[24,25] and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.[26] In Fig. 2, $l_\perp$ stands for the lattice parameter perpendicular to the conducting plane, i. e. $1/c^*$ for β-(BEDT-TTF)$_2$I$_3$, and $1/a^*$ for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, whereas $l_{//}$ stands for the lattice parameter along the conducting plane which is defined here as $2(ab\sin\gamma)^{1/2}$ for β-(BEDT-TTF)$_2$I$_3$, and $(2bc)^{1/2}$ for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ just for the purpose of fair comparison with each other and also with $l_\perp$. In both β-(BEDT-TTF)$_2$I$_3$ and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, application of hydrostatic pressure results in compression of lattice parameters in each direction, so that both $l_\perp$ and $l_{//}$ shrink although the amount of shrinkage is not the same among each other. Thus, the effect of hydrostatic pressure involves decrease of both in-plane ($l_{//}$) and out-of-plane ($l_{\perp}$) lattice parameters. So we need another way to change these parameters in order to separate the two effects. As such an example we would like to consider the role of uniaxial pressure in the following section.

In the third model,[21] Tc is expected to change via change in the frequency of intramolecular vibration as well as electron-molecular vibration coupling constants. This point will be discussed later.

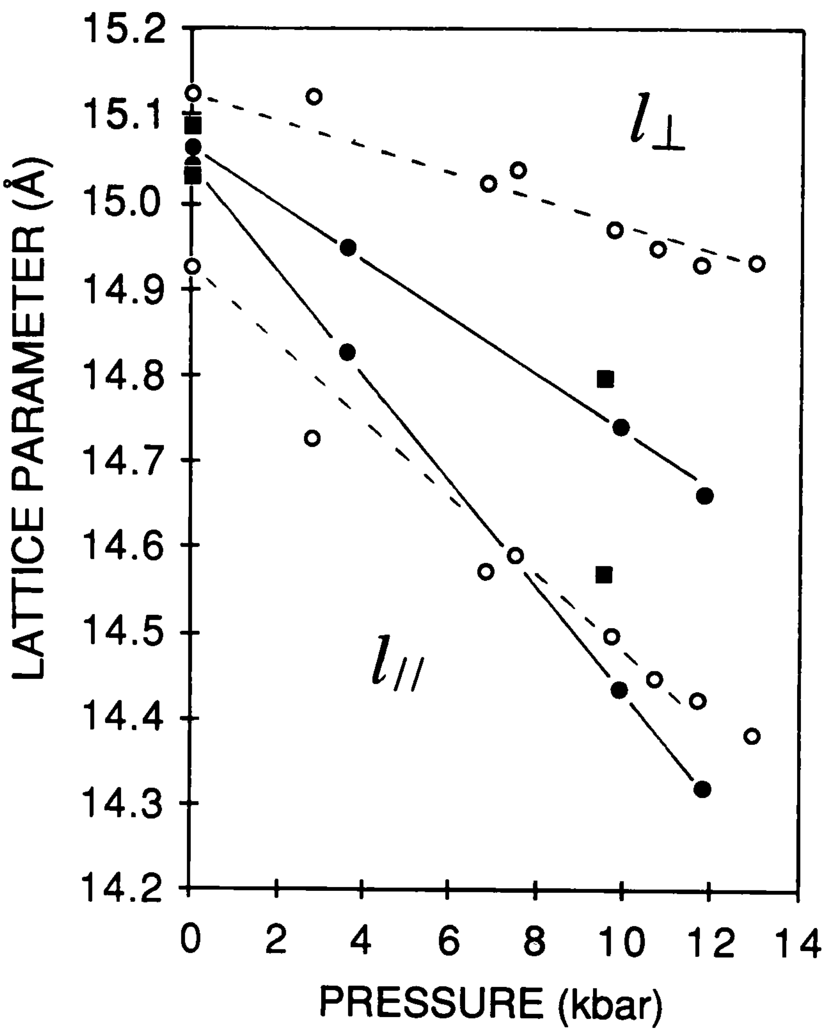

FIGURE 2 Effect of hydrostatic pressure on the lattice parameters of β-(BEDT-TTF)$_2$I$_3$ (●,[24] ■[25]) and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (O[26]).

ROLE OF UNIAXIAL PRESSURE

As we have seen in Fig. 2, the effect of hydrostatic pressure involves decrease of both in-plane ($l_{//}$) and out-of-plane ($l_{\perp}$) lattice parameters. On the other hand, uniaxial pressure perpendicular to the plane is expected to cause a *decrease* in the distance ($l_{\perp}$) between the conducting planes accompanied by some *increase* in the in-plane lattice parameters ($l_{//}$). Thus combination of the two experiments is expected to identify the dominance between *intraplane* and *interplane* interactions. Figure 3 shows the effect of uniaxial pressure on the superconducting transition of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. A uniaxial pressure applied perpendicular to the conducting plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ revealed that Tc decreases by uniaxial compression as ΔTc=-0.01~0.02 K/bar. One way to interpret this result is as follows. The decrease in Tc by application of both hydrostatic and uniaxial pressure indicates that the common lattice parameter which changes in the same direction, i.e. $l_{\perp}$, is dominating the change of Tc in this case.

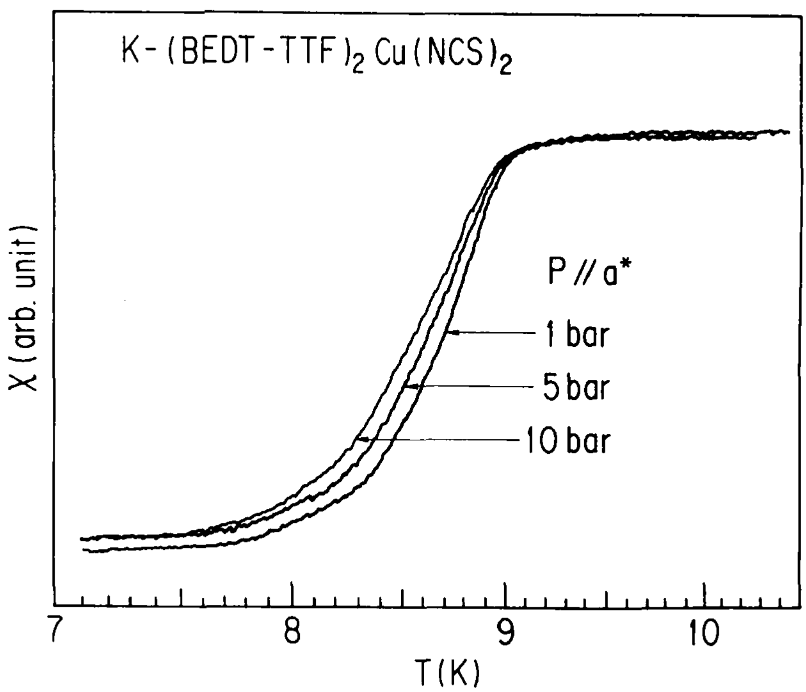

FIGURE 3 Effect of uniaxial pressure on the superconducting transition of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

This simple interpretation seems to suggest that *interplane* interaction is important in the case of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$. However we should refrain from regarding this result as a general feature applicable to other systems. Actually, some preliminary results on a similar experiment indicate an opposite tendency in the case of the high-Tc state of β-$(BEDT\text{-}TTF)_2I_3$, suggesting that the role of uniaxial pressure can be different from one material to the other.

ESTIMATION OF THE ISOTOPE EFFECT

Now, we will discuss the third possibility. In this model on the mechanism of superconductivity by Yamaji,[21] the attractive interaction mediated by intramolecular vibration is incorporated into the BSC theory, and Tc is expected to change via change in frequency of intramolecular vibration as well as electron-molecular vibration coupling constants.

It is well known that there is a strong interaction between the HOMO and totally symmetric intramolecular vibration modes in the TTF-analog molecules. Actually it it a common practice to use the central C=C distance in order to estimate the charge transfer of each TTF-analog molecule. This strong electron-molecular vibration interaction was shown to provide remarkably large attractive interactions between current carriers in the conduction band made of HOMO's on the basis of the BCS derivation.[21] Assuming that electronic state density N(0) is constant in the whole band extending from -D to D, the following solution for Tc was obtained:

$$Tc=1.13\omega_0 \exp\{-\cfrac{1}{\lambda_0-\cfrac{1}{x_1-\cfrac{1}{\lambda_1-\cfrac{1}{x_2-\cfrac{1}{\cdots\cfrac{}{\lambda_{n-1}-\cfrac{1}{x_n+\cfrac{1}{\lambda_n}}}}}}}}\} \qquad (1)$$

where, λ_0=N(0)V, λ_i=N(0)·2$g_i^2\omega_i$/N (i=1, · · · , n-1);
$x_i=\ln(\omega_i/\omega_{i-1})$ (i=1, · · · , n), and λ_n=-N(0)U=-μ, $h\omega_n$=D
Details of the estimation of Tc is given elsewhere.[21]

Our purpose is to get a reasonable estimation of the isotope effect of Tc in BEDT-TTF based superconductors. Calculation of the intramolecular vibration of BEDT-TTF is under way. In this paper we present an estimation based on the Yamaji model,[21] which uses the TTF molecule in place of BEDT-TTF. All the a_g modes of TTF have been studied and their coupling constants with the HOMO electron is published.[27] We performed a normal co-ordinate calculation of the in-plane modes of TTF using the same geometrical parameters and force constants as those reported by Bozio et al.[28,29] and calculated the isotope shift in the frequency of these vibrations by changing only the mass of corresponding atoms, leaving force constants unchanged. Table I shows the result of calculation of isotope shift for all the a_g modes of intramolecular vibration of the TTF molecule, where we substituted four hydrogen atoms with deuterium(d4), two inner carbon atoms with ^{13}C (inner^{13}C), two outer carbon atoms with ^{13}C (outer^{13}C), four carbon atoms with ^{13}C (all^{13}C) and four sulfur atoms with ^{34}S (all ^{34}S). Since all the substituted atoms in this case have heavier mass, we obtained isotope shift to lower frequency for all the intramolecular vibrations listed in Table I. In order to calculate Tc using eq. (1), we need the values of interaction constants g_i for each case. The values for normal TTF molecule (h4) are given in Table I. Here we simply employed the relation $\lambda_i \propto \omega_i^{-2}$ (i.e. $g_i \propto \omega_i^{-3/2}$) and calculated Tc as shown in Table I.

TABLE I Isotope shift of intramolecular vibration, a_g modes ω_i(cm^{-1}) (i=1-7) of the TTF molecule, and Tc .

	h4 (g_i)	d4	inner^{13}C	outer^{13}C	all ^{13}C	all ^{34}S
ω_1	232(0.16)	229	232	229	229	228
ω_2	465(1.33)	464	465	464	464	452
ω_3	734(0.49)	712	734	717	717	726
ω_4	1087(0.16)	779	1087	1085	1085	1087
ω_5	1511(0.62)	1495	1468	1468	1454	1511
ω_6	1554(0.23)	1545	1538	1541	1495	1554
ω_7	3074(0.03)	2284	3074	3063	3063	3074
Tc(K)	3.85	5.24	4.52	4.86	5.24	5.23

It is interesting to note that substitution by heavier atoms resulted in lower intramolecular vibration frequency (normal isotope effect) but higher Tc (inverse isotope effect). This model has two advantages; that is, it provides a qualitative explanation for both the inverse isotope effect as reported by Oshima et al. for κ-(BEDT-TTFd8)$_2$Cu(NCS)$_2$,[30] and the pressure effect on the same argument. Pressure is also considered as a primary effect to increase the a_g mode frequencies, decreasing the electron-a_g-mode couplings, thus decreasing Tc rapidly.

SUMMARY

We have discussed the origin of the strong pressure dependence of Tc, and showed the usefulness of application of uniaxial pressure with some experimental results. The intramolecular-vibration-mediated superconductivity model has been shown to provide qualitative explanation for both the pressure effect and the inverse isotope effect.

REFERENCES

1. D. Jerome, A. Mazaud, M. Ribault and K. Bechgaard, J. Phys. (Paris) Lett., 41, L95 (1980).
2. See for example, M. Tokumoto in Proc. 1st ISSP Symposium on the Physics and Chemistry of Organic Superconductors (Springer-Verlag, to be published).
3. M. Tokumoto, N. Kinoshita, K. Murata, H. Bando and H. Anzai, in Proc. MRS 1989 Fall Meeting "Advanced Organic Solid State Materials" (to be published).
4. H. Anzai, M. Tokumoto, K. Takahashi and T. Ishiguro, J. Cryst. Growth, 91, 225 (1988).
5. M. Tokumoto, H. Anzai, K. Murata, K. Kajimura and T. Ishiguro, Jpn. J. Appl. Phys., 26-S3, 1977 (1987); *idem*, Synth. Metals, 27, A251 (1988).
6. T. J. Emge, P. C. Leung, M. A. Beno, A. J. Schultz, H. H. Wang, L. M. Soma and J. M. Williams, Phys. Rev., B30, 6780 (1984).
7. P. C. W. Leung, T. J. Emge, M. A. Beno, H. H. Wang, J. M. Williams, V. Petricek and P. Coppens, J. Am. Chem. Soc., 107, 6184 (1985).
8. J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn, A. J. Schultz and M. -H. Wangbo, Prog. Inorg. Chem., 35, 51 (1987).
9. V. B. Ginodman, A. V. Gudenko, L. N. Zherikhina, V. N. Laukhin, E. B. Yagubskii, P. A. Kononovich and I. F. Shegolev, Acta Polymerica 39, 533 (1988).

10. S. Kagoshima, Y. Nogami, M. Hasumi, H. Anzai, M. Tokumoto, G. Saito and N. Mori, Solid State Commun., 69, 1177 (1989).
11. S. Kagoshima, M. Hasumi, Y. Nogami, N. Kinoshita, H. Anzai, M. Tokumoto and G. Saito, Solid State Commun., 71, 843 (1989).
12. T. Sasaki, N. Toyota, M. Hasumi, T. Osada, S. Kagoshima, H. Anzai, M. Tokumoto and N. Kinoshita, J. Phys. Soc. Jpn., 58, 3477 (1989).
13. L. J. Azevedo, E. L. Venturini, J. E. Schirber, J. M. Williams, H. H. Wang and T. J. Emge, Mol. Cryst. Liq. Cryst., 119, 389 (1985).
14. K. Murata, M. Tokumoto, H. Anzai, H. Bando, G. Saito, K. Kajimura and T. Ishiguro, J. Phys. Soc. Jpn., 54, 2084 (1985).
15. K. Murata, M. Tokumoto, H. Bando, H. Tanino, H. Anzai, N. Kinoshita, K. Kajimura, G. Saito and T. Ishiguro, Physica, 135B, 515 (1985).
16. J. E. Schirber, L. J. Azevedo, J. F. Kwak, E. L. Venturini, P. C. W. Leung, M. A. Beno, H. H. Wang and J. M. Williams, Phys. Rev., B33, 1987 (1986).
17. K. Murata, Y. Honda, H. Anzai, M. Tokumoto, K. Takahashi, N. Kinoshita, T. Ishiguro, N. Toyota, T. Sasaki and Y. Muto, Synth. Metals, 27, A341 (1988).
18. V. N. Laukhin, E. E. Kostyuchenko, Yu. V. Sushko, I. F. Schegolev and E. B. Yagubskii, JETP Lett., 41, 81 (1985).
19. K. Oshima, T. Mori, H. Inokuchi, H. Urayama, H. Yamochi and G. Saito, Synth. Metals, 27, A165 (1988).
20. A. Nowack, M. Weger, D. Schweizer and H. J. Keller, Solid State Commun., 60, 199 (1986)
21. K. Yamaji, Solid State Commun., 61, 413 (1987).; *idem*, Synth. Metals, 27, A115 (1988).
22. B. Rothaemel, H.Brunner, D. Schweitzer and H. J. Keller, Phys. Rev., B34, 704 (1986).
23. Y. Maniwa, T. Takahashi, K. Murata and G. Saito, Physica, 143B, 506 (1986).
24. H. Tanino, K. Kato, M. Tokumoto, H. Anzai and G. Saito, J. Phys. Soc. Jpn., 54, 2390 (1985).
25. V. N. Morchanov, R. P. Shibaeva, V. N. Kachinskii, E. B. Yagubskii, V. N. Simonov, B. K. Vainshtein, Dokl. Akad. Nauk. SSSR, 286, 637 (1986) [Sov. Phys. Doklady 31, 6 (1986)].
26. D. Chasseau, J. Gaultier, H. Houbib, M. Rahal, L. Ducasse, M. Kurmo and P. Day, in Proc. MRS 1989 Fall Meeting "Advanced Organic Solid State Materials" (to be published).
27. N. O. Lipari, M. J. Rice, C. B. Duke, R. Bozio, A. Girlando and C. Pecile, Int. J. Quantum Chem.: Quantum Chem. Symp. 11, 583 (1977).
28. R. Bozio, A. Girlando and c. Pecile, Chem. Phys. Lett., 52, 503 (1977).
29. R. Bozio, I. Zanon, A. Zirlando and C. Pecile, J. Chem. Phys., 71, 2282 (1979).
30. K. Oshima, H. Urayama, H. Yamochi and G. Saito, Synth. Metals, 27, A473 (1988).