JOURNAL OF
Materials
CHEMISTRY

# Electrical properties and crystal structures of metallic TMVT salts

**Hiroyuki Nishikawa,*[a] Tatsuo Sato,[a] Takeshi Kodama,[a] Isao Ikemoto,[a] Koichi Kikuchi,*[a] Hiroyuki Anzai[b] and Jun-ichi Yamada*[b]**

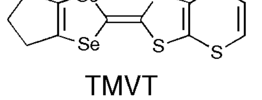
[a]*Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192–0397, Japan. E-mail: hiron@comp.metro-u.ac.jp, kikuchi-koichi@c.metro-u.ac.jp*
[b]*Department of Material Science, Faculty of Science, Himeji Institute of Technology, 1479–1 Kanaji, Kamigori-cho, Ako-gun, Hyogo 678–1297, Japan. E-mail: yamada@sci.himeji-tech.ac.jp*

***Received 12th October 1998, Accepted 8th December 1998***

The TMVT-based salts $(TMVT)_2X$ ($X^- = AsF_6^-$ and $ClO_4^-$) have been characterized by X-ray crystallography, electrical resistivity measurements, thermoelectric power measurements and EPR studies. Although an increase in resistivity was observed in both salts, the thermoelectric power indicated that these salts retain essentially metallic states. In contrast with this result, the tight-binding band calculation of these salts suggested that their Fermi surfaces are quasi-one-dimensional and inclined to be nested. The X-ray crystallographic analyses revealed that their structures are similar to that of $(TMVT)_2PF_6$, and consist of donor stacks with no dimerization, wherein there are several chalcogen···chalcogen contacts shorter than the sum of the van der Waals radii within and between the stacks.

## Introduction

For ET-based superconductors [ET = bis(ethylenedithio)tetrathiafulvalene], the π-electronic system of the conducting component should be extended to its periphery to increase the $T_c$.[1] However, neither of the two known vinylene analogues of ET, symmetrical VT [bis(vinylenedithio)tetrathiafulvalene] and unsymmetrical EVT [ethylenedithio(vinylenedithio)tetrathiafulvalene], have given metallics salts stable at low temperature, despite the fact that these donors possess extended π-systems due to replacement of one or both ethylene end groups of ET with vinylene groups.[2,3] On the other hand, our preliminary study on the development of new organic metals composed of vinylenedithio-substituted DSDTF (diselenadithiafulvalene) donors has revealed that the vinylene analogue of TMET-STF [trimethylene(ethylenedithio)diselenadithiafulvalene], *viz.* TMVT [trimethylene(vinylenedithio)diselenadithiafulvalene] provides several metallic salts. In particular, $(TMVT)_2PF_6$ shows metallic behaviour down to 4.2 K.[4] In this salt, the TMVT donor molecules form a columnar structure with short chalcogen···chalcogen intermolecular contacts within and between stacks; the molecular structure of TMVT is approximately planar, in contrast with the fact that the two vinylene end groups of VT in $(VT)_2PF_6$, which undergoes an MI (metal-to-insulator) transition at around 180 K, are a long way out of the molecular plane.[3] The donor arrangement and conformation in $(TMVT)_2PF_6$ may be responsible for its metallic conductivity. Thus, whether such an arrangement and conformation are common in metallic TMVT-based salts or not is an important question for the development of organic metals. In this paper, we present the structural and electrical properties of other metallic TMVT salts.



TMVT

## Experimental

### Synthesis of TMVT salts

According to the controlled-current electrocrystallization method,[5] the TMVT salts were prepared from 34 mg (0.08 mmol) of TMVT and 0.32 mmol of the corresponding tetra-n-butylammonium salt in 16 ml of PhCl or TCE at 20 °C under nitrogen for 35 days. During the course of the electrocrystallization, when the first microcrystal was observable after applying the current, the crystal growth was stopped by turning off the current and the mixture allowed to stand without the applied current until further growing microcrystals were no longer observed. Subsequently, the crystal growth was started again by turning on the current, the value of which was identical with that of the current that was turned off.

### Measurement of physical properties

The measurement of the temperature dependence of the resistivity (2–300 K) was carried out by the four-probe dc method using gold wire contacted to a gold electrode deposited on the crystal surface by thermal evaporation. The crystals were black plates with a typical size of 0.5 × 0.25 × 0.03 mm. For the measurement of the resistivity within the *bc* plane, gold wires were fixed to four gold contacts arranged linearly using gold paint. For the measurement of the resistivity along the *a** axis, two pairs of gold wires were fixed to gold contacts on the surfaces of the sample crystal corresponding to the *bc* plane.

A plate-like single crystal was used for the measurement of thermopower. The method has been described previously.[6]

The EPR data were obtained using an X-band spectrometer with a rectangular microwave cavity (JEOL JES-RE3X). The EPR spectra were measured using a single crystal for $(TMVT)_2AsF_6$, and powder for $(TMVT)_2ClO_4$, because the size of the crystals obtained was rather small and the signal-to-noise ratio was poor. The static field was always applied perpendicular to the crystal plane of $(TMVT)_2AsF_6$, corresponding to the direction of the *a** axis.

### X-Ray crystallography

Crystal data were collected at 293 K using a MacScience MXC18 diffractometer with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) or Cu-Kα ($\lambda = 1.54178$ Å) radiation. The $\omega$–$2\theta$ scans were employed for data collection and Lorentz and polarization corrections were applied. Analytical absorption corrections were carried out by the difabs method.[7] The structure was solved by direct methods and refined by full-

**Table 1** Crystal data of radical cation salts of TMVT

| | $(TMVT)_2AsF_6$ | $(TMVT)_2ClO_4$ |
|---|---|---|
| Chemical formula | $C_{22}H_{16}S_8Se_4AsF_6$ | $C_{22}H_{16}S_8Se_4ClO_4$ |
| Formula weight | 1041.64 | 952.23 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $C2/c$ | $C2/c$ |
| Unit cell parameter: $a$/Å | 32.384(7) | 32.720(12) |
| $b$/Å | 7.207(2) | 7.127(4) |
| $c$/Å | 13.102(3) | 13.045(6) |
| $\beta$(°) | 97.18(2) | 106.22(3) |
| $V$/Å$^3$ | 3033.9(12) | 2921.1(22) |
| $Z$ | 4 | 4 |
| $D_c$/g cm$^{-3}$ | 2.280 | 2.144 |
| $\lambda$/Å | 1.54178 | 0.71073 |
| $\mu$/mm$^{-1}$ | 12.8135 | 5.6479 |
| Crystal size/mm | 0.35 × 0.3 × 0.03 | 0.25 × 0.25 × 0.05 |
| $2\theta_{max}$ (°) | 103.18 | 57.26 |
| Min/max transmission | 0.511/1.831 | 0.721/1.367 |
| Total data | 3015 | 4850 |
| Independent data | 2539 | 4255 |
| Observed data [$I > 2\sigma(I)$] | 2485 | 3595 |
| Number of variables | 187 | 167 |
| $R$, $Rw$ | 0.070, 0.075 | 0.061, 0.065 |
| $\Delta\rho_{max}$ | 0.94 | 1.28 |
| $\Delta\rho_{min}$ | −0.90 | −0.85 |

matrix least-squares. All atoms except for H and O atoms were refined with anisotropic displacement parameters, while O atoms were refined using isotropic approximation. The positions of H atoms were determined by calculation. All calculations were performed using the CRYSTAN program (MacScience). Crystallographic data for $(TMVT)_2AsF_6$ and $(TMVT)_2ClO_4$ are summarized in Table 1.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/134. The crystallographic data is available in CIF format from the RSC web site, see: http://www.rsc.org/suppdata/jmc/1999/693.

### Calculation of band structures

The band structure calculations were performed on a Pentium 75 personal computer using the programs of Professor T. Mori.[8] The overlap integrals $S_{ij}$ between HOMOs of adjacent donor molecules were calculated on the basis of the extended Hückel MO method. The band structures and the shapes of the Fermi surfaces were obtained by the tight-binding method, using the transfer integrals $t_{ij}$ from the equation $t_{ij} = E\ S_{ij}$, where $E$ is the energy level of the HOMO of the donor (−10 eV).

## Results and discussion

Fig. 1 shows the temperature dependence of resistivity along the $a^*$ axis of the $AsF_6$ and $ClO_4$ salts. Both salts exhibited metallic conducting behaviour down to low temperature. The resistivities within the $bc$ plane of both salts are also metallic, although there were observed many resistance jumps, probably caused by microcracks caused by the thermal constraints as the temperature decreased. The room temperature conductivities of the $ClO_4$ salt within the $bc$ plane and along the $a^*$ axis were 135 and $10^{-2}$ S cm$^{-1}$. Those of the $AsF_6$ salt were 125 and $10^{-2}$ S cm$^{-1}$. The ratios of the anisotropy of conductivity within the $bc$ plane of the $AsF_6$ and $ClO_4$ salts were 2 and 6, respectively. These small values indicate that both salts have a comparatively two-dimensional character. As shown in Fig. 1, the $AsF_6$ and $ClO_4$ salts show metallic behaviour down to low temperature, but they exhibit an upturn of resistivity at 15 and 7 K, respectively, in contrast with the $PF_6$ salt. These upturns are broad and small in both salts, so both salts may also retain an intrinsically metallic state down to 4.2 K.

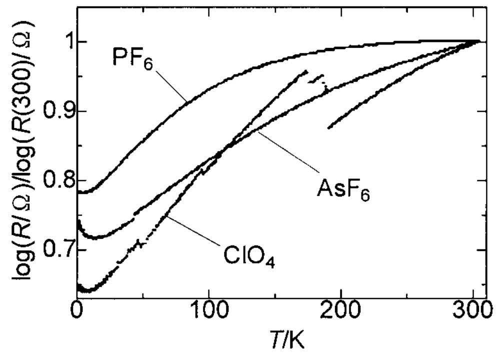


**Fig. 1** Temperature dependence of the resistivity of the $AsF_6$, $ClO_4$ and $PF_6$ salts measured along the $a$ axis.

Fig. 2 shows the temperature dependence of the thermoelectric power ($S$) of the $ClO_4$ and $AsF_6$ salts. The room temperature thermoelectric powers were 11 and 26 μV K$^{-1}$ for the $ClO_4$ and $AsF_6$ salts, respectively. The thermoelectric powers of both salts decrease almost linearly with decreasing temperature, although the slope of $S$ to temperature gradually changed at around 100 K. Such a T-linear tendency of thermoelectric power is characteristic of the metallic state, so both salts are metallic at least down to 4.2 K.

The temperature dependence of the peak-to-peak linewidth and the intensity of the EPR spectra are depicted in Fig. 3. The EPR spectra of both salts are broad, and the linewidths at room temperature are 303 and 290 G for the $ClO_4$ and $AsF_6$ salts, respectively. These large linewidths were generally observed in salts based on donors containing selenium atoms. The linewidths decrease gradually with decreasing temperature

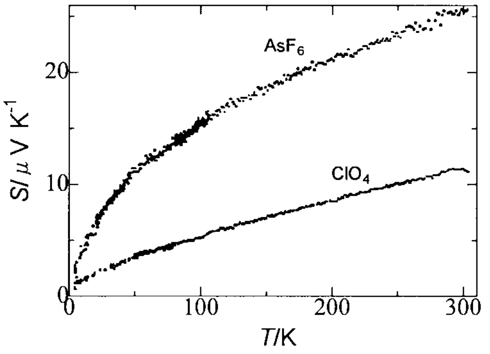


**Fig. 2** Temperature dependence of the thermopower of the $AsF_6$ and $ClO_4$ salts.

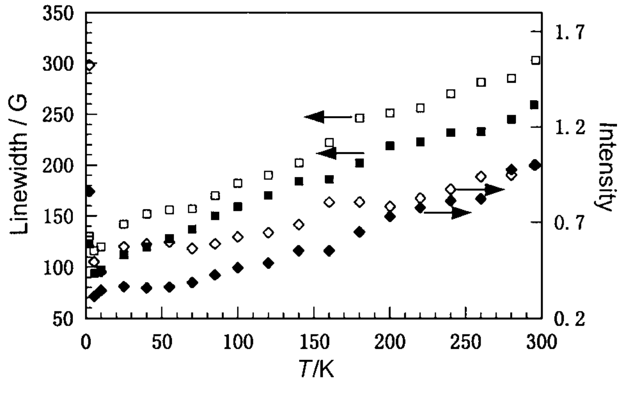


**Fig. 3** Temperature dependence of the EPR linewidth and intensity for (□, ◇) $(TMVT)_2AsF_6$ and (■, ◆) $(TMVT)_2ClO_4$.

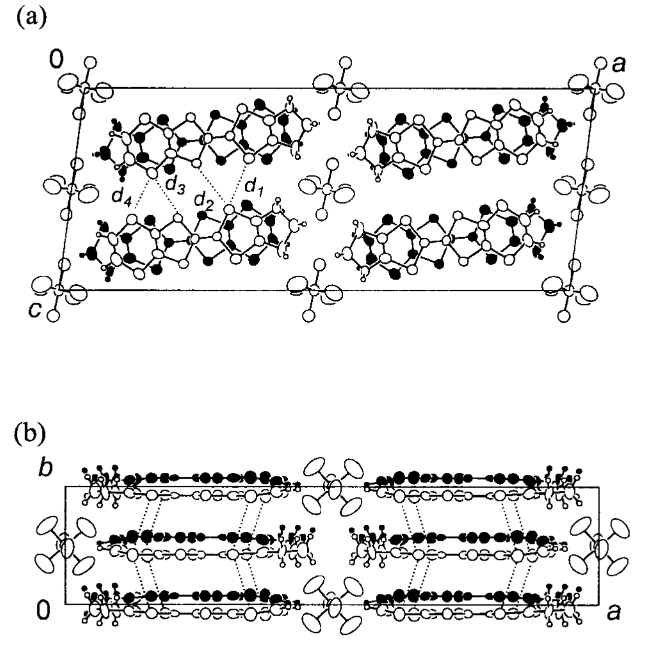


**Fig. 4** Crystal structure of $(TMVT)_2AsF_6$: (a) interstack shorter Se···Se contact (<4.00 Å): $d_1=3.712(2)$ Å; Se···Se contact (<3.85 Å): $d_2=3.811(3)$ Å; S···S contacts (<3.70 Å): $d_3=3.529(5)$ Å, $d_4=3.472(5)$ Å; (b) intrastack shorter Se···Se contacts between the front molecules drawn by open circles.

to 110–140 G at liquid helium temperature, and show no anomaly. The EPR intensity of each sample is almost independent of temperature below 70 K. This temperature dependence of the intensity is peculiar to the metallic state, and the lack of anomalies indicates that there is no magnetic transition at low temperature. This is consistent with the observed thermoelectric powers.

Fig. 4 and 5 show the crystal structures of $(TMVT)_2AsF_6$ and $(TMVT)_2ClO_4$, respectively. Both salts crystallized in the monoclinic space group $C2/c$ with unit cell volumes and axial lengths comparable to those of the $PF_6$ salt [$(TMVT)_2PF_6$: monoclinic, $C2/c$, $a=32.119(6)$, $b=7.174(1)$, $c=13.084(2)$ Å, $\beta=97.30(1)°$, $V=2990.4(8)$ Å$^3$, $Z=4$]. The thermal parameters of the O atoms in the $ClO_4$ anion and the F atoms in the $AsF_6$ anion are significantly larger than those of the other atoms. While the $AsF_6$ salt is isostructural with the $PF_6$ salt, a difference is observed in the position of the anions between the $ClO_4$ and $AsF_6$ salts. The $ClO_4$ anions locate on the two-fold axis, while the $AsF_6$ anions lie on the inversion centers. However the structures of the donor layers are very similar in both salts. The TMVT donor molecule forms stacks along the $b$ axis in both salts. The neighboring TMVT molecules in a stack are related by a two-fold screw axis and their molecular plane is almost perpendicular to this axis. Therefore the TMVT molecules form donor stacks with no dimerization, similar to the $PF_6$ salt. The intermolecular distance, which is the same as half of lattice constant $b$, becomes larger as the size of the anions increases [3.564 Å for $(TMVT)_2ClO_4$, 3.589 Å for $(TMVT)_2PF_6$ and 3.604 Å for $(TMVT)_2AsF_6$].

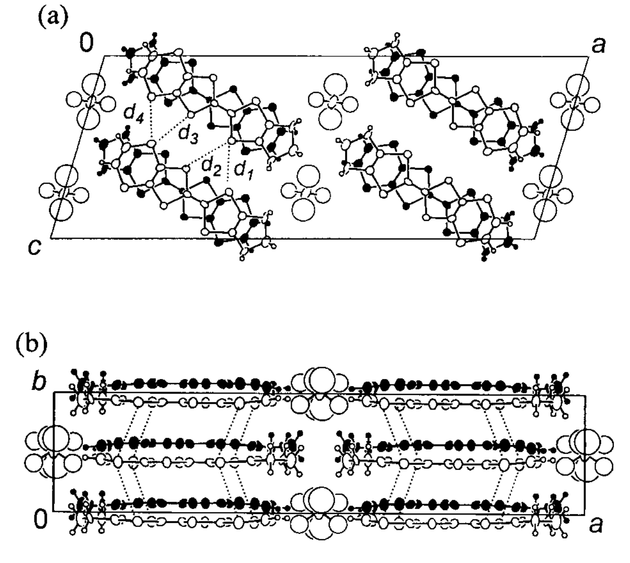


**Fig. 5** Crystal structure of $(TMVT)_2ClO_4$: (a) interstack shorter Se···Se contact (<4.00 Å): $d_1=3.705(2)$ Å; Se···Se contact (<3.85 Å): $d_2=3.803(3)$ Å; S···S contacts (<3.70 Å): $d_3=3.519(5)$ Å, $d_4=3.434(5)$ Å; (b) intrastack shorter Se···Se contacts between the front molecules drawn by open circles.

As illustrated in Fig. 4(a) and 5(a), there also exist several chalcogen···chalcogen contacts shorter than the sum of the van der Waals radii between the stacks in both salts. The pattern of the short contacts is the same as that in the $PF_6$ salt. The existence of these shorter interstack contacts adds some two-dimensional character to these salts. This is consistent with the small anisotropy of electrical conductivity within the $bc$ plane. In both salts, similar to the $PF_6$ salt, the molecular structure of TMVT is approximately planar, in contrast with the fact that the two vinylene end groups of VT in $(VT)_2PF_6$ are out of the plane. This favors intermolecular interactions, producing the metallic conduction. A crystal structure similar to those of the TMVT salts was observed in $(DMtTSF)_2ReO_4$.[9] In this salt, the donor molecule DMtTSF has a planar structure and also shows metallic behavior down to low temperature.[10]

In order to investigate the electronic structure in detail, the band structures of $(TMVT)_2X$ ($X^-=AsF_6^-$ and $ClO_4^-$) were calculated from their crystal structures. The calculations were carried out for a primitive cell with $a_p=(a-b)/2$, $b_p=b$, $c_p=c$, $\alpha_p=\alpha$, $\beta_p=105.84°$, $\gamma_p=102.29°$, and $a_p=(a-b)/2$, $b_p=b$, $c_p=c$, $\alpha_p=\alpha$, $\beta_p=97.01°$, $\gamma_p=77.45°$ for the $ClO_4$ and $AsF_6$ salts, respectively. In Fig. 6, the overlap integrals for the $ClO_4$ and $AsF_6$ salts are summarized. For both salts, the overlap integrals ($p1$, $p2$) between the stacks are about 1/3 of those ($b$) in the stacking direction. The overlaps for the $ClO_4$ salt are slightly larger than those for the $AsF_6$ salt, which correspond to the size of the anions. The ratios of the interstack to intrastack overlap integrals for metallic TMVT salts are larger than those of TMTSF salts (1 : 10) and column B of $(TMET\text{-}STF)_2BF_4$ (1 : 5).[11] Thus, the two-dimensionality of TMVT salts is larger than that of TMTSF salts. The Fermi surface of $(TMVT)_2AsF_6$ is shown in Fig. 7(b). The Fermi surface of the $ClO_4$ salt is almost the same. As shown in Fig. 7(a), the upper two bands are partially filled, and there exist two pairs of Fermi surfaces associated with these two bands. Both Fermi surfaces are open perpendicular to the stacking axis, so $(TMVT)_2X$ ($X^-=AsF_6^-$ and $ClO_4^-$) has quasi-one-

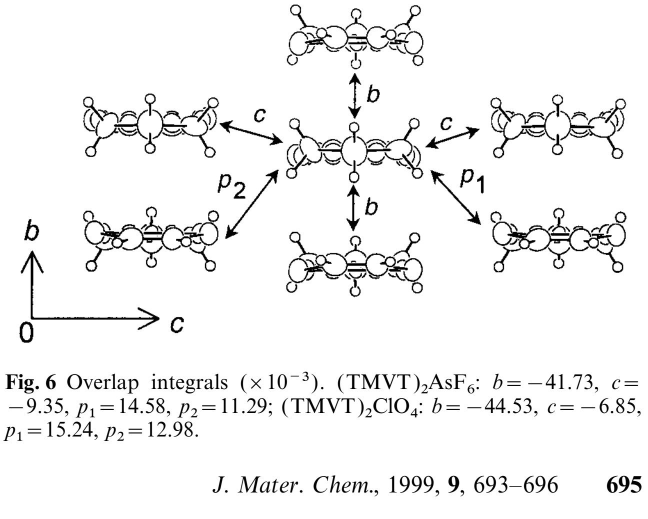


**Fig. 6** Overlap integrals ($\times10^{-3}$). $(TMVT)_2AsF_6$: $b=-41.73$, $c=-9.35$, $p_1=14.58$, $p_2=11.29$; $(TMVT)_2ClO_4$: $b=-44.53$, $c=-6.85$, $p_1=15.24$, $p_2=12.98$.

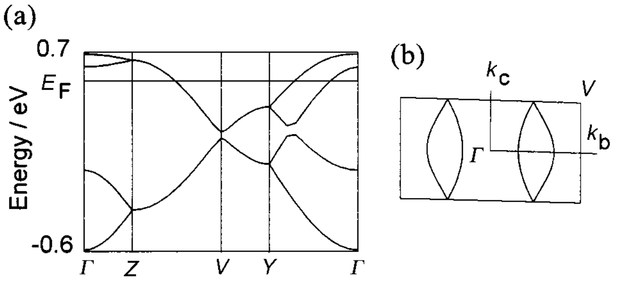


**Fig. 7** (a) Band structure and (b) Fermi surface of $(TMVT)_2AsF_6$.

dimensional character with relative two-dimensionality due to large distortions of the surfaces along the transverse direction. Taking the shape of the Fermi surfaces into account, the vector $b^*/2$ or $(b^*+c^*)/2$ seems to nest the Fermi surfaces easily and cause the metal-to-insulator transition.

Although the band structures of $(TMVT)_2X$ ($X^- = AsF_6^-$ and $ClO_4^-$) suggest the existence of the metal-to-insulator transitions in these salts by the nesting of Fermi surfaces, the measurements of transport properties indicate that both salts retain a metallic state at least down to 4.2 K. Such findings were also reported for salts with open but highly distorted Fermi surfaces.[12] It is an important question for the development of organic metals whether the large distortion prevents the nesting of Fermi surfaces or not.

## Conclusion

The thermopower measurements indicate that $(TMVT)_2X$ ($X^- = AsF_6^-$ and $ClO_4^-$) retain a metallic state at least down to 4.2 K, similar to the $PF_6$ salt, although there were observed upturns in the temperature dependence of the electrical resistivity. From EPR studies, the lack of magnetic transitions was confirmed for both salts at low temperature. The X-ray analysis revealed that the metallic TMVT salts have similar crystal structures, although a difference in the position of the anions exists. In the crystalline state, the donor molecules construct stacks without dimerization and the transverse intermolecular interactions are fairly large, in contrast with TMTSF salts. The TMVT donor molecules in these salts are planar, unlike VT molecules in $(VT)_2PF_6$. Although the band structures of $(TMVT)_2X$ ($X^- = AsF_6^-$ and $ClO_4^-$) suggest the existence of metal-to-insulator transitions due to nesting of the Fermi surface, both salts retained their metallic behaviour down to low temperature.

## References

1 H. Yamochi, T. Komatsu, N. Natsukawa, G. Saito, T. Mori, M. Kusunoki and K. Sakaguchi, *J. Am. Chem. Soc.*, 1993, **115**, 11319.

2 H. Nakano, K. Miyawaki, T. Nogami, Y. Shirota, S. Harada and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2604.

3 H. Kobayashi, A. Kobayashi, T. Nakamura, T. Nogami and Y. Shirota, *Chem. Lett.*, 1987, 559.

4 J. Yamada, S. Satoki, H. Anzai, K. Hagiya, M. Tamura, Y. Nishio, K. Kajita, E. Watanabe, M. Konno, T. Sato, H. Nishikawa and K. Kikuchi, *Chem. Commun.*, 1996, 1955.

5 H. Anzai, J. M. Delrieu, S. Takasaki, S. Nakatsuji and J. Yamada, *J. Cryst. Growth*, 1995, **154**, 145.

6 K. Saito, H. Kamio, Y. Honda, K. Kikuchi, K. Kobayashi and I. Ikemoto, *J. Phys. Soc. Jpn.*, 1989, **58**, 4093; K. Saito, Y. Yoshino, K. Kikuchi, K. Kobayashi and I. Ikemoto, *J. Phys. Soc. Jpn.*, 1993, **62**, 1001.

7 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

8 T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 627.

9 K. Kikuchi, K. Yakushi, H. Kuroda, I. Ikemoto and K. Kobayashi, *Mol. Cryst. Liq. Cryst.*, 1985, **125**, 345.

10 P. Delhaes, E. Dupart, J. Amiell, C. Coulon, J. M. Fabre, L. Giral, D. Chasseau and B. Gallois, *J. Phys.*, 1983, **C44**, 1239.

11 R. Kato, K. Yamamoto, Y. Okano, H. Tajima and H. Sawa, *J. Chem. Soc., Chem. Commun.*, 1986, 947.

12 T. Mori, Y. Misaki, H. Fujiwara and T. Yamabe, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 2685.

*Paper 8/07893I*