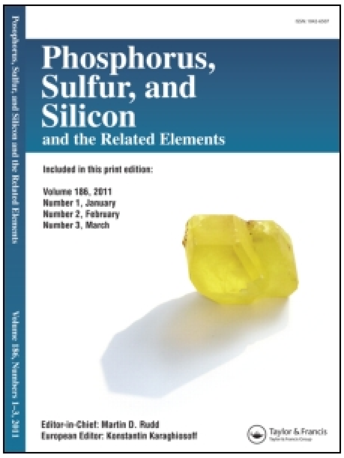
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Organic Metals Containing Tellurium

Dwaine O. Cowan[a]; Richard McCullough[a]; Allan Bailey[a]; Knud Lerstrup[a]; Daniel Talham[a]; Donald Herr[a]; Michael Mays[a]
[a] Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

To cite this Article Cowan, Dwaine O. , McCullough, Richard , Bailey, Allan , Lerstrup, Knud , Talham, Daniel , Herr, Donald and Mays, Michael(1992) 'Organic Metals Containing Tellurium', Phosphorus, Sulfur, and Silicon and the Related Elements, 67: 1, 277 — 294

To link to this Article: DOI: 10.1080/10426509208045849

URL: http://dx.doi.org/10.1080/10426509208045849

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1992, Vol. 67, pp. 277–294
© 1992 Gordon and Breach Science Publishers S.A.
Reprints available directly from the publisher
Printed in the United Kingdom
Photocopying permitted by license only

ORGANIC METALS CONTAINING TELLURIUM

DWAINE O. COWAN, RICHARD MCCULLOUGH, ALLAN BAILEY, KNUD LERSTRUP, DANIEL TALHAM, DONALD HERR, MICHAEL MAYS
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

Abstract Examination of the structural and electronic trends among organic metals and organic superconductors, which are composed of complex salts of heterocyclic π-donors, has been greatly facilitated by the preparation and study of a number of new tellurium containing organic π-donors. These studies required that a number of new synthetic strategies be developed. A brief review of these methods leading up to and including the recent synthesis of tetratellurafulvalene (TTeF) is provided. The increase in electrical conductivity on going from S to Se to Te in the series (TXF-TCNQ) (where X=S, Se, Te) is shown to be consistent with the square of the bandwidths or to an increase in intrachain interaction ($\sigma \propto W_T^2$). While TTeF-TCNQ has not been found to undergo a transition to a superconducting state as the temperature is lowered at ambient pressure neither does it undergo a metal to insulator transition as is observed for TTF-TCNQ (T_{max} = 59K) or for TSF-TCNQ (T_{max} = 40K). This change in behavior is likely due, at least in part, to the increased interchain interaction and more two-dimensional character. Tight-binding (extended Hückel) electronic band structure calculations indicate that while the structure is more 2-D than TTF-TCNQ, the Fermi surface is not closed and the material is still best described as a quasi-one-dimensional organic metal.

Downloaded At: 14:56 29 January 2011

INTRODUCTION

Two primary objectives have motivated the synthesis and study of tellurium π-donors. The first is the search for structure property correlations to aid in the design and understanding of organic metals and organic superconductors. That is, how does the exchange of selenium or tellurium for sulfur in the donors affect the solid state structure, electrical conductivity (dc to microwave), thermoelectric power, magnetic susceptibility (both static and spin), and optical properties (linear and nonlinear) of the complex salts derived from these donors. The second objective is a more practical one, to chemically increase the dimensionality of these systems in order to circumvent the pathological metal-to-insulator transition (Peierls transition) so prevalent in quasi-one-dimensional molecular networks. If the metallic ground state can be retained to low temperatures new superconductors may be observed. While this increased interchain interaction may suppress the metal-to-insulator transition, the increased intrachain interaction ought to produce a wider bandwidth metal and higher electrical conductivity, but give a lower transition temperature to a superconducting state than the corresponding S or Se compound, assuming they could be made superconducting in some other way. This is a consequence of the fact that to a first approximation the density of states at the Fermi level is proportional to one over the bandwidth.

$$D(E_F) \propto 1/W_T$$

Within the weak coupling limit ($U_oD(E_F)<<1$) of the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity the transition temperature is given by the following equation:

$$T_c = 1.14\ \theta \exp[-1/U_oD(E_F)]$$

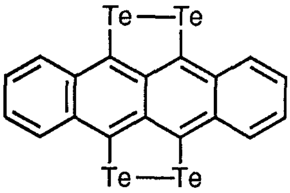
where θ is the Debye temperature, $D(E_F)$ is the density of states at the Fermi level, and U_o is the electron lattice interaction. Since the metals formed from the organic tellurium π-donors have wider bandwidths and lower density of states (same number of levels spread over a larger energy) than the corresponding selenium or sulfur compounds, the tellurium compounds might be expected to have lower superconducting transition temperatures. This speculation however, is based on the weak coupling limit of the BCS theory and at the present time the mechanism for superconductivity in the organic materials is unknown. A more detailed examination of the factors that influence electrical conductivity and superconductivity of organic metals can be found in references [1], [2], and [3].

Downloaded At: 14:56 29 January 2011

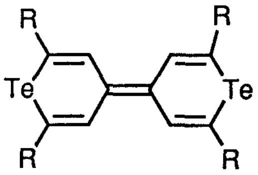
SYNTHESIS OF TELLURIUM CONTAINING Π-DONORS

The synthesis of tellurium containing π-donors was reviewed by Cowan and Kini.[4] Since that review, a number of new donors have been prepared and complexes derived from these donors synthesized and studied. As a consequence of this new work, a more detailed understanding of both the chemistry and physics is accessible. Only donors where the tellurium is incorporated in the heterocyclic ring will be discussed here. This is an arbitrary division which unfortunately excludes the interesting set of compounds with alkyltellurium groups attached to the TTF or TSF skeleton.[5] For example, even the neutral tetra(telluramethyl)tetrathiafulvalene ($TTeC_1$-TTF) has a conductivity of $10^{-5}\Omega^{-1}cm^{-1}$ and has exceptionally large hole and electron mobilities for an organic compound ($\mu_h = 28.5$ $cm^2/V{\cdot}s$; $\mu_e = 18.6$ $cm^2/V{\cdot}s$). These properties have been attributed to the short Te, Te contacts in the solid state. This infinite tellurium chain structure with the polarizable pendent TTF groups is a unique structural motif. Saito and coworkers have recently presented more information on this class of compounds.[5b]

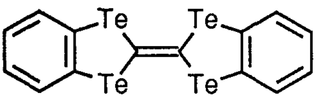
Downloaded At: 14:56 29 January 2011



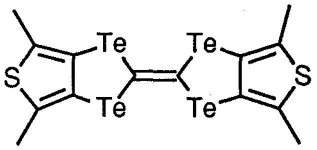
TTeT



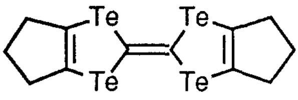
R_4 - BTeP



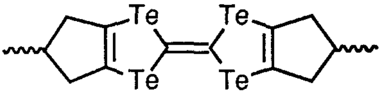
DBTTeF



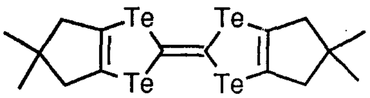
BDMT-TTeF



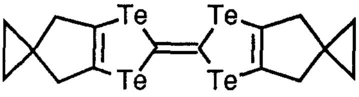
HMTTeF



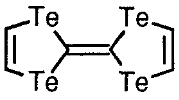
DMHM-TTeF



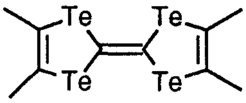
TMHM-TTeF



CpHM-TTeF



TTeF



TMTTeF

FIGURE 1 Tellurium Containing π - Donors, TMTTeF is presently unknown

Tetratellurotetracene, TTeT

Both tetrathiotetracene[6] and tetraselenotetracene[7] form complex salts [$(TTT)_2I_3$; $(TST)_2I$; $(TST)_2Cl$] which have room temperature electrical conductivities in excess of $10^3\Omega^{-1}cm^{-1}$; and in the case of $(TST)_2Cl$ this compound remains metallic to at least 26K with a conductivity of $2x10^4\Omega^{-1}cm^{-1}$. These results indicate that the synthesis of salts of the more polarizable TTeT could produce molecular metals with equivalent or higher conductivities. Tetratellurotetracene (TTeT) was prepared and studied by two groups in 1982.[8] Sandman and coworkers prepared TTeT in 13% yield by allowing sodium ditelluride formed in DMF from tellurium powder and sodium metal, to react with tetrachlorotetracene. This compound, like many of the higher molecular weight tellurium compounds, is not very soluble in organic solvents. It can be recrystallized from chlorobenzene and the long wavelength absorption in chlorobenzene is red shifted compared to TSeT [λ_{max}763nm (log ε 4.16) vs λ_{max}716nm (log ε 4.1)]. In the solid state the very short Te···Te interstack contacts (3.701Å) provide hope that if ion-radical salts can be prepared from TTeT they too will have strong interstack interaction. While some complex salts have been prepared, the lack of a good solvent has impeded the preparation of a large variety of salts.[9] Other groups have altered the number of rings and the ring fusion, for example, anthracene rather than tetracene; or added methyl groups to enhance the donor properties of the molecule and to impart a greater solubility. Some success has been achieved in this area as noted in the paper by Ogura and coworkers.[10]

Bi(telluropyranylidene), R_4-BTeP

Detty and coworkers added lithium telluride under basic conditions to diacetylenic ketones to form the telluropyranones in better than fifty percent yields. This Michael like product could be converted quantitatively into the thione with Lawesson's reagent and then coupled with the extrusion of sulfur by heating the thione in xylene with copper to form the desired R_4-BTeP.[11,12] Using this procedure a wide variety of bipyranylidenes could be prepared, R = H, Me, *t*-Bu, Ph. While the chemistry and electrochemistry of these interesting donors has been explored in some detail, little work has been done yet to characterize the electrical properties of the charge transfer salts ($TCNQ^-$, $TCNQF_4^-$, DDQ^-) and the inorganic complex salts [I_3^-, BF_4^-, PF_6^-, $Cu(NCS)_2^-$] of these donors.

Dibenzotetratellurafulvalene, (DBTTeF) and Bis(dimethylthiopheno)tetratellurafulvalene, (BDMT-TTeF)

Cowan, Lerstrup and coworkers prepared DBTTeF by allowing tellurium to react with dilithiobenzene in THF to give the lithium salt of benzene-1,2-ditellurate. Reaction of this salt with tetrachloroethylene gave a 10% yield of DBTTeF.[13,14] Cyclic voltammetry gave the following results for the first oxidation potential for the series DBTTF, DBTSF,

Downloaded At: 14:56 29 January 2011

DBTTeF: $E_{1/2}(1)$, 0.71V, 0.78V, and 0.70V. The increase and then decrease in the oxidation potential indicates that two factors, which have opposite effects in the series S, Se, Te are important. For the TTF framework the HOMO is assigned as an antibonding π-orbital of b_{1u} symmetry. In the series S, Se, Te the resonance integral $\beta_{C\text{-}X}$ will become smaller owing to the longer bond lengths of the C-X bonds. This has the effect of pushing up the antibonding HOMO less on going from sulfur to tellurium (stabilizing the HOMO) and making it harder to remove an electron, see Figure 2. However, the opposite trend is expected based on the valence state ionization potentials for the series S, Se, Te. That is, the valence state ionization potentials decrease in the series S, Se, Te. This raises the basis orbital energy of the heteroatom, and therefore tends to increase the energy of the HOMO, making it easier to remove an electron. It seems likely that these two opposing factors account for the unusual trend in $E_{1/2}(1)$ values. In addition, the separation between the first and second oxidation potential ($\Delta E_{1/2}$) decreases in the series DBTTF > DBTSF > DBTTeF. This is consistent with the predicted affect of the heteroatom change on the on-site coulombic repulsion, that is, the ease with which two positive charges can be placed on the same molecule.

Downloaded At: 14:56 29 January 2011

Bis(dimethylthiopheno)tetratellurafulvalene, BDMT-TTeF, combines the presence of the tetratelluraethylene core which ought to increase the molecule polarizability, interchain interaction and bandwidth with the dimethylthiopheno rings which could also help increase the interchain interaction (increase the dimensionality). BDMT-TTeF was prepared by a procedure similar to that used to prepare DBTTeF. 3,4-Dibromo-2,5-dimethylthiophene in THF was allowed to react with 2 equivalents of *t*-BuLi then 1 equivalent of tellurium, and the sequence was repeated. Tetrachloroethylene was then added and the mixture was slowly warmed to room temperature. A brown solid was isolated by filtration, which upon extraction with CS_2 gave BDMT-TTeF in 75% yield. Recrystallization from 1, 1, 2-trichloroethane gave shiny bronze-colored (reflected light), blood-red (transmitted light) crystals. Again, the solid state structure seems to be dominated by the Te···Te interdonor interactions. This results in the neutral donor being nonplanar in the solid.[15,16]

It is rather surprising that so few metallic complexes have been prepared to date from the dibenzo series of compounds (DBTTF, DBTSF and DBTTeF) and from BDMT-TTeF. Even those which might be considered metallic have low conductivity values [DBTSF-2,5-TCNQCl_2, $20\Omega^{-1}cm^{-1}$]. Simple molecular orbital calculations indicate that the HOMO for these aryl fused ring systems is quite similar to that for the unsubstituted ring system. That is, the corresponding wave function coefficients are almost identical. There is however, a large difference in the energy which is reflected in the $E_{1/2}(1)$ values for the two series of compounds. The donors containing the aryl ring systems are harder to oxidize by 0.2 to 0.4V than the unsubstituted molecules. It would seem that this difference could be

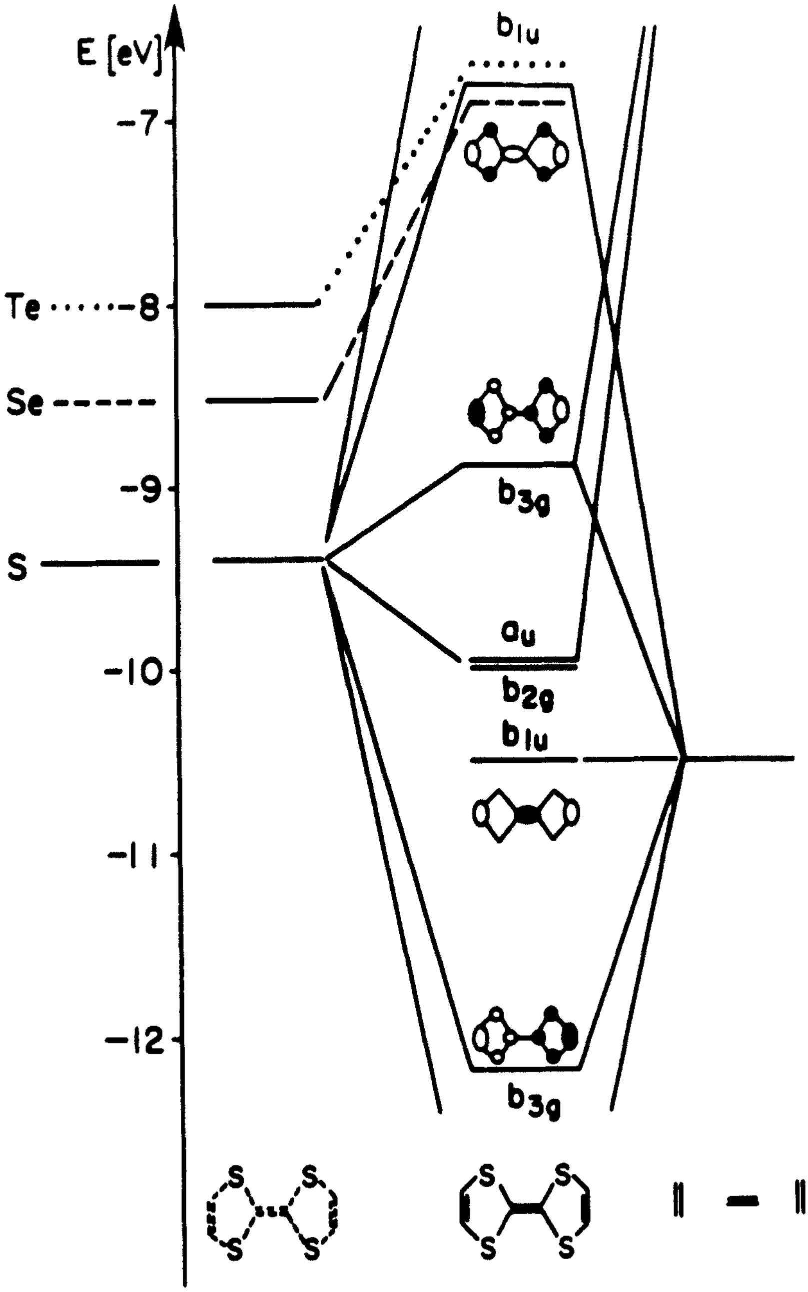


Figure 2 ZDO Molecular Orbital Model for TTF and how the energy of the HOMO (b_{1u}) changes as the Valence State Ionization Potential and Resonance Integral change for the Se and Te compounds. For a detailed discussion of the ZDO method applied to TTF see reference [13b]

Downloaded At: 14:56 29 January 2011

compensated for by choice of the acceptor. The on-site Coulombic repulsion could be a more important factor in the aryl fused systems than in the others molecules.

Hexamethylenetetratellurafulvalene, (HMTTeF) and Related Compounds

Wudl and Aharon-Shalom[17] prepared hexamethylenetetratellurafulvalene (HMTTeF) by the following set of reactions. 1,2-Dibromocyclopentene was allowed to react with *t*-BuLi in THF at -80°C, tellurium metal was added at -15°C and the sequence repeated a second time to form the 1,2-dilithioditelluride. When tetrachloroethylene was added to this solution at -78°C, HMTTeF was formed in a 32% yield of crude products (CS_2 extractable solids). The fraction that was less soluble in CS_2 proved to be HMTTeF. The other fraction was later shown by Saito[18] to be tetratelluradicyclopenta [b,g] naphthalene (TTeDCN) the six-six fused ring heterocycle. Wudl also found that the oxidation potential for HMTTeF was less than the corresponding Se compound but larger than the S compound. He proposed that "ionization in the sulfur fulvalene occurs primarily from the π-bonded network, whereas ionization in the tellurium fulvalene originates from the tellurium lone pairs". This seems less likely to us than the explanation we have presented for the same phenomenon observed in the DBTXF series of donors and already reviewed in this paper. While Wudl and Aharon-Shalom presented some preliminary data on one complex (TCNQ) prepared from HMTTeF, it remained for Saito and coworkers[19] to prepare and examine a comprehensive set of charge transfer complexes. One of the interesting surprises which is still not completely understood, is that $TCNQF_4$ forms a complex with HMTTeF which has a high conductivity ($0.3\Omega^{-1}cm^{-1}$, pellet; where TTF-TCNQ was $5\Omega^{-1}cm^{-1}$). This was the first time that a $TCNQF_4$ complex did not give a Mott-Hubbard insulator. They proposed that the increased bandwidth due to the large tellurium atoms and the large molecular polarizability of HMTTeF overcame the tendency of unit charge transfer to produce a state where the short-range Coulomb repulsion between conduction electrons on the same molecular site (U_{eff}) is not extensively reduced by screening. When U_{eff} is greater than the bandwidth (4t), a Mott-Hubbard insulator is normally produced. While more work needs to be done, later studies[20,21] indicate that the charge transfer is probably close to unity.

Single crystal conductivity studies[20] on the TCNQ salt and the DMTCNQ salt showed both to be metallic with room temperature conductivity values between 1000 and $2000\Omega^{-1}cm^{-1}$ and to pass through a broad maxima at T_{max} = 243K (TCNQ) and 130K (DMTCNQ) with a gradual decrease in conductivity below T_{max}. We found [21] similar results except our room temperature conductivities were not as high as Saito's (TCNQ, 1400 vs 550; DMTCNQ 1800 vs 460). For our salts the conductivity increased to lower temperatures (TCNQ, 243K vs 73K; DMTCNQ 130K vs 83K). In both studies the crystal quality, as attested to by the poor X-ray diffracting characteristics, could explain the

Downloaded At: 14:56 29 January 2011

difference observed. In 1986, Sano and coworkers reported[22] the preparation and study of several complex salts of HMTTeF with inorganic counterions, $(\mathrm{HMTTeF})_n\mathrm{X}$ where X = Cl, Br, I, PF_6, AsF_6, and ClO_4. The PF_6, AsF_6, and ClO_4 salts were semiconductors. The halide salts $(\mathrm{HMTTeF})_2$ X were found to exhibit metallic conductivities to low temperatures. The single crystal conductivity results for HMTTeF salts are summarized in Table 1.

TABLE I Single Crystal Conductivity Studies on HMTTeF Salts

Counterion	σ_{RT}	T_{max}	σ_{77K}	σ_{5K}
TCNQ (20)	1400	243	600	
(21)	550	73	910	
DMTCNQ (20)	1800	130	2600	
(21)	460	83	1000	
Br (22)	350	100		18
Cl (22)	360	170		2
I (22)	390	120		4

σ units $\Omega^{-1}\mathrm{cm}^{-1}$

A real problem in growing good quality crystals of the charge transfer salts of HMTTeF and the complex inorganic salts of HMTTeF is that the salts need to be much less soluble than the very insoluble neutral precursor HMTTeF.

$$2\mathrm{HMTTeF} \xrightarrow[-e]{\mathrm{TBA}^+\mathrm{X}^-} (\mathrm{HMTTeF})_2^+\ \mathrm{X}^-$$

$$\mathrm{HMTTeF} \xrightleftharpoons{\mathrm{Acceptor}} \mathrm{HMTTeF\text{-}ACCEPTOR}$$

It appears that in many cases HMTTeF has a solubility that is comparable to the salts that we are trying to prepare. Attempts to work at higher temperatures or to find a more appropriate solvent have not met with success. In light of this, we have prepared HMTTeF like donors with alkyl groups (methyl and cyclopropyl) in the 5-and 5'- positions.[23,24] The purpose for adding the alkyl groups was to increase the solubility of the π-donor while still providing sufficient overlap to form a reasonable conduction band. The synthesis of the 1,2-vinyl dibromide precursors is shown in Figure 3. Their conversion into DMHM-TTeF, TMHM-TTeF and CpHM-TTeF follows the procedure used to make HMTTeF with a few modifications. In this procedure a vinyl dibromide is successively treated with two equivalents of tert-butyllithuim followed by addition of elemental tellurium and the procedure then repeated. The resulting ditelluride dianion is reacted with tetrachloroethylene

Downloaded At: 14:56 29 January 2011

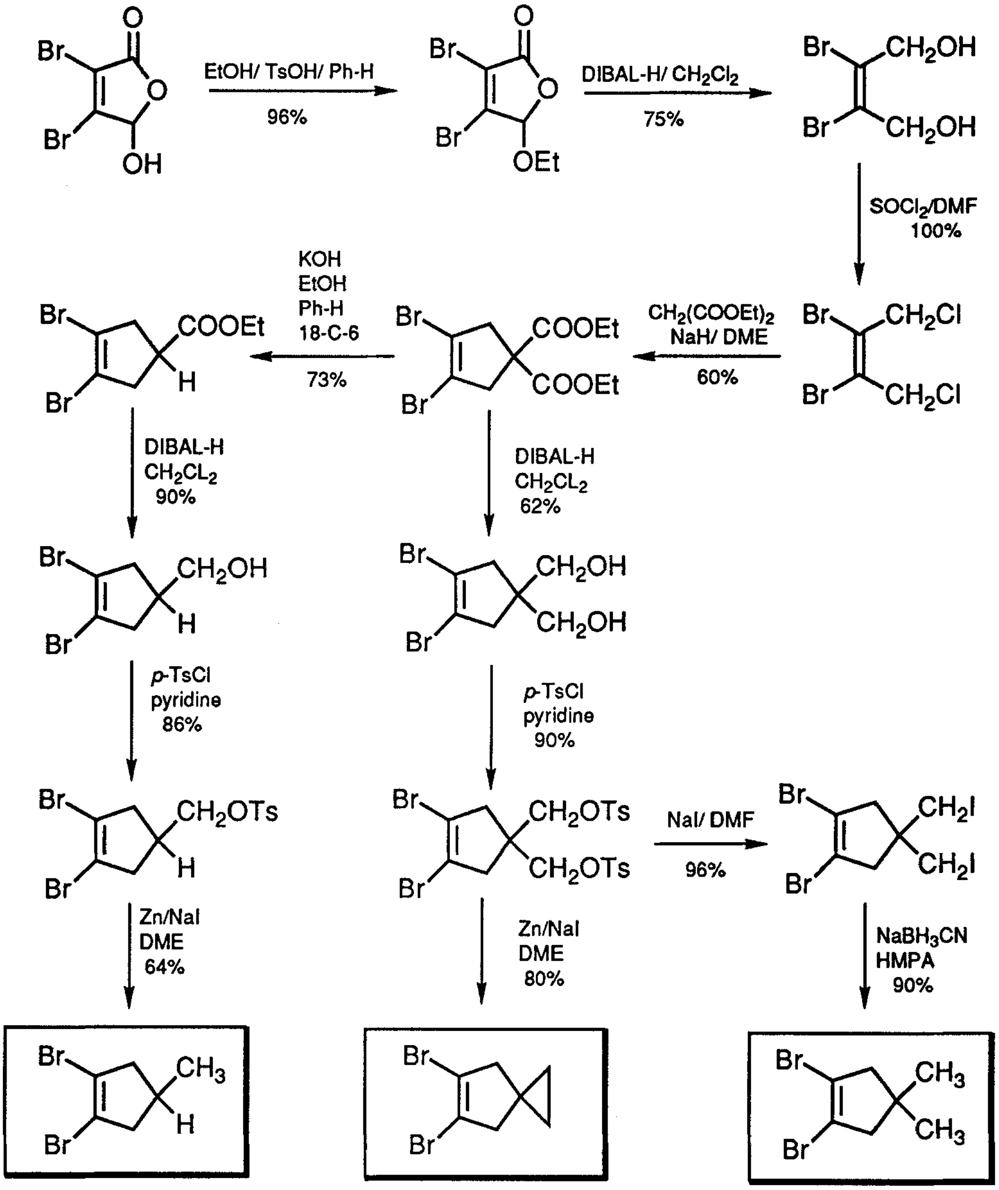


FIGURE 3 Synthesis of 1,2 - Vinyl Dibromides

Downloaded At: 14:56 29 January 2011

to give the tetratellurafulvalene. If freshly prepared microcrystalline tellurium is used in the reaction, the entire reaction sequence can be done at -78°C. This helps to eliminate the formation of some unwanted byproducts. The 1932 procedure for the formation of the microcrystalline tellurium involves the formation of "$TeCl_4$" and then its reduction back to tellurium metal (see Figure 4).[25] In addition, the use of two equivalents of *t*-BuLi in the metal halogen exchange reaction also helps reduce side reactions[26]. After the metal halogen exchange occurs the *t*-BuBr formed is destroyed by the second equivalent of *t*-BuLi. This removal of *t*-BuBr from the reaction mixture eliminates the cross coupling reaction and the alkylation of the telluride anion. The problems that can occur with the *n*-BuLi exchange and how they are eliminated with *t*-BuLi are shown in Figure 5. The formation of isobutane and isobutylene from *t*-BuLi and *t*-BuBr in THF takes place at a reasonable rate even at -78°C.

As expected, the solution electrochemical characteristics are essentially identical for the new donors, TMHM-TTeF, DMHM-TTeF, CpHM-TTeF and HMTTeF. The formation of metallic salts from these more soluble donors has met with very limited success. Apparently, the methyl groups and the cyclopropyl groups reduce overlap in the slipped stack solid state structure by forcing the molecules farther apart. This increases the likelihood that mixed stack and other nonconducting phases will form. While work is continuing, to date only $(DMHM\text{-}TTeF)_2Br$ shows metallic like properties. The resistance profile as a function of temperature for a single crystal of $(DMHM\text{-}TTeF)_2Br$ is given in Figure 6. The resistance or conductivity remains almost constant to low temperatures.

Downloaded At: 14:56 29 January 2011

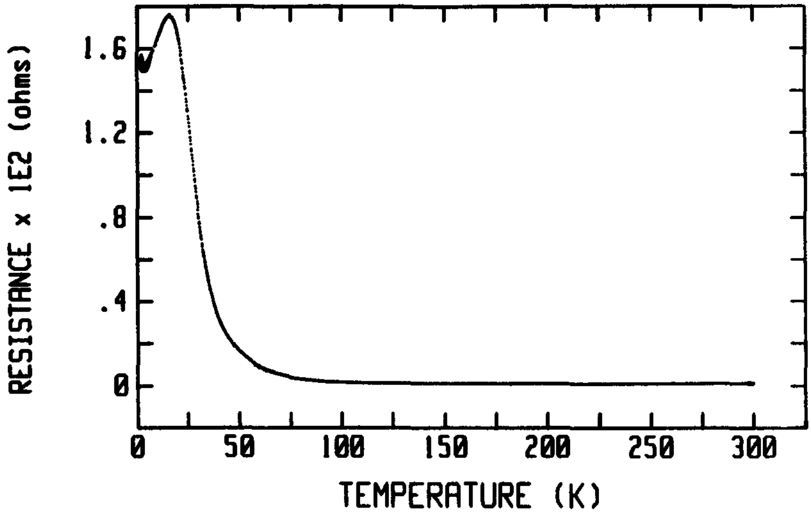


Figure 6 Resistance as a function of temperature for a single crystal of $(DMHM\text{-}TTeF)_2Br$. $\sigma_{300} = 27\Omega^{-1}cm^{-1}$

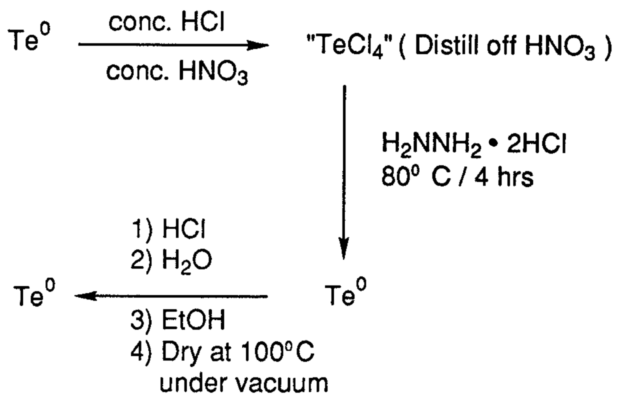


FIGURE 4 Preparation of Microcrystalline Tellurium

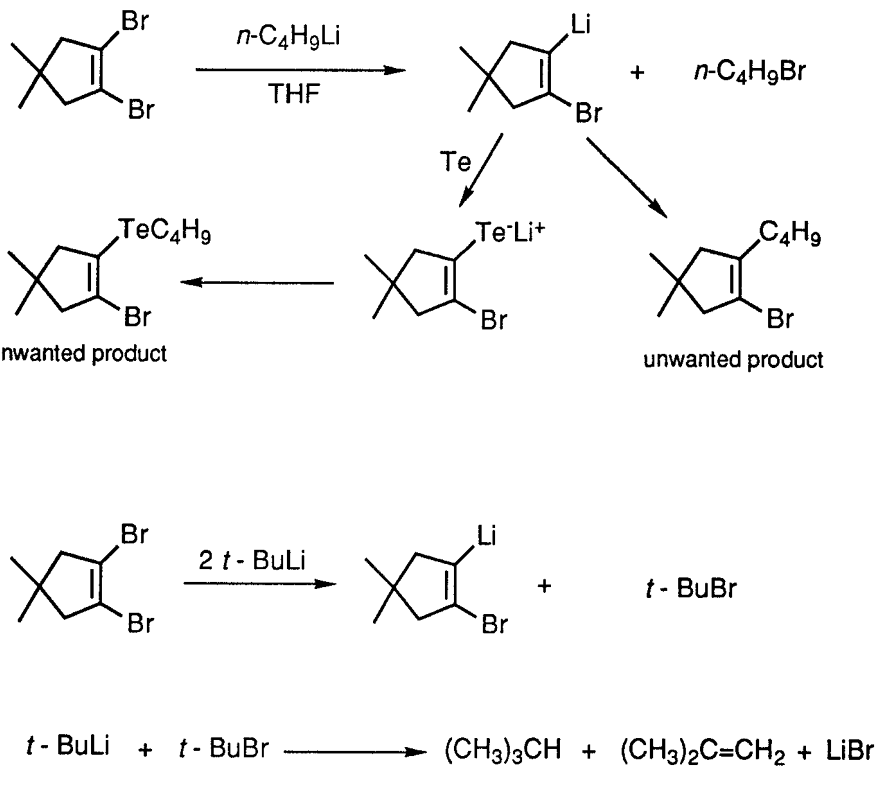


FIGURE 5 Metal Halogen Exchange Reactions

Downloaded At: 14:56 29 January 2011

Downloaded At: 14:56 29 January 2011

Tetratellurafulvalene (TTeF)

The methods used for the synthesis of DBTTeF and HMTTeF have not been useful in the synthesis TTeF. In the DBTTeF synthesis the *o*-dilithiobenzene was prepared from the corresponding mercury compound. Divinyl mercury compounds are generally unknown. The HMTTeF synthesis, using the 1,2-bromocyclopentene only works because at low temperatures the 1-bromo-2-lithiocyclopentene does not eliminate LiBr as a five membered ring acetylene (cyclopentyne) would be formed. This elimination reaction readily takes place in acyclic compounds. If a more electropositive atom is attached to the vinyl carbon, such as Hg or Sn the elimination should be circumvented. We were interested in using a trialkyltin group although the starting material *Z*-1,2-bis(trimethylstannyl) ethylene was initially unavailable. Two encouraging results concerning the utilization of tin chemistry in the synthesis of TTeF were then published.[27,28] Mitchell and coworkers reported in 1983 the synthesis of the *Z* isomer of 1,2-bis(trimethylstannyl) ethylene by the Pd(0) catalyzed addition of hexamethylditin to acetylene.[27] Reich and coworkers a year later showed that 2,3-bis(trimethylstannyl) - 1,3-butadiene reacted with two equivalents of methyllithium and two equivalents of Se to give the 2,3-diselenide dianion of 1,3-butadiene in 55% yield.[28] We have used Mitchell's distannylalkene to prepare TTeF (See figure 7). 1,2-Bis(trimethylstannyl)ethylene was treated with *n*-BuLi at -78°C and then with microcrystalline tellurium at the same temperature. After all of the tellurium had reacted the first two steps were repeated and 0.5 equivalent of tetrachloroethylene was added at -78°C to react with the 1,2-dilithioditelluride. This gave about a 5% yield of TTeF that had been purified by chromatography (2x) and recrystallization.[29,30] The yield seems to be limited by several factors: the position of the equilibrium of the transmetallation reaction, *n*-BuLi and the trimethyltin species; the reaction with tetrachloroethylene which gives rise to polymeric products as well as some of the six-membered ring isomer (this latter product makes the purification of TTeF somewhat laborious); and the oxidation of TTeF (presumably during workup) to form products like the insoluble $TTeF(OH)_8$. Since we can trap the 1,2-dilithioditelluride with *cis* - $PtCl_2(PPh_3)_2$ and isolate the resulting platinum coordination compound in 28% yield, we know that the first four steps in the reaction proceed at least to that extent. Several modifications of the TTeF synthesis are being pursued so that TTeF can be used in further chemical synthesis.

STUDY OF TELLURIUM Π-DONOR SALTS

Information on some tellurium π-donor salts has been presented in the earlier sections along with the synthesis of the donor inasmuch as so little work has been done on the salts. This is a consequence of the fact that crystal formation is difficult and the quality of the crystals once formed is often poor. For TTeF the results are much more promising.[31-33]

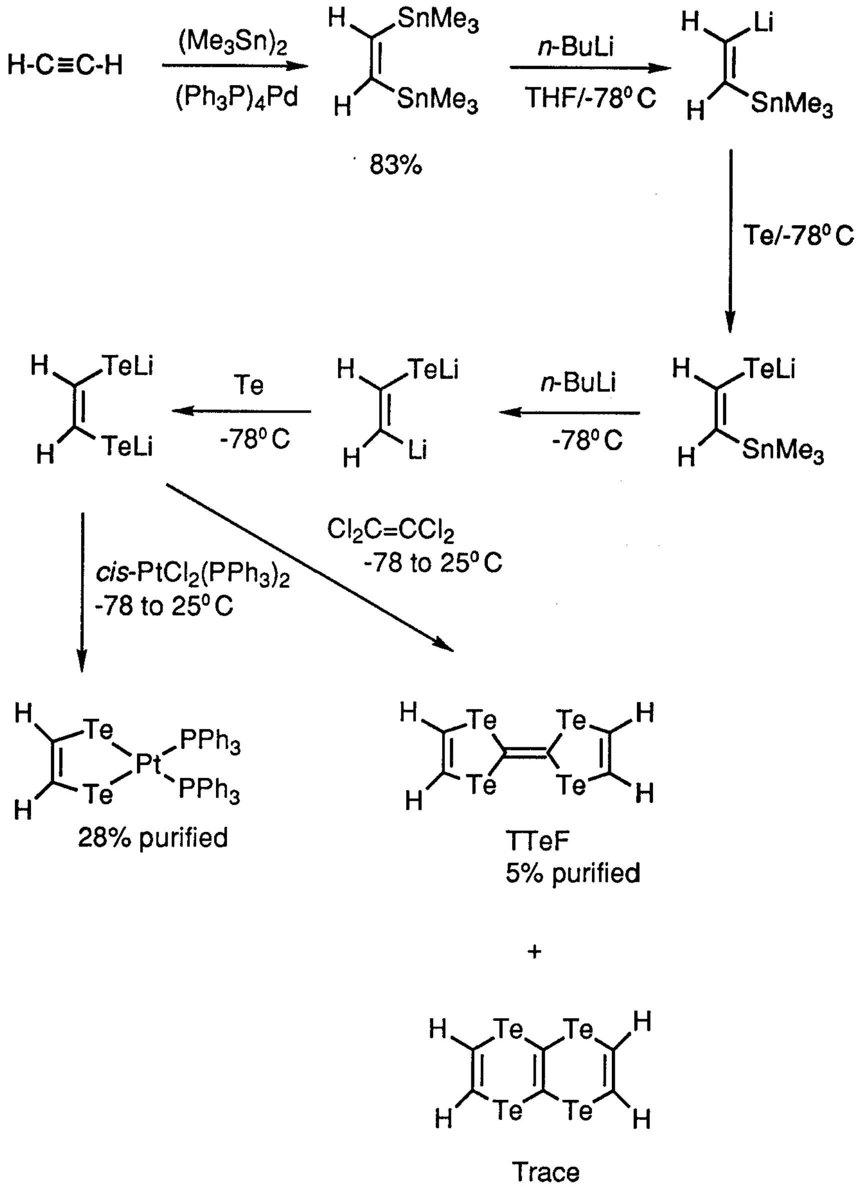


FIGURE 7 Synthesis of TTeF

Downloaded At: 14:56 29 January 2011

Downloaded At: 14:56 29 January 2011

TTeF-TCNQ

Because TTeF solutions are easily oxidized and are somewhat water sensitive, crystals were grown in a glove box with an inert atmosphere of high purity helium. A black (metallic, segregated stack) phase of TTeF-TCNQ was formed when warm chlorobenzene solutions of TTeF and TCNQ were mixed and the solvent allowed to evaporate.[31,32] However, only fine powders were obtained in quantities to small to fully characterize. Shiny black needles of TTeF-TCNQ have been prepared by carefully layering a CS_2/TTeF solution with a CH_3CN/TCNQ solution (1-5mM each) in a straight or H cell.[31,32] Even these crystals were brittle and generally multiply twinned. The X-ray crystal structure indicates that there are layers of donor molecules which have intermolecular Te···Te contacts not only along the intrastack direction but also along the interstack directions.[33] These donor layers alternate with layers of acceptor molecules. This mode of packing is somewhat similar to that observed for some phases of $(TMTSF)_2X$ and $(BEDT\text{-}TTF)_2X$ salts. A tight-binding electronic band structure calculated based on the crystal structure indicates that the donor bandwidth is quite large (2.49 eV double - zeta Slater orbitals) while the TCNQ bandwidth is almost the same for TTF-TCNQ, TSF-TCNQ as it is for TTeF-TCNQ.[33] A number of physical parameters for TCNQ salts of TTF, TSF and TTeF are collected in Table 2.

TABLE II Comparison of TCNQ Salts of TTF, TSF and TTeF

Parameter	TTF-TCNQ	TSF-TCNQ	TTeF-TCNQ
$\sigma_{300K}(\Omega^{-1}cm^{-1})$	500 ± 100	800 ± 100	2,200 ± 300
$\sigma_{max}/\sigma_{300K}$	~ 14	~ 12	~ 9.5
T_{max} (K)	59	40	<2
Stacking axis (Å)	3.819	3.876	3.947
Z (e^-)	0.59	0.63	0.71
σ_{300K} ratio[a]	1	1.2-2.3	3.2-6.3
$[W_T]^2$ ratio[b]	1	1.5	3.1
W_D (eV)	0.85	1.52	2.49
W_A (eV)	1.37	1.31	1.36

a) σ_{300K} ratio $\equiv \sigma_{TXF\text{-}TCNQ}/\sigma_{TTF\text{-}TCNQ}$ (300K)

b) $[W_T]^2$ ratio $\equiv ([W_D]^2 + [W_A]^2) / ([W_{TTF}]^2 + [W_{TCNQ}]^2)$; All bandwidths (W) based on calculations with double-zeta Slater type orbitals.

The room temperauture electrical conductivity of TTeF-TCNQ is greater than 2,000 $\Omega^{-1}cm^{-1}$ with a few samples as high as 3,000 $\Omega^{-1}cm^{-1}$. Since the conductivity is inversely proportional to the square of the density of states at the Fermi level it should also be proportional to the bandwidth squared.

$$\sigma \propto 1/[D(E_F)]^2 \propto [W_T]^2 = [W_D]^2 + [W_A]^2$$

The calculated $[W_T]^2$ ratios based on double-zeta bandwidths, 1:1.5:3.1 are in excellent agreement with the experimental conductivity ratios, 1:1.2 - 2.3:3.2 - 6.3 for TCNQ salts of TTF, TSF and TTeF (see Table 2). While TTeF-TCNQ has not been found to undergo a transition to a superconducting state as the temperature is lowered at ambient pressure, neither does it undergo a metal to insulator transition as is observed for TTF-TCNQ (T_{max} = 59K) or for TSF-TCNQ (T_{max} = 40K). This change in behavior is likely due, at least in part, to the increased interchain interaction and more two-dimensional character. The tight-binding electronic band structure calculations confirm that the Fermi surface is more 2-D than that of TTF-TCNQ; but it is not closed and the material still has considerable 1-D character. Since Pouget has observed superlattice structure (from diffuse X-ray scattering) for TTeF-TCNQ, it is possible that the TCNQ chains undergo a Peierls (charge-density) modulation while the TTeF chains relatively unaffected.[34] The superlattice structure is certainly pertinent to the electronic structure since the degree of charge transfer calculated from the X-ray data is the same as that calculated from the infrared data (Z = 0.71).[35]

Downloaded At: 14:56 29 January 2011

Other TTeF Salts

Only preliminary data is available on a few other salts of TTeF. This data is summarized in Table III. The $TCNQF_4$ and DMTCNQ salts undergo metal-to-semiconductor transitions at about 95K and 175K, respectively. The gap energy given in terms of a temperature (15K, 110K) is extremely low in both cases. Work is in progress on the complex salts of TTeF, but to date only a semiconducting perchlorate salt ($\sigma_{300K} = 4\Omega^{-1}cm^{-1}$) has been examined. A considerable opportunity exists for the preparation of complex salts of TTeF and other tellurium π-donors if a suitable solvent can be uncovered and used in the electrochemical salt formation.

TABLE III TTeF Salts

Parameter	TCNQ	$TCNQF_4$	DMTCNQ	ClO_4
$\sigma_{300K}(\Omega^{-1}cm^{-1})$	2,200	330	123	4
$\sigma_{max}/\sigma_{300K}$	9.5	2.7	1.6	—
T_{max} (K)	<2	95	175	—
E_g (K)[a]	—	~15	~110	(0.24eV)
S_{300K} (μV/K)	3.5	2.7	2.5	

a) Eg below T_{max} for the $TCNQF_4$ and DMTCNQ salts. The ClO_4^- salt is a semiconductor over the temperature range examined.

ACKNOWLEDGEMENTS

The authors acknowledge the assistance of colleagues whose names appear on many of the cited articles from The Johns Hopkins University. Special thanks are extended to Drs. T. O. Poehler and T. J. Kistenmacher for their collaborative efforts. We thank Mr. Greg Yep for help with drawings and proofreading. Dwaine Cowan wishes to thank Drs.: Kenichi Fukui, Tokio Yamabe, Kazuyoshi Tanaka, Gunzi Saito, Noboru Sonoda, Nobuaki Kambe, Masaru Kimura and Shinsuke Inoue for their warm hospitality during his recent visit to Japan to present this paper. Our work on tellurium chemistry has been supported by the National Science Foundation through the Division of Materials Research (DMR-8921071).

Downloaded At: 14:56 29 January 2011

REFERENCES

1. D.O. Cowan, in New Aspects of Organic Chemistry I. Proceedings of the 4th International Conference on New Aspects of Organic Chemistry, edited by Z. Yoshida, T. Shiba and Y. Ohshiro (Kadansha Ltd., Tokyo; and VCH, 1989), pp. 177-225.
2. D. O. Cowan, R. Elsenbaumer, F. Wudl, J. Collman, G. Saito, and P. Erk, in Organic Superconductivity, edited by V. Kresin, and W. A. Little (Plenum Press, New York, 1990), pp 295-316.
3. D. O. Cowan and F. M. Wiygul, Chemical and Engineering News, 64, (29), 28-45 (1986).
4. D. O. Cowan and A. Kini, in The Chemistry of Organic Selenium and Tellurium Compounds, edited by S. Patai (John Wiley and Sons, London, 1987), Vol. II, Chap. 12, pp. 463-494.

5. (a) H. Inokuchi, K. Imaeda, T. Enoki, T. Mori, Y. Maruyama, G. Saito, N. Okada, H. Yamochi, K. Seki, Y. Higuchi, and N. Yasuoka, Nature, 329, 39 (1987); (b) see also G. Saito, H. Yamochi, N. Iwasawa, H. Murofushi, and T. Tachikawa, Proceedings of this conference.
6. (a) G. Mihaly, A. Janossy, and G. Gruner, Solid State Commun., 22, 771 (1977); (b) L. C. Isett and E. A. Perez-Albuerne, Solid State Commun., 21, 433 (1977).
7. (a) V. N. Laukhin, A. I. Kotov, M. L. Khidekel, I. F. Schegalev, and E. B. Yagubskii, JETP Letters, 28, 284 (1978); (b) P. Dalhaes, C. Coulon, S. Flandrois, H. Hilti, C. W. Mayer, and G. Rihs, J. Chem. Phys., 73, 1452 (1980).
8. (a) D. J. Sandman, J. C. Stark, and B. M. Foxman, Organometallics, 1, 739 (1982); (b) D. J. Sandman, J. C. Stark, G. P. Hamill, W. A. Burke, B. M. Foxman, Mol. Cryst. Liq. Cryst., 86, 79 (1982); (c) R. P. Shibaeva and V. F. Kaminshii, Cryst. Struct. Commun., 10, 663 (1981).
9. (a) H. Miyamoto, K. Takimiya, Y. Aso, T. Otsubo, and F. Ogura, Synth Met., 42, 2389 (1991); (b) T. Otsubo, N. Sukenobe, Y. Aso, and F. Ogura, Synth. Met., 27, B509 (1988).
10. K. Takimiya, Y. Aso, T. Otsubo, and F. Ogura, Proceedings of this Conference.
11. (a) M. R. Detty and B. J. Murray, J. Org. Chem., 47, 1148 (1982).
(b) M. R. Detty, B. J. Murry, and J. H. Perlstein, Tetrahedron Lett., 24, 539 (1983).
12 M. R. Detty, B. J. Murray, and M. D. Seidler, J. Org. Chem., 47, 1968 (1982).
13. (a) K. Lerstrup, D. Talham, A. Bloch, T. Poehler, and D. O. Cowan, J. Chem. Soc., Chem. Commun., 336 (1982); (b) R. Gleiter, M. Kobayashi, J. Spanget-Larsen, J. P. Ferraris, A. N. Bloch, K. Bechgaard, and D. O. Cowan, Ber. Bunsenges. Phys. Chem., 79, 1218 (1975).
14. K. Lerstrup, M. Lee, F. M. Wiygul, T. J. Kistenmacher, and D. O. Cowan, J. Chem. Soc., Chem. Commun., 294 (1983); 15. K. A. Lerstrup and D. O. Cowan, J. de Physique, Paris, 44, C3-1247, (1983).
16. K. Lerstrup, D. O. Cowan, and T. J. Kistenmacher, J. Am. Chem. Soc., 106, 8303 (1984).
17. F. Wudl and E. Aharon-Shalom, J. Am. Chem. Soc., 104, 1154 (1982).
18. N. Okada, G. Saito, and T. Mori, Chem. Lett., 311 (1986).
19. G. Saito, T. Enoki, H. Inokuchi, H. Kumagai, and J. Tanaka, Chem. Lett., 503 (1983).
20. G. Saito, H. Kumagai, J. Tanaka, T. Enoki, and H. Inokuchi, Mol. Cryst. Liq. Cryst., 120, 337 (1985).
21. D. O. Cowan, M. Mays, M. Lee, R. McCullough, A. Bailey, K. Lerstrup, T. Kistenmacher, T. Poehler, and L-Y. Chiang, Mol. Cryst. Liq. Cryst., 125, 191 (1985).

Downloaded At: 14:56 29 January 2011

22. (a) S. Matsuzaki, Z. S. Li, M. Sano, Chem. Lett., 1343 (1986), (b) S. Matsuzaki, Z. S. Li, and M. Sano, Synth. Met., 19 399 (1987). (c) Z. S. Li, S. Matsuzaki, M. Onomichi,
M. Sano, and G. Saito, Synth. Met., 16, 71 (1986).
23. K. Lerstrup, A. Bailey, R. McCullough, M. Mays, D. Cowan, and T. Kistenmacher, Synth. Met., 19, 647 (1987).
24. A. B. Bailey, R. D. McCullough, M. D. Mays, D. O. Cowan, and K. Lerstrup, Synth. Met., 27, B425 (1988).
25. O. Clauder, Z. Anal. Chem., 89, 270 (1932).
26. E. J. Corey and D. J. Beamers, J. Am. Chem. Soc., 94, 7210 (1972).
27. (a) T. N. Mitchell, A. Amamria, H. Killing, and D. Rutschow, J. Organomet. Chem., C45, 241 (1983); (b) T. N. Mitchell, A. Amamria, H. Killing, and D. Rutschow, J. Organomet. Chem., 304, 257 (1986).
28. H. T. Reich, K. E. Yelm, and I. L. Reich, J. Org. Chem., 49, 3438 (1984).
29. R. D. McCullough, G. B. Kok, K. A. Lerstrup, and D. O. Cowan, J. Am. Chem. Soc., 109, 4115 (1987).
30. R. D. McCullough, M. D. Mays, A. B. Bailey, and D. O. Cowan, Synth. Met., 27, B487 (1988).
31. M. D. Mays, R. D. McCullough, D. O. Cowan, T. O. Poehler, W. A. Bryden, and T. J. Kistenmacher, Solid State Commun., 65, 1089 (1988).
32. M. D. Mays, R. D. McCullough, A. B. Bailey, D. O. Cowan, W. D. Bryden, T. O. Poehler, and T. J. Kistenmacher, Synth. Met., 27, B493 (1988).
33. D. O. Cowan, M. D. Mays, T. J. Kistenmacher, T. O. Poehler, M. A. Beno, A. Kini, J. M. Williams, Y-K. Kwok, D. Carlson, L. Xiao, J. J. Novoa, and M-H. Whangbo, Mol. Cryst. Liq. Cryst., 181, 43 (1990).
34. J. P. Pouget, M. D. Mays, and D. O. Cowan, unpublished observations.
35. J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler, and D. O. Cowan, J. Am. Chem. Soc., 103, 2442 (1981).

Downloaded At: 14:56 29 January 2011