Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: E. M. Engler , V. Y. Lee , R. R. Schumaker , S. S. P. Parkin , R. L. Greene & J. C. Scott (1984): Synthesis of Biethylenedithiolylene-Tetrathiafulvalene Donors (BEDT-TTF) and Electrochemical Preparation of their Charge Transfer Complexes, Molecular Crystals and Liquid Crystals, 107:1-2, 19-31

To link to this article: http://dx.doi.org/10.1080/00268948408072069

Mol. Cryst. Liq. Cryst. 1984, Vol. 107, pp. 19-31
0026-8941/84/1072-0019/$18.50/0

SYNTHESIS OF BIETHYLENEDITHIOLYLENE-TETRATHIAFULVALENE DONORS (BEDT-TTF) AND ELECTROCHEMICAL PREPARATION OF THEIR CHARGE TRANSFER COMPLEXES

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Abstract: Various synthetic procedures for preparing BEDT-TTF are critically examined. Starting from readily available thiapendione, BEDT-TTF can be made in a high yield, simple, two-step synthesis. Electrochemical crystal growth of charge transfer complexes of BEDT-TTF typically involves the formation of multiple phases and stoichiometries. In the case of perrhenate (ReO_4^-) at least five different complexes have been identified. Controlled preparation of the superconducting phase ($(BEDT\text{-}TTF_2ReO_4)$) remains an elusive goal.

INTRODUCTION

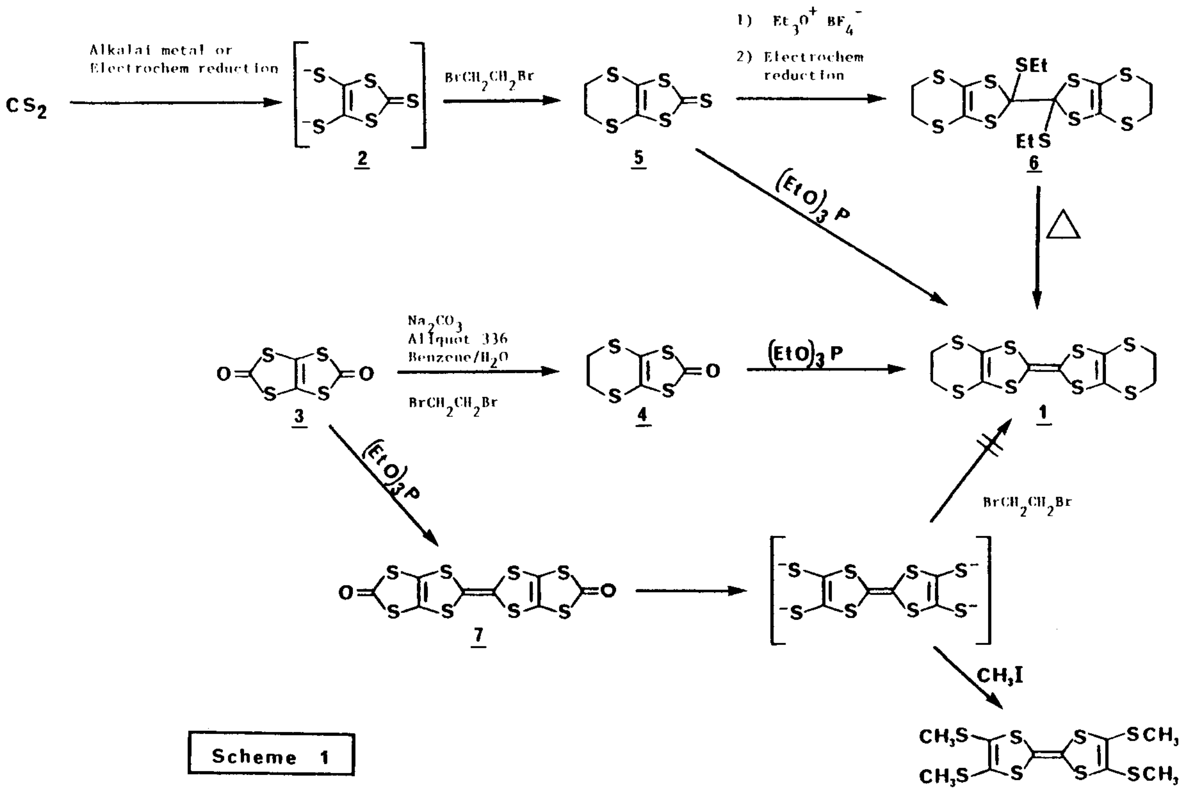
The last decade of research on organic conductors based on tetrathiafulvalene derivatives has witnessed a steady march in the progress of enhancing metallic properties and in uncovering a wide variety of interesting solid state phenomena. Table I traces this progress from the initial discovery of marginal metallic behavior in TTF-TCNQ through various selenium modifications where stabilization of the metallic phase occurred, to the present stage of organic superconductors based on TMTSF and BEDT-TTF Bechgaard salts.[1] Out of such work, has come a realization of the importance of enhancing interstack interactions as a means of stabilizing the tendency of these quasi-one-dimensional metals to charge or spin driven lattice distortions of the Fermi surface.

The most recent development in TTF based solids has involved the donor, bisethylenedithiolylene-tetrathiafulvalene (1,BEDT-TTF), where a novel two-dimensional electronic structure was reported by Saito and coworkers (see Table I, ref. l,m). Electrical anisotropies for directions parallel/perpendicular to the stacking axis near unity were discovered due to a unique "side by side" stacking of the donors, in contrast to the typical "face to face" stacking of such charge transfer complexes.[2] Subsequently, in a structure related to the Bechgaard 2:1 salts, superconductivity was discovered in BEDT-TTF perrhenate providing the first manifestation of this phenomena in an organosulfur-based solid (see Table I, ref. n).

In this paper we will provide a critical evaluation of the synthetic approaches for preparing BEDT-TTF. While BEDT-TTF can be synthesized[3] by several procedures, we will describe here the method that we have found to be the most convenient and reliable. Further, details of the conditions of electrochemical crystal growth will be presented which is particularly critical for BEDT-TTF where multiple phases have been a common feature of crystal growth in contrast to TMTSF or TMTTF complexes.

Synthesis of BEDT-TTF

Scheme I illustrates the various synthetic approaches for preparing BEDT-TTF from commercially available starting materials. Alkali metal (K or Na in DMF)[4] or electrochemical[5] reduction of carbon disulfide had been employed initially for preparing 4,5-dithiolate-1,3-dithiole-2-thione (2) which can be isolated as the dianion salt or reacted in-situ with alkyl halides. In the latter case,


CS2
Alkalai metal or Electrochem reduction
2
BrCH2CH2Br
5
1) Et3O+ BF4-
2) Electrochem reduction
SEt
EtS
6
(EtO)3P
△
3
Na2CO3
Aliquot 336
Benzene/H2O
BrCH2CH2Br
4
(EtO)3P
1
(EtO)3P
7
BrCH2CH2Br
CH3I
CH3S
SCH3

Scheme 1

however, by-products in the reaction can complicate isolation of the alkylated product and lead to variable yields. Isolation of 2 as the Zn salt[4] provides a more stable material for further reaction. Thermal rearrangement of 2 to its 1,2-dithiol-3-thione isomer can be troublesome, if the alkali reduction procedure is not carefully followed.[6]

Alternately, thiapendione (3)[7] can be converted in a simple convenient procedure[8,9] to the carbonyl precursor 4 for coupling to BEDT-TTF (yields for 3 to 4 conversion ~80-90%). The reaction involves selective base opening of only one of the two carbonyls of thiapendione using a benzene-water solvent mixture with an alkyl ammonium phase transfer reagent and sodium carbonate with gentle warming and subsequent addition of 1,2-dibromoethane. A detailed, large-scale synthesis of thiapendione has recently been reported.[8,10] Thiapendione is a stable, white, crystalline solid which can be conveniently handled for further reaction. This useful synthetic building block has enabled the preparation of a wide variety of oligomeric and BEDT-like deviatives of TTF. Table II summarizes some examples.

Both -thione 5 and -one 4 can be coupled directly to BEDT-TTF on refluxing in freshly distilled triethyl phosphite under nitrogen. We have found, however, that higher yields (typically ~80% for coupling 4 *versus* ~25% for 5) and more easily isolated product are obtained when using 4. In fact, on cooling the triethyl phosphite solution, BEDT-TTF crystallizes out and is isolated by simple filtration. Recrystallization several times from carbon disulfide-ethylacetate gave BEDT-TTF (as orange needles) suitable for charge transfer salt preparations.

An alternate coupling procedure[11] involving thione alkylation, reductive coupling to an ortho-thio oxalate and subsequent pyrolysis

TABLE I Progress in the properties of organic metals based on TTF derivatives.

Year	Material	Properties	Reference
1973	TTF-TCNQ	metallic state discovered in an organic solid metal-insulator transition ($T_{M\text{-}I}$ at 53°K)	a,b
1974	TSeF-TCNQ DSeDTF-TCNQ	isostructural Se-analogs prepared ($T_{M\text{-}I}$ at 28°K)	c,d
1975	$(TTF)_x(TSeF)_{1-x}TCNQ$	organic alloys	e,f
1975	HMTSeF-TCNQ	high conductivity maintained at low temperature ($T_{M\text{-}I}$~16°K)	g
1976	HMTSeF-TCNQ	$T_{M\text{-}I}$ suppressed under pressure	h
1980	$(TMTSF)_2X$ $X{=}PF_6$	conductivity at T_{max} $>10^5$/ohm-cm (Bechgaard salts)	i
1980	$(TMTSF)_2X$	organic superconductivity discovered in $X{=}PF_6$ under pressure and ClO_4 at ambient pressure (T_C~1°K)	j,k
1982	$(BEDT\text{-}TTF)_2\text{-}ClO_4(Cl_3C_2H_3)_{0.5}$; $\beta\text{-}(BEDT\text{-}TTF)_2PF_6$	new two-dimensional organic metals	l,m
1983	$(BEDT\text{-}TTF)_2ReO_4$	first sulfur-based organic superconductor (T_C~2°K)	n

TABLE I (continued)

[a]J. Ferraris, D. O. Cowan, V. Walutka, Jr. and J. H. Perlstein, J. Am. Chem. Soc., 95, 948 (1973); [b]L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito and A. J. Heeger, Solid State Commun., 12, 1125 (1973); [c]E. M. Engler and V. V. Patel, J. Am. Chem. Soc., 96, 7376 (1974); [d]S. Etemad, T. Penney, E. M. Engler, B. A. Scott and P. E. Seiden, Phys. Rev. Lett., 34, 741 (1975); [e]Y. Tomkiewicz, E. M. Engler and T. D. Schultz, Phys. Rev. Lett., 35, 456 (1975); [f]E. M. Engler, B. A. Scott, S. Etemad, T. Penney and V. V. Patel, J. Am. Chem. Soc., 99, 5909 (1977); [g]A. N. Bloch, D. O. Cowan, K. Bechgaard, R. E. Pyle, R. H. Banks and T. O. Poehler, Phys. Rev. Lett., 34, 1561 (1975); [h]J. R. Cooper, M. Weger, D. Jerome, D. Lefur, K. Bechgaard, A. N. Bloch and D. O. Cowan, Solid State Commun., 19, 749 (1976); [i]K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen and N. Thorup, Solid State Commun., 33, 1119 (1980); [j]D. Jerome, A. Mazaud, M. Ribault and K. Bechgaard, J. Phys. Lett. (Orsay, France), 41, L-95 (1980); [k]K. Bechgaard, K. Carneiro, F. B. Rasmussen, M. Olsen, G. Rindorf, C. S. Jacobsen, H. J. Pedersen and J. C. Scott, J. Am. Chem. Soc., 103, 2440 (1981); [l]G. Saito, T. Enoki, K. Toriumi and H. Inokuchi, Solid State Commun., 42, 557 (1982); [m]H. Kobayashi, T. Mori, R. Kato, A. Kobayashi, Y. Sasaki and G. Saito, Chem. Lett., 581 (1983); [n]S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott and R. L. Greene, Phys. Rev. Lett., 50, 270 (1983).

has not shown any advantages over the phosphite coupling method. Another procedure, which in principle, should readily provide 1 involves coupling of thiapendione to dithiapendione (7)[7] and subsequent base reaction of the carbonyls to tetrathiolate intermediate 8. While reaction with methyl iodide occurs near quantitatively, alkylation with dihaloethane gave no BEDT-TTF in our attempts.

Electrocrystallization of BEDT-TTF Charge Transfer Salts

In contrast to TMTTF and TMTSF anion salts where typically a single phase dominates, BEDT-TTF complexes are characterized by multiple phases and stoichiometries. Electrochemical crystal growth[12] techniques have been shown to be essential to obtaining high quality single crystals for solid state characterization. In brief, the procedure involves oxidation, under low, controlled currents (~0.1-50 microamps) or voltages (0.2-1.0 volts *versus* s.c.e.), a solution of donor plus appropriate electrolyte (tetra-alkyl ammonium salts).

Since our initial discovery of the superconducting phase (see Table I) of BEDT-TTF_2ReO_4, we have been unable to identify a set of experimental conditions that uniquely selects for this phase.[13] Five distinct complexes have been made by ourselves[14,15] involving BEDT-TTF and ReO_4^-, and Kobayashi and coworkers[2] have reported an additional one. Table III summarizes some data on these materials. We have explored a wide variety of variations in the crystal growth parameters which are summarized in Table IV. The usual precautions were taken in carrying out these crystal preparations. Both donor and electrolyte were recrystallized at least two times and vacuum dried. Solvent was freshly distilled over drying agents under N_2 and passed over neutral alumina prior to use. Oven dried glassware and electrochemically cycled Pt electrodes were employed. Crystal runs were carried out on a vibrationless table in the dark. The general conclusions from this work are:

- Variation of solvent and current appears to have a greater effect on crystal size and composition than changes in constituent concentrations, temperature, and electrode material and form.
- Considerable variations can occur from run to run. From our experience in this area, it appears that subtle nucleation processes at the electrode interface dominate which phase is formed.
- The 2:1 superconducting phase is obtained as a mixture with crystals of other complexes, typically the α-3:2 phase. No unique set of growth conditions have been defined.[13] Typically, using THF or methylene chloride as a solvent, low currents (<1 microamp), produces preferentially the α-3:2 phase while higher currents (>10 microamps) produce the 2:1:0.5 phase. Intermediate currents produce the 2:1 phase on an approximate basis that 50% of the crystal runs will have some 2:1 phase. The β-3:2 phase is produced at about the same frequency. When mercury is used as an electrode in methylene chloride, the γ-3:2 phase is more commonly found, but also as a mixture of crystals of the other phases. The characteristic shape of the crystals for the various phases permits ready identification once experience has been gained.

SUMMARY

The preparation of BEDT-TTF from thiapendione can be effected in a one day, simple procedure in overall yield of approximately 80%. Thiapendione is also a convenient synthetic starting point for a wide variety of new systematic modifications of BEDT-TTF.[9] Electrochemical preparation of charge transfer complexes with

TABLE II TTF derivatives prepared from thiapendione.

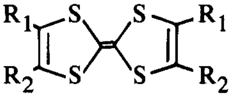
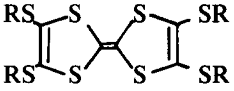
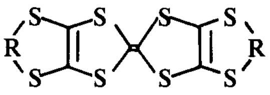
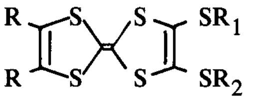
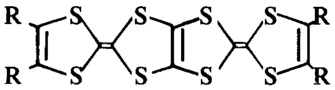
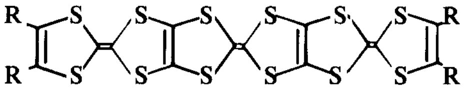
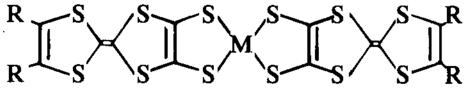
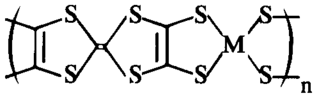
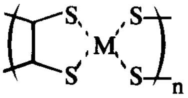
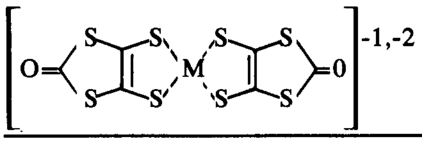
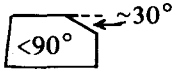
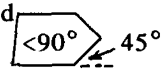
Compound	Substituents	Reference
	R_1/R_2=H, alkyl	8,10
	R=alkyl,CO	7
	R= $(CH_2)_n$, -CH=CH-	8,10
	R=CN, CF_3, CO_2CH_3 R_1,R_2=alkyl, R_1/R_2=CO	7,a,b
	R=CN, CF_3, CO_2CH_3	7,a,b
	R=CF_3	a
	R=CF_3, CN, CO_2CH_3 M=Ni,Pt,Pd	7,b,c
	M=Ni,Pt,Pd	c,d
	M-Ni,Pt,Pd	c,d

TABLE II (continued)

Compound	Substituents	Reference
	M=Ni,Pd,Pt	d

[a] R. R. Schumaker and E. M. Engler, *J. Am. Chem. Soc.*, *102*, 6651 (1980); [b] E. M. Engler, V. V. Patel and R. R. Schumaker, *J. Chem. Soc., Chem. Comm.*, 516 (1979); [c] N. Martinez-Rivera, E. M. Engler and R. R. Schumaker, *ibid.*, 184 (1979); [d] H. Poleschner, W. John, G. Kempe, E. Hoyer and E. Fanghanel, *Z. Chem.*, *18*, 345 (1978).

TABLE III Complexes of BEDT-TTF with perrhenate.

Complex	Shape	Unit Cell Parameters	Conductivity (1 ohm-cm) T_{max} (°K)
$(BEDT\text{-}TTF)_2ReO_4$	elongated plates 	7.78, 12.59, 16.97 73.0°, 79.9°, 89.1°	~20 (metallic), 81°
α-$(BEDT\text{-}TTF)_3(ReO_4)_2$	thin plates 	8.50, 30.57, 9.41 89.6°	~50 (weakly metallic), 88°
β-$(BEDT\text{-}TTF)_3(ReO_4)_2$	elongated plates 	9.28, 16.11, 8.37 91.7°, 97.1°, 102.0	~100 (weakly metallic),~100°
γ-$(BEDT\text{-}TTF)_3(ReO_4)_2$	chunky crystals ---	16.30, 12.01, 12.42 91.2°	~1 (semiconducting)
$(BEDT\text{-}TTF)_2(ReO_4)(THF)^{a}_{0.5}$	twisted needles	--------	~1 (semiconducting)^b
$(BEDT\text{-}TTF)(ReO_4(THF)^c$	--------	12.68, 8.04, 19.29 97.7°	10^{-2} (semiconducting)

[a]Composition by elemental analysis; [b]polycrystalline measurement; [c]From ref. 2.

BEDT-TTF is typified by multiple phases and stoichiometries. Six distinct phases of BEDT-TTF with perrhenate have been identified. The superconducting (BEDT-TTF)$_2$ReO$_4$ cannot, in our hands, be prepared reliably and uniquely, but repeated preparations of this material have been made under a variety of conditions as a mixture of crystals of other phases.

TABLE IV Parameters varied in electrocrystallization runs.

Parameter	Variation
Solvent	THF, CH_2Cl_2, CH_3CN, $CHCl_2CHCl$, C_6H_5Cl
Current	0.1-20 microamps
Concentration	
Donor	10^{-4}-10^{-3} molar
Electrolyte	0.02-0.2 molar
Temperature	0° (THF, CH_2Cl_2) 50° (CH_3CN, C_6H_5Cl) 80° (C_6H_5Cl)
Electrode	
Material	Pt, Graphite, Ag, Au, Cu, Ni
Form	Pt: wire, foil, mesh loop, evaporated film

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11. P. R. Moses and J. Q. Chambers, J. Am. Chem. Soc., 96, 945 (1974).
12. This technique was applied by Bechgaard (see reference i in Table I) on the $TMTSF_2X$ complexes. For a description and summary of previous work see: E. M. Engler, R. L. Greene, P. Haen, Y. Tomkiewicz, K. Mortensen and J. Berendzen, J. Mol. Cryst. Liq. Cryst., 79, 371 (1982).

13. J. Williams *et al.*, have reported that the 2:1 phase forms out of 1,1,2 trichloroethane. We have tried their description repeatedly and have not been able to confirm their result. Our results indicate predominate formation of the α-3:2 and β-3:2 phases.
14. K. Carneiro, J. C. Scott and E. M. Engler, Phys. Rev. B, in press.
15. For a detailed description of the structure of these complexes see: S. S. P. Parkin, E. M. Engler, V. Y. Lee and R. R. Schumaker, to be published.