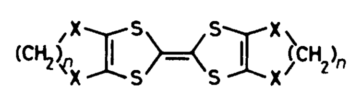
Bis(ethylenediseleno)tetrathiafulvalene: Convenient One-pot Synthesis and *X*-Ray Crystal Structure

Aravinda M. Kini,* Bradley D. Gates, Mark A. Beno, and Jack M. Williams
Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

An efficient, one-pot synthetic procedure for the preparation of the title electron-donor starting from tetrathiafulvalene, and its crystal structure as determined by *X*-ray diffraction, are presented.

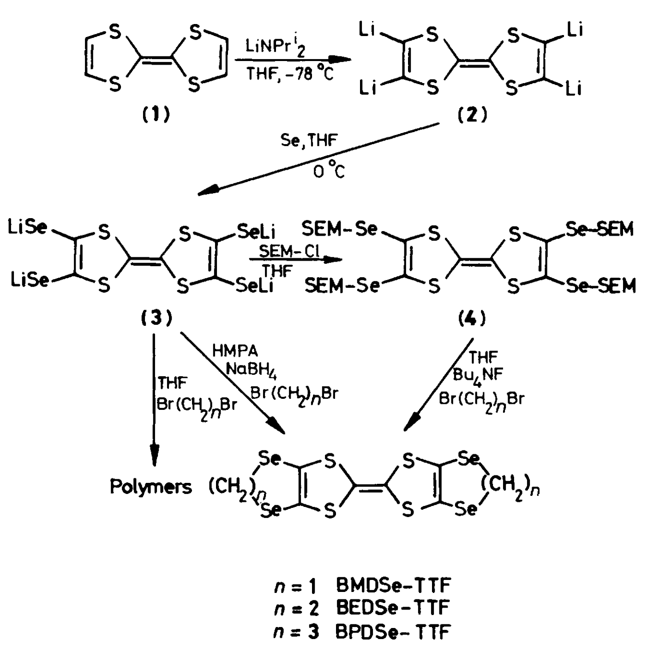
Bis(ethylenedithio)tetrathiafulvalene, BEDT-TTF, has now yielded ten ambient pressure superconductors and the superconducting transition temperatures (T_c) of these materials have been rapidly rising. A T_c of *ca.* 1.5 K in β-(BEDT-TTF)$_2$I$_3$ was first reported in 1984[1] and with the recent finding[2] and verification[3] of T_c *ca.* 10 K in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, a new high in T_c for organic systems has now been achieved. The presence of two-dimensional S · · · S networks in the radical-cation salts of BEDT-TTF, which favours the formation of a two-dimensional electronic band structure, is now generally believed to be the underlying reason for these rapid strides. The structure–property relationship found in β-(BEDT-TTF)$_2$X salts ($X^- = I_3^-$, AuI_2^-, IBr_2^-)[4] and our recent finding[5] of a large (the largest known in any superconductors) negative pressure dependence of T_c (−3 K/kbar) in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, have suggested that the expansion of the crystallographic unit cell in both types of structures is the empirical method of choice for further raising T_c in these systems. Incorporation of selenium and tellurium in BEDT-TTF is an attractive way to accomplish the unit cell enlargement, in addition to perhaps enhancing the dimensionality, owing to the larger size and greater polarizability of selenium and tellurium atoms compared to sulphur. In this connection, we are interested in the mixed S/Se and S/Te analogues of BEDT-TTF, bis(ethylenediseleno)tetrathiafulvalene (BEDSe-TTF) and bis(ethyleneditelluro)tetrathiafulvalene (BEDTe-TTF), wherein the outer sulphur atoms of BEDT-TTF are replaced by selenium and tellurium. Lee[6] and Nigrey *et al.*[7] have recently reported the synthesis of BEDSe-TTF independently *via* two different methods. We present here a one-pot procedure as a convenient alternative for the preparation of BEDSe-TTF, and report its crystal structure as determined by single-crystal *X*-ray diffraction.

Acidity of the vinylic protons of tetrathiafulvalene (TTF) (**1**) was first recognized by Green, who demonstrated the proton–lithium exchange by treatment of TTF with strong bases such as BuLi or lithium di-isopropylamide.[8] More recently, Aharon-Shalom *et al.*[9] and Lee[6] utilized the tetralithiation of TTF and subsequent chalcogen insertion into the carbon-lithium bonds of tetralithio-TTF (**2**) in their syntheses of tetrakis(alkylchalcogeno)-TTF, and BMDSe-TTF and BEDSe-TTF respectively. In the latter case (see Scheme 1), attempted intramolecular, alkylative ring closure of tetraselenolate ion (**3**) with dibromoalkanes led to polymeric products, which were obviously formed by predominantly intermolecular alkylation, even under high dilution conditions.[6] This problem was overcome by Lee, by first alkylating the tetraselenolate ion (**3**) with a silicon-containing protecting



X = S; *n* = 2 BEDT-TTF
X = Se; *n* = 1 BMDSe-TTF
X = Se; *n* = 2 BEDSe-TTF
X = Se; *n* = 3 BPDSe-TTF
X = Te; *n* = 2 BEDTe-TTF

Figure 1. BEDT-TTF and its analogues.



Scheme 1

group (trimethylsilylethoxymethyl, SEM) and then carrying out the intramolecular alkylation with dibromoalkanes by slow deprotection of SEM groups mediated by fluoride ion, resulting in moderate yields (35%) of BEDSe-TTF.[6] The formation of polymeric products even under these conditions was nevertheless noted. Nigrey *et al.*[7] synthesized BEDSe-TTF by a four-step sequence starting from 1,3-dithiole-2-thione.

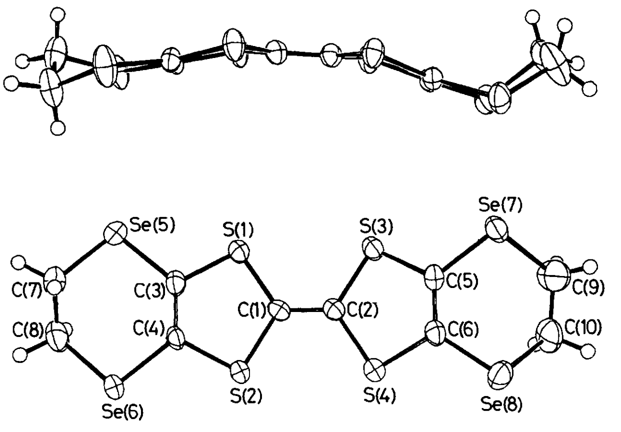


Figure 2. Atom numbering scheme and molecular conformation of neutral BEDSe-TTF.

Table 1. Intramolecular distances and selected S · · · S(Se) intermolecular contacts in BEDSe-TTF and BEDT-TTF.

Interatomic distances/Å

Atoms	BEDSe-TTF	BEDT-TTF[a]
S(1)–C(1)	1.758(6)	1.764
S(1)–C(3)	1.760(6)	1.757
S(2)–C(4)	1.752(6)	1.747
S(2)–C(1)	1.765(6)	1.760
S(3)–C(2)	1.760(6)	1.753
S(3)–C(5)	1.761(6)	1.755
S(4)–C(6)	1.754(6)	1.755
S(4)–C(2)	1.763(6)	1.753
C(1)–C(2)	1.329(8)	1.319
C(3)–C(4)	1.326(8)	1.335
C(5)–C(6)	1.330(8)	1.328
Se(S)(5)–C(3)	1.886(6)	1.727
Se(S)(5)–C(7)	1.954(7)	1.801
Se(S)(6)–C(4)	1.900(6)	1.744
Se(S)(6)–C(8)	1.940(8)	1.803
Se(S)(7)–C(5)	1.903(6)	1.751
Se(S)(7)–C(9)	1.946(7)	1.804
Se(S)(8)–C(6)	1.901(6)	1.747
Se(S)(8)–C(10)	1.931(7)	1.800
C(7)–C(8)	1.440(11)	1.430
C(9)–C(10)	1.483(10)	1.494

Intermolecular S · · · S(Se) contacts ≤3.7 Å

Atoms[b]	BEDSe-TTF	BEDT-TTF[a]
S(1)–S(2^{i})	3.700(3)	3.686
S(2)–S(4^{ii})	3.686(2)	3.623
S(3)–Se(S)(8^{iii})	3.542(2)	3.482
Se(S)(5)–Se(S)(6^{iii})	3.785(1)	3.692
Se(S)(7)–Se(S)(8^{iii})	3.644(1)	3.545

[a] Co-ordinates taken from ref. 12, standard deviations 0.007—0.012 Å.
[b] Symmetry operations for second atom: (i) $1 - x, -y, 1 - z$; (ii) $2 - x, -y, 1 - z$; (iii) $x - 1, y, z$.

We liked the synthetic potential of the easily generated tetralithio-TTF (**2**), which could serve as a central precursor to a variety of S/Se and S/Te analogues of BEDT-TTF and other tetrathiafulvalene derivatives. We speculated that the intermolecular alkylation of the tetraselenolate (**3**) with dibromoalkanes, yielding a polymeric product, was strongly favoured in the solvent (THF) employed by Lee,[6] because to a large measure the tetraselenolate ion was poorly solvated. In fact, when it is generated in THF, it precipitates as a pale orange solid. We then reasoned that if the tetraselenolate ion (**3**) is sufficiently solvated, as expected in dipolar aprotic solvents,[10] it would be prone to intramolecular alkylation because once the dibromoalkane molecule enters the solvent sphere of the solvated tetraselenolate ion, it would react with the tetraselenolate ion within the solvent sphere faster than with that outside the solvent sphere. Thus, in dipolar aprotic media, the intramolecular alkylation (yielding *e.g.* BEDSe-TTF) should take a strong preference over intermolecular alkylation (yielding a polymeric product) and this expectation has now been realized experimentally by us. Replacement of the solvent THF, after the generation of the tetraselenolate ion (**3**), by a dipolar aprotic solvent such as hexamethylphosphoramide (HMPA) and subsequent addition of dibromoalkanes has resulted in good yields of bis(alkyleneseleno)tetrathiafulvalenes, with substantially less polymeric by-product. Additionally, it has been possible virtually to eliminate the polymeric by-product by addition of sodium borohydride prior to the addition of dibromoalkanes. The function of sodium borohydride is to cleave any intermediates containing

Se–Se linkages, most likely formed by adventitious oxygen-promoted oxidation of the tetraselenolate ion. Typical yields obtained from several runs for the preparation of BEDSe-TTF† were in the range of 84—95% (crude) and 42—57% after one recrystallization from chloroform. Clearly, the need for isolating the SEM-protected intermediate (**4**) by the use of expensive SEM-Cl is eliminated and therefore our method represents a superior and convenient alternative to the methods of Lee[6] and Nigrey *et al.*[7] The procedure works equally well for the preparation of BMDSe-TTF (25—35% yield after one recrystallization from chloroform) and BPDSe-TTF (47—65% after one recrystallization from chloroform) by use of the appropriate dibromoalkanes.

There is ample literature precedence where the degree of oxidation (or reduction) of electron donors (or acceptors) in their radical-cation (or radical-anion) salts can be inferred from the changes in certain bond lengths upon oxidation (or reduction).[11] Therefore, we have determined the crystal structure of the neutral donor BEDSe-TTF by *X*-ray diffraction. Crystal data‡ indicate that the crystals of neutral BEDSe-TTF are isostructural to those of neutral BEDT-TTF.[12] The molecular bond distances (see Figure 2 for numbering scheme) and intermolecular S · · · S(Se) contact distances for BEDSe-TTF and BEDT-TTF are shown in Table 1. It is clear that the substitution of outer S atoms of BEDT-TTF by larger Se atoms does not affect the central TTF portion of the molecule but does result in the expansion of the intermolecular distances and the enlargement of the unit cell (1449.6 to 1544.0 Å^3). Therefore, the charge-transfer salts derived from BEDSe-TTF should possess an expanded donor–donor network compared to the corresponding BEDT-TTF salts, provided the same structure type is retained in both cases. Moreover, since the majority of the HOMO contribution is located on the central TTF portion of the molecule,[13] expansion of the donor–donor network should produce narrower electronic conduction bands and result in a higher density of states at the Fermi level and hence higher superconducting transition temperatures for BEDSe-TTF salts. Experimental verification of this conjecture must await the preparation of appropriate radical-cation salts of BEDSe-TTF, and investigations of their crystal structures and electrical properties. Such studies, as well as the preparation of related tellurium containing donors, are currently underway in our laboratory.

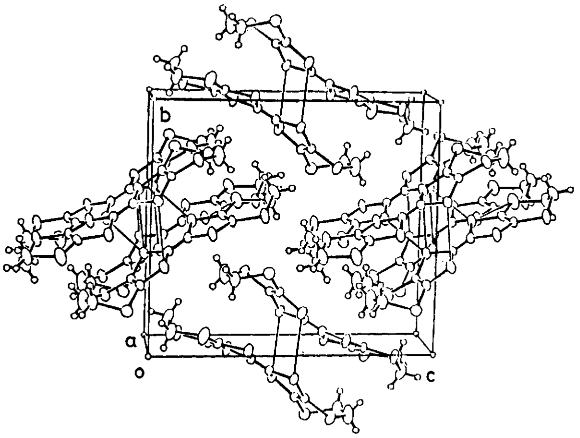


Figure 3. Molecular packing observed in neutral BEDSe-TTF, which is identical to that of neutral BEDT-TTF.

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under contract number W-31-109-ENG-38. B. D. G. is an Undergraduate Research Participant sponsored by the Argonne Division of Educational Programs from Northern Illinois University, DeKalb, Illinois.

Received, 25th July 1988; Com. 8/02998I

References

1 E. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, P. A. Kononovich, M. V. Kartsovnik, A. V. Zvarykina, and L. I. Buravov, *J.E.T.P. Lett.*, 1984, **39**, 12.

2 H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, *Chem. Lett.*, 1988, 55.

3 S. Gartner, E. Gogu, I. Heinen, H. J. Keller, T. Klutz, and D. Schweitzer, *Solid State Commun.*, 1988, **65**, 1531; K. D. Carlson, U. Geiser, A. M. Kini, H. H. Wang, L. K. Montgomery, W. K. Kwok, M. A. Beno, J. M. Williams, C. S. Cariss, G. W. Crabtree, M.-H. Whangbo, and M. Evain, *Inorg. Chem.*, 1988, **27**, 965.

4 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. Whangbo, *Prog. Inorg. Chem.*, 1987, **35**, 51.

5 J. E. Schirber, E. L. Venturini, A. M. Kini, H. H. Wang, J. R. Whitworth, and J. M. Williams, *Physica C*, 1988, **152**, 157.

6 V. Y. Lee, *Synth. Met.*, 1987, **20**, 161.

7 P. J. Nigrey, B. Morosin, and J. F. Kwak, in 'Novel Superconductivity,' eds. S. A. Wolf and V. Z. Kresin, Plenum, New York, 1987, 171; P. J. Nigrey, *J. Org. Chem.*, 1988, **53**, 201.

8 D. C. Green, *J. Org. Chem.*, 1979, **44**, 1476.

9 E. Aharon-Shalom, J. Y. Becker, J. Bernstein, S. Bittner, and S. Shaik, *Tetrahedron Lett.*, 1985, 2783.

10 J. March, 'Advanced Organic Chemistry,' Wiley, New York, 1985, 317.

11 See *e.g.*, T. J. Kistenmacher, T. J. Emge, A. N. Bloch, and D. O. Cowan, *Acta Crystallogr. Sect. B.*, 1982, **38**, 1193; H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, and H. Inokuchi, *Chem. Lett.*, 1984, 183; M. A. Beno, U. Geiser, K. L. Kostka, H. H. Wang, K. S. Webb, M. A. Firestone, K. D. Carlson, L. Nunez, M.-H. Whangbo, and J. M. Williams, *Inorg. Chem.*, 1987, **26**, 1912, and references therein.

12 H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 301.

13 M.-H. Whangbo, J. M. Williams, P. C. W. Leung, M. A. Beno, T. J. Emge, and H. H. Wang, *Inorg. Chem.*, 1985, **24**, 3500.

---

† To a solution of lithium di-isopropylamide (10 mmol), generated from di-isopropylamine and Bu^{n}Li in 50 ml of THF at −78 °C, tetrathiafulvalene (2.5 mmol) was added. After stirring at −78 °C for 90 min, a lemon yellow suspension of tetralithio-TTF (**2**) resulted. Selenium powder (freshly opened sample, 200 mesh, 10 mmol) was then added and the reaction mixture gradually warmed to 0 °C and stirred for 2 h. During this time selenium dissolved and the tetraselenolate (**3**) formed as a pale orange precipitate. THF was removed by vacuum distillation and the orange residue was treated with 40 ml of dry, deoxygenated HMPA and sodium borohydride (10 mmol). The mixture was stirred at room temperature for 1 h and then cooled to 0 °C. A solution of 5 ml of 1,2-dibromoethane in 10 ml of dry, deoxygenated HMPA was then added and the mixture allowed to warm to room temperature and stirred overnight. Resultant pale orange, gelatinous mixture was poured into 500 ml of methanol and the precipitated solid was collected by Buchner filtration. After drying *in vacuo*, 1.20—1.36 g (84—95%) of crude BEDSe-TTF was obtained as an orange solid. This was digested in 1.5 l of boiling chloroform, hot filtered, concentrated to about 300 ml, and chilled overnight to obtain BEDSe-TTF as dark orange crystals (yield 42—57%), m.p. 220—222 °C (decomp.).

‡ *Crystal data*: $C_{10}H_8S_4Se_4$, M = 572.25, monoclinic, space group $P2_1/n$, unit cell at 298 K: a = 6.834(1), b = 14.066(1), c = 16.112(2) Å, β = 94.52(1)°, U = 1544.0(3) Å^3, D_c = 2.462(1) g/cm^3 for Z = 4. Data with $4.0° \leq 2\theta \leq 45.0°$ were collected on a Syntex P2$_1$ diffractometer with monochromatic Mo-K_α radiation (λ = 0.71073 Å) and corrected for Lorentz, polarization, and absorption effects, μ_c = 99.1 cm^{-1}. R (F) = 0.062 for 2580 independent reflections with F_o >0.0. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.