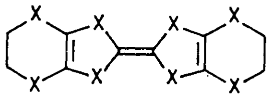
Bis(ethylenediseleno)tetraselenafulvalene (BEDSe-TSeF)

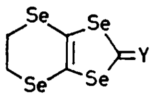
V. Y. Lee, E. M. Engler,* R. R. Schumaker, and S. S. P. Parkin
IBM Research Laboratory, 5600 Cottle Road, San Jose, CA 95193, U.S.A.

The title compound, synthesized from 4,5-ethylenediseleno-1,3-diselenol-2-one (5,6-dihydro-1,3,4,7-tetraselenainden-2-one) *via* trimethyl phosphite coupling, has been characterized and several charge-transfer salts of this new π-donor have been prepared.

Charge-transfer salts of bis(ethylenedithio)tetrathiafulvalene[1] (**1**, X = S: BEDT-TTF) have been thrust to the forefront of organic metals research with the discovery of a novel two-dimensional metallic structure[2] and, recently, superconductiv-



(1)



(2) a; Y = Se
b; Y = O

ity.[3] We report here the first synthesis of the selenium analogue of BEDT-TTF: bis(ethylenediseleno)tetraselenafulvalene (**1**, X = Se: BEDSe-TSeF) [bi(5,6-dihydro-1,3,4,7-tetraselena-inden-2-ylidene)].

While the synthesis of BEDSe-TSeF follows from literature precedents, the actual method for obtaining this new π-donor was not so straightforward. Electrochemical reduction[4] of carbon diselenide did not initially provide the expected 4,5-diselenolate-1,3-diselenole-2-selone intermediate, but mainly triselenocarbonate. We discovered, however, that warming of the reaction to 40 °C, not recognized previously,[4] was necessary to obtain the desired diselenolate intermediate. Addition of excess of 1,2-dibromoethane provided 4,5-ethylene-1,3-diselenole-2-selone [(**2a**); m.p.: 123—125 °C (decomp.); i.r.(KBr, cm^{-1}): 895 (C=Se); ^{1}H n.m.r. (CS$_2$, δ): 3.40; *m/z* M^+: 464)]. Alkali metal reduction (potassium naphthalide in tetrahydrofuran) also afforded the diselenoate intermediate.

Selone coupling using trialkyl phosphite bases has been the standard technique for preparing a wide variety of tetraselenafulvalenes.[5–7] Surprisingly, we were unable to effect coupling using trialkyl phosphites (methyl or ethyl) under heating either neat or in aromatic solvents (benzene, toluene). However, using mercury(II) acetate in acetic acid (**2a**) was converted into the 2-one derivative [(**2b**); m.p.: 109 °C, i.r. (KBr, cm^{-1}): 1680 (C=O); ^{1}H n.m.r. (CS$_2$, δ): 3.48] which could be smoothly coupled with triethyl phosphite in refluxing benzene to give BEDSe-TSeF (**1**, X = Se) as brick-red microcrystals after CS$_2$ extraction [approximate yield from CSe$_2$: 10%; m.p.: 235—240 °C (decomp.); i.r. (KBr, cm^{-1}): 2920w, 1405w, 1260m, and 690m].†

The low solubility of BEDSe-TSeF has hampered our ability to grow single crystals of charge-transfer salts readily with this donor. However, we have had some initial success using electrocrystallization techniques[8] at elevated temperatures (40—45 °C) in tetrahydrofuran. Preliminary results have provided crystals of reasonable quality of BEDSe-TSeF with ReO$_4$ and ClO$_4$ anions as 1 : 1 complexes with room temperature conductivities in the range of 10^{-1}—10^{-2} Ω cm^{-1}

We thank A. Schweiger for help in electrochemical crystal growth. This work was supported in part by the Office of Naval Research.

Received, 21st December 1982; Com. 1465

References

1 M. Mizuno, A. F. Garito, and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1978, 18.

2 G. Saito, T. Enoki, K. Toriumi, and H. Inokuchi, *Solid State Commun.*, 1982, **42**, 557; G. Saito, T. Enoki, and H. Inokuchi, *Chem. Lett.*, 1982, 1345; H. Kobayashi, A. Kobayashi, G. Saito, T. Enoki, and H. Inokuchi, *J. Am. Chem. Soc.*, to be published.

3 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.*, 1983, **50**, 270.

4 E. M. Engler, D. C. Green, and J. Q. Chambers, *J. Chem. Soc., Chem. Commun.*, 1976, 148.

5 M. Narita and C. U. Pittman, Jr., *Synthesis*, 1976, 489.

6 E. M. Engler, B. A. Scott, S. Etemad, T. Penney, and V. V. Patel, *J. Am. Chem. Soc.*, 1977, **99**, 5909.

7 K. Bechgaard, D. O. Cowan, A. N. Bloch, and L. Henriksen, *J. Org. Chem.*, 1975, **40**, 746.

8 E. M. Engler, R. Greene, P. Haen, Y. Tomkiewicz, K. Mortensen, and J. Berendzen, *Mol. Cryst. Liq. Cryst.*, 1982, **79**, 371, and references cited therein.

---

† Satisfactory elemental analysis obtained.