Synthesis, Crystal Structure, and Charge-transfer Salts of Dibenzotetraselenafulvalene (DBTSF)

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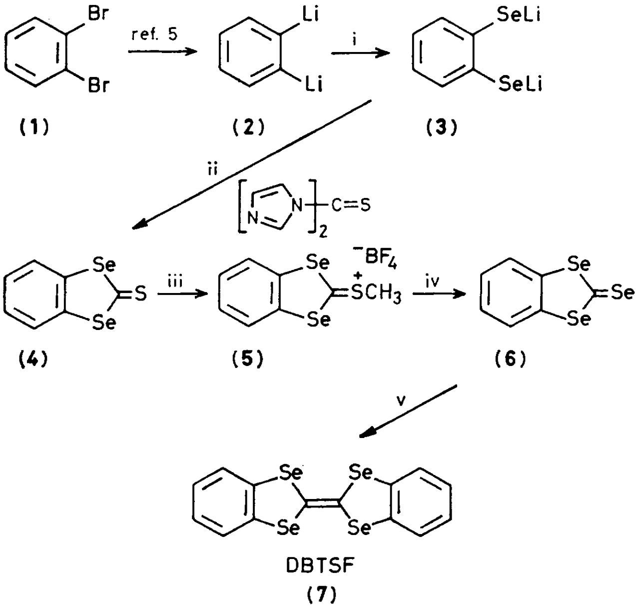
The synthesis and crystal structure of the title compound (DBTSF) and electrical characterization of some of its charge-transfer salts (ranging from insulators to metals) are reported.

Studies of low-dimensional organic salts have benefitted greatly from the availability of several tetrathiafulvalene (TTF) donors, including TTF and its derivatives formed by extending the σ-bond framework (TMTTF and HMTTF) or the π-orbital system (DBTTF).[1]‡ The next logical, but chemically demanding step has been the preparation of a parallel series of tetraselenafulvalenes (TSF). Specifically, the synthesis of selenafulvalene donors has led to considerable insight into the roles of donor and acceptor stacks near phase transition phenomena (TSF–TCNQ and its solid solutions with TTF–TCNQ),[2] the realization of semi-metallic behaviour for a binary, segregated-stack system (HMTSF–TCNQ),[3] and the first organic superconductor $(TMTSF)_2PF_6$ and its analogues.[4]‡ In this report, we describe the synthesis of a new tetraselenafulvalene donor, dibenzotetraselenafulvalene† (**7**), its crystal structure, and a preliminary survey of its charge-transfer salts.

As shown in Scheme 1, compound (**4**) was prepared from 1,2-dilithiobenzene (**2**), derived from 1,2-dibromobenzene (**1**) *via* *o*-phenylenemercury following a known procedure.[5] The reaction time for converting (**1**) into (**2**) was shortened from four days to two days by allowing Li to react with a trace amount of dibromoethane prior to the addition of the mercury compound.

The deep-red solution of (**2**) was filtered under Ar, cooled to −30 °C, and diluted with 3 volumes of tetrahydrofuran (THF). In the following step, elemental Se was added, and the reaction mixture was stirred at −30 °C to −20 °C for *ca.* 2 h. Subsequently, separate solutions of 1.2 equiv. of thiocarbonyl di-imidazole in THF and 1 equiv. of acetic acid in THF were added slowly and simultaneously; during this addition, the temperature was maintained at −40 °C and then was allowed over a 3-h period to reach room temp. The reaction mixture was stirred for *ca.* 20 h, filtered, and evaporated to give a brown crystalline product. Recrystallization from CCl_4 gave (**4**) as bright yellow needles (56% yield based on *o*-phenylenemercury; m.p. 147—148 °C).



Scheme 1. i, Se, Et_2O–THF; ii, $MeCO_2H$; iii, $(MeO)_2CH^+BF_4^-$, CH_2Cl_2; iv, H_2Se; v, Ph_3P, C_6H_6.

Compound (**4**) was quantitatively converted into (**6**) by methylating the thione with an excess of dimethoxycarbenium tetrafluoroborate in CH_2Cl_2 at room temp. for 2 h followed by the addition of 1 vol. of MeOH and an excess of H_2Se at −30 °C. The solution, with stirring (20 h), was allowed to come to room temp. Cooling the reaction mixture in dry ice and filtering yielded (**6**) as red crystals. Recrystallization from CCl_4 gave deep-red needles which melted with decomposition at 175—177 °C.

The coupling of (**6**) to give (**7**) was achieved by suspending (**6**) in a minimal amount of benzene with 1.5 equiv. of triphenylphosphine and stirring the mixture at room temp. for two weeks. Filtration and recrystallization from CCl_4 gave (**7**)§ as red platelets which melted at 288—291 °C [maximal yield *ca.* 65%, based on (**2**)].

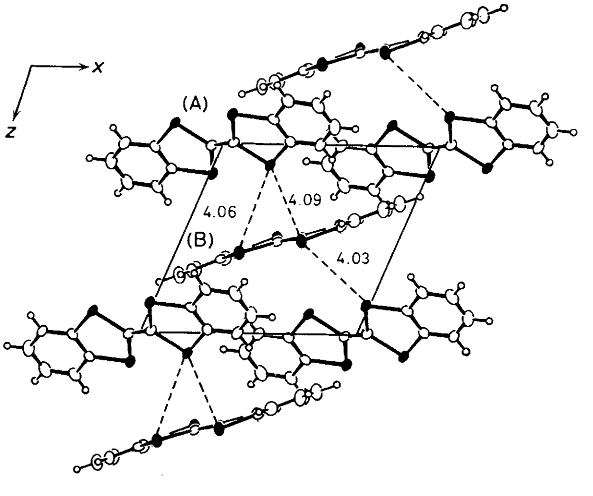


Figure 1. The (010) projection of the crystal structure of DBTSF (**7**). The molecule labelled A is centred at (0,0,0), while molecule B is centred at (1/2,0,1/2). Se atoms are shaded and closest Se · · · Se contacts (A) are indicated.

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‡ TMTTF = tetramethyl-, HMTTF = hexamethylene-, and DBTTF = dibenzo-tetrathiafulvalene. TMTSF = tetramethyl-, HMTSF = hexamethylene-, and DBTSF = dibenzo-tetraselenafulvalene. TCNQ = tetracyanoquinodimethane.

§ I.r. and high-resolution mass spectroscopy were consistent with the formulation (**7**). Peak matching of the parent ion of composition $C_{14}H_8{}^{80}Se_3$, nominal mass 498 μ, resulted in the following M_{calc} = 497.7232; M_{obs} = 497.7243. The parent ion showed an isotope pattern identical with the calculated pattern. Elemental analysis was satisfactory (calc: C, 34.15; H, 1.63; found: C, 34.08; H, 1.66).

Diffraction quality crystals were obtained from CS_2–C_6H_{12}. *Crystal data:* triclinic, space group $P\bar{1}$, a = 9.590(3), b = 9.847(3), c = 8.967(3) Å, α = 115.61(2), β = 113.10(3), γ = 74.07(3)°, U = 696.7 Å^3; two independent molecules per cell, each required to possess C_i symmetry. Conventional refinement has led to an R value of 0.075 based on 3598 X-ray diffraction data.¶ The molecular geometry of DBTSF is very similar to that of its S-containing homologue DBTTF,[6] with the expected expansion in molecular size owing to the increase in the average of the Se–C bond lengths (1.894 Å) relative to the average S–C bond length (1.753 Å) in DBTTF. However, the DBTSF donor is significantly more chair shaped (average dihedral angle between the tetraselenaethylene plane and the diselenabenzene ring is *ca.* 10°) than the DBTTF donor (in which the corresponding dihedral angle is *ca.* 4°). In further contrast with DBTTF,[6] intermolecular stacking is not a dominant feature of the crystal structure of DBTSF (see Figure 1); rather, Se · · · Se intermolecular contacts near the van der Waals separation (4.0 Å) dominate. In this sense the structural motif of DBTSF is more reminiscent of that of the closely related tetraselenafulvalene, TMTSF.[7]

Electrochemical growth of several salts of DBTSF (7) with various inorganic and organic acceptors (Table 1) has also been accomplished. The $(DBTSF)_nX$ salts ($X = ClO_4^-$, PF_6^-, or AsF_6^-) have room-temperature conductivities that are somewhat smaller than the $(TMTSF)_2X$ salts (Table 1), which are superconductors at very low temperatures (*ca.* 1—2 K).[4] The binary organic salts DBTSF–TCNQ and DBTSF–2,5-$TCNQF_2$ are probably mixed-stack compounds, based on their low conductivity, low fractional charge transfer,[8] and general similarity to their DBTTF congeners.[6] In contrast, DBTSF–2,5-$TCNQCl_2$ is a good electrical conductor and is probably a fractionally-charged, two-chain organic metal as is DBTTF–2,5-$TCNQCl_2$.[9] Finally, DBTSF–$TCNQF_4$ is a unit-charged Mott insulator with structural, electrical, and magnetic properties comparable to HMTSF–$TCNQF_4$.[10]

Table 1. Conductivity and charge-transfer data.

Compound	Conductivity/Ω^{-1} cm^{-1} (295 K) Compaction pellet	Conductivity/Ω^{-1} cm^{-1} (295 K) Single crystal	Z[a]
$(TMTSF)_2ClO_4$	4.4	600	0.5[c]
$(DBTSF)_nX$[b]	1×10^{-2}	1	0.5
DBTSF–TCNQ	1.7×10^{-10}	2.3×10^{-6}	0.33[d]
DBTSF–2,5-$TCNQF_2$	1.8×10^{-7}	—	0.40[d]
DBTSF–2,5-$TCNQCl_2$	2.0×10^{-1}	20	0.86[d]
DBTSF–$TCNQF_4$	7.0×10^{-6}	7.9×10^{-4}	1.00[d]

[a] Z = fractional charge per cation. [b] $X = ClO_4^-$, PF_6^-, or AsF_6^-; the composition and conductivity of the DBTSF salts vary slightly depending upon the solvent in which they are prepared. When the salts are grown in chlorobenzene, elemental analysis indicates that a small amount of chlorobenzene is incorporated in that salt, and n is *ca.* 2. [c] From ref. 4. [d] Evaluated from the CN stretch frequency (see ref. 8).

We gratefully acknowledge support of the Solid State Chemistry Program, Division of Materials Research, of the National Science Foundation. M. L. thanks the Exxon Education Foundation for a fellowship.

Received, 12th November 1982; Com. 1295

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¶ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.