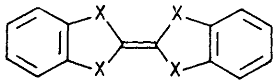
Dibenzotetraselenafulvalene (DBTSF). Synthesis and Conducting Salts

Ib Johannsen,*[a] Klaus Bechgaard,[a] Kell Mortensen,[b] and Claus Jacobsen[b]

[a] *Department of General and Organic Chemistry, H. C. Ørsted Inst., DK-2100 Copenhagen, Denmark*
[b] *Physics Laboratory III, Technical University of Denmark, DK-2800 Lyngby, Denmark*

Dibenzotetraselenafulvalene has been synthesized from 1,2,3-benzoselenadiazole; charge-transfer salts based on the product show semiconducting properties.

The discovery of a superconducting ground state in cation-radical salts of tetramethyltetraselenafulvalene (TMTSF)[1] has increased the interest in the search for new donors of the fulvalene type. In this context we have been interested in the effects of extending the π-orbital system in fulvalene type donors. In the case of tetrathiafulvalene the π-orbital exten-

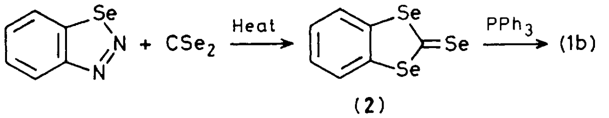


(1)

a; X = S

b; X = Se

Scheme 1



sion going to dibenzotetrathiafulvalene, DBTTF (**1a**), results in a substantial increase in the electrochemical oxidation potential (0.47 to 0.72 V).† Recently the synthesis of dibenzotetratellurafulvalene has been reported.[2]

We report a two step synthesis of dibenzotetraselenafulvalene DBTSF [bi(benzo-1,3-diselenol-2-ylidene)], and the formation of some charge-transfer salts with it. A similar method has been reported earlier for the synthesis of another tetraselenafulvalene.[3]

1,2,3-Benzoselenadiazole[4] (0.06 M in xylene) was thermolysed in the presence of a twofold excess of carbon diselenide,[5] (reflux, $1\frac{1}{2}$ h), yielding the red benzo-1,3-diselena-2-selone (**2**) (69%), decomp. above 183 °C. Coupling of (**2**) (0.04 M in toluene) with 130% excess of triphenylphosphine (reflux, 2 h), treatment with sulphur to convert unchanged triphenylphosphine, and chromatography (silica, toluene) gave the orange-red DBTSF (**1b**)‡ in 66% yield (Scheme 1).

The substituted analogue, 4,4′,5,5′-tetramethyldibenzotetraselenafulvalene (TMDBTSF), was synthesized using a similar procedure giving slightly lower yields. The dimethylselone melts at 155—160 °C and TMDBTSF melts above 350 °C. The photoelectron ionisation potential of DBTSF is 6.90 eV. For DBTTF a value of 6.64 eV[6] is obtained and no major differences in orbital sequence are observed.

Table 1. Room temperature conductivities and low temperature activation energies.

Compound	σ (300 K)/Ω^{-1} cm^{-1}	E_A/eV
DBTSF$(TaF_6)_{0.61}$	20	0.075
DBTSF$(AsF_6)_{0.67}$	3	0.24
DBTSF$(SbF_6)_{0.72}$	0.5	0.080

DBTSF forms a 1 : 1 charge-transfer complex with tetrafluoro-7,7,8,8-tetracyanoquinodimethane. It has a rather low room temperature conductivity, $3 \times 10^{-4}\,\Omega^{-1}\,cm^{-1}$, indicating the formation of a mixed-stack compound or a Mott-insulator.

Better conductivities are obtained in single-stack systems with inorganic counterions. Black needle-like crystals of DBTSF$(TaF_6)_{0.61}$, DBTSF$(AsF_6)_{0.67}$, and DBTSF$(SbF_6)_{0.72}$ were formed by electrocrystallisation (constant current, 4 μA) from 1,1,2-trichloroethane solutions of DBTSF (2 mM) containing the appropriate n-butylammonium salts (25 mM) as electrolytes. Four-probe conductivity data on single crystals show semiconductor-type temperature dependence. Room temperature conductivities and low temperature activation energies are given in Table 1. The conductivities obtained are of the same magnitude as those of the corresponding sulphur analogues, for example DBTTF$(BF_4)_{0.8}$.[7]

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† Measured under the same conditions as mentioned for DBTSF.

‡ M.p. 291—293 °C (corr.); elemental analysis, found C 34.26, H 1.76%, calc. C 34.17, H 1.64%; i.r. (KBr) ν_{max} 3400w, 1440m, 1430w, 1250w, 1100m, 750s, and 690w cm^{-1}; u.v.-vis. (MeCN–tetrahydrofuran) λ_{max} 221 (log ϵ 4.45), 286(4.21), 320sh(3.70), and 470(2.20) nm; ^{1}H n.m.r. ($CDCl_3$, Me_4Si) δ 7.1—7.4(m); $E_{\frac{1}{2}}$ (1) = 0.78 V (*vs.* sat. calomel electrode at Pt-button electrode, CH_2Cl_2, 0.1 M $Bu^n_4N^+$ BF_4^-).

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