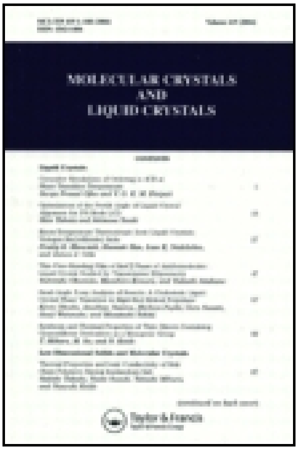

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Synthesis of A New Series of Tetrachalcogen Fulvalenes and Their Charge Transfer Cohpiexes

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SYNTHESIS OF A NEW SERIES OF TETRACHALCOGEN FULVALENES AND THEIR CHARGE TRANSFER COMPLEXES

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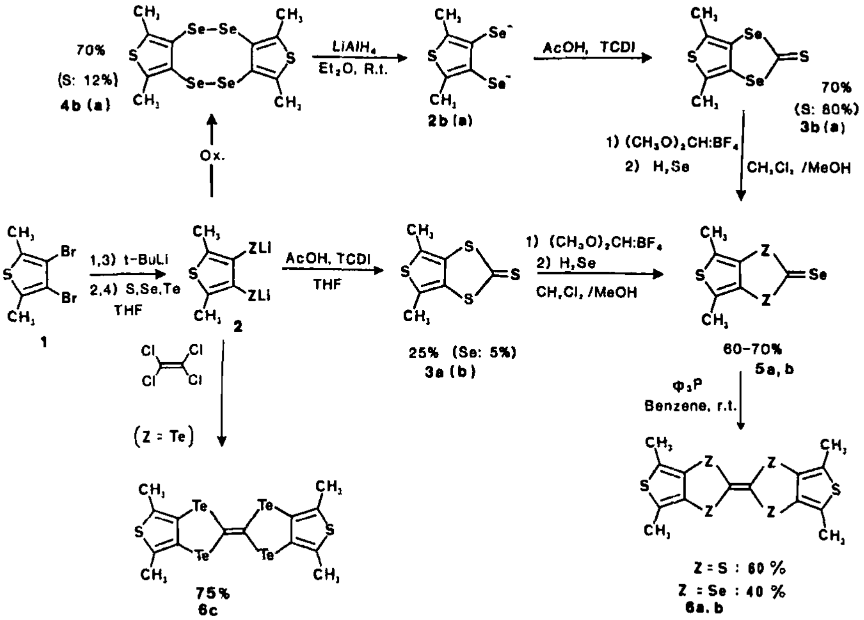
Abstract *The synthesis of a new series of fulvalene-type π-donors and their charge-transfer complexes are described together with the crystal structure of the tetratellurafulvalene derivative.*

In our systematic investigation of new π-donors based on the fulvalene molecule, we have succeeded in the synthesis of a new series of tetrachalcogen fulvalenes.[1] The synthesis is outlined in Scheme 1 and the preparation includes the following new compounds: 4,6-dimethylthieno[4,5-d]-1,3-dithiole-2-thione (3a, mp 110-111°C) and -2-selone (5a, mp 134-135°C), 4,6-dimethylthieno[4,5-d]-1,3-diselenole-2-thione (3b, mp 125-126°C), and -2-selone (5b, mp 154-155°C), 1,3,6,8-tetramethyl[1,2,5,6]-tetrathiocino[3,4-c:7,8-c′]dithiophene (4a, mp 274°C decomp.), and the corresponding tetraselenocin (4b, mp 272°C) $\Delta^{2,2'}$bi-4,6-dimethylthieno[3,4-d]-1,3-dithiole (BDMT-TTF) (6a, mp 295-297°C) together with the -1,3-diselenole (6b, mp 313-315°C) and -1,3-ditellurole (6c, mp 295-298°C decomp.) analogs (BDMT-TSF and BDMT-TTeF).

The common precursor 3,4-dibromo-2,5-dimethylthiophene (1) was converted to the dichalcogen dianion (2) in a four-step reaction using t-butyllithium for the halogen-lithium exchange followed by the addition of the appropriate element. The tellurium dianion (2c) was reacted with tetrachloroethylene to give BDMT-TTeF (6c) directly, whereas the sulfur and selenium analogs (2a and 2b) were reacted with thiocarbonyldiimidazole (TCDI) to give 3a and 3b. As indicated in the scheme a higher yield of 3b was obtained by first oxidizing 2 to 4b which was then easily purified and subsequently reduced to 2b. Alkylation of 3 and reaction with hydrogen selenide gave the corresponding selones 5a and 5b which by treatment with triphenylphosphine for several days gave 6a and 6b.



SCHEME 1 The synthesis of BDMT-TXF.

The solid-state molecular structure of BDMT-TTeF was determined by single crystal X-ray diffraction methods and is illustrated in Figure 1. It is particularly interesting to compare the molecular geometry of BDMT-TTeF with that of HMTTeF,[2] the only other tetratellurafulvalene for which the solid-state molecular structure is known. The most dramatic difference lies in the adopted molecular conformation. Clearly shown in Figure 1, BDMT-TTeF exhibits a very asymmetric boat conformation, with dihedral angles of 16.0° and 47.1° between the plane defined by the four Te atoms and the dimethylthieno-3,4-ditellural moieties. In contrast, HMTTeF displays a symmetric chair conformation,[2] with analogous dihedral angles of only 7.7° and -8.2°. Despite the outwardly dissimilar conformations, the interesting finding is that the mean Te-C (2.106Å) and central double bond (1.331Å) lengths and the mean C-Te-C (89.2°) and Te-C-

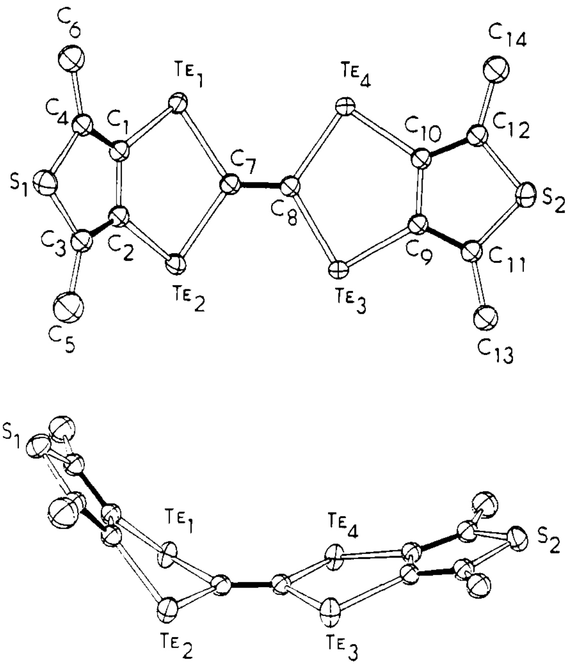


FIGURE 1 Two views of the solid-state molecular structure of BDMT-TTeF.

Te (113.0°) bond angles in BDMT-TTeF are quite similar to those reported[2] for HMTTeF (2.100Å, 1.356Å, 90.4°, and 114.4°, respectively.

A number of charge transfer complexes have been made from 6a, b and c with TCNQ, $TCNQF_4$, PF_6^- and AsF_6^-. The complexes are all semiconductors with rather low room temperature conductivities ($10^{-3}\ \Omega^{-1}\ cm^{-1} - 10^{-10}\ \Omega^{-1}\ cm^{-1}$) due to either full charge transfer ($TCNQF_4$ complexes) or to the formation of mixed stacks (TCNQ complexes). Electrochemically grown salts with PF_6^- or AsF_6^- as counterions showed similar low room temperature conductivities. Only the BDMT-TTeF-AsF_6 salt showed a significantly higher conductivity (~ 50 $\Omega^{-1}\ cm^{-1}$) than the rest of the complexes prepared so far, but this recent result is based on a single four-probe measurement and further studies are planned.

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