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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 THE IR CHARGE TRANSFER COMPLEXES

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Abstract The synthesis of a new series of fulvalene-type m-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 diamion (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 16.00 and 47.10 between the plane defined by the dimethylthieno-3,4-ditellural the four Te atoms and In contrast, moieties. HMTTeF displays a symmetric chair conformation, with analogous dihedral angles of only 7.70 and Despite the outwardly dissimilar conformations, the interesting finding is that the mean Te-C (2.106Å) and central double bond (1.331A) lengths and the mean C-Te-C (89.20) and Te-C-

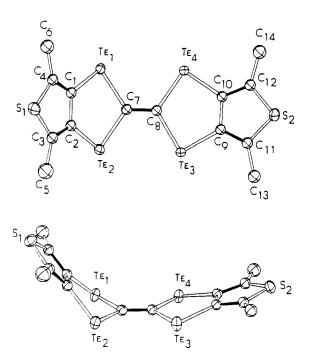


FIGURE 1 Two views of the solid-state molecular structure of BDMT-TTeF.

Te (113.0°) bond angles in BDMT-TTeF are quite similar to those reported² for HMTTeF $(2.100\text{\AA}, 1.356\text{\AA}, 90.4^{\circ}, \text{ and } 114.4^{\circ}, \text{ respectively.}$

A number of charge transfer complexes have been made from 6a, b and c with TCNQ, TCNQF4, PF6 and AsF6. The complexes are all rather semiconductors with low room temperature conductivities $(10^{-3} \Omega^{-1} \text{ cm}^{-1} - 10^{-10} \Omega^{-1} \text{ cm}^{-1})$ due to either full charge transfer (TCNQF $_{\perp}$ complexes) or to the formation of mixed stacks (TCNQ complexes). Electrochemically grown salts with PF6or AsF₆ as counterions showed similar low room temperature conductivities. Only the BDMT-TTeF-AsF₆ salt showed a significantly higher conductivity (~ 50 Ω^{-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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REFERENCES

- K. Lerstrup and D. Cowan, <u>J. Phys. (Paris)</u>, <u>44</u>, C3-1247 (1983).
- P. Carrol, M. Lakshmikantham, M. Cava, F. Wudl, E. Aharon-Shalom and S. Cox, <u>J. Chem. Soc., Chem. Comm.</u> 1316 (1982).