

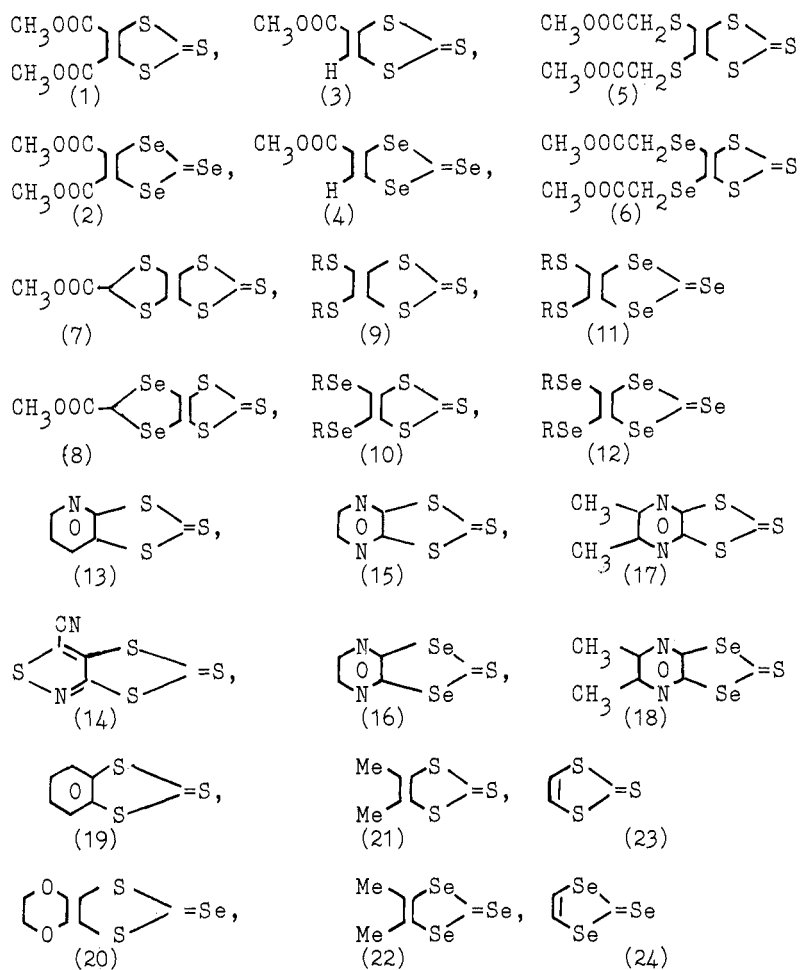
## New tetraheterafulvalenes, metal 1,2-diheterolenes and some of their products

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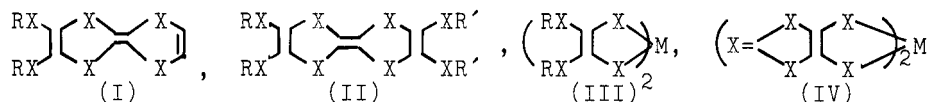
**Abstract** - A number of tetraheterafulvalenes and metal 1,2-diheterolenes prepared were converted to their charge transfer complexes, cation radical salts and cation deficient metal 1,2-diheterolenes by chemical or electrochemical procedures. Some of these compounds were found to be conducting solids.

Using the compounds (1)-(24) as starting materials, a number of tetraheterafulvalenes of the types (I) and (II) and metal 1,2-diheterolenes of the types (III) and (IV) have been prepared by methods similar to those reported in



(a):R=CH<sub>3</sub>, (b):2R=CH<sub>2</sub>, (c):2R=CH<sub>2</sub>CH<sub>2</sub>, (d):2R=CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>  
 (e):2R=CH(CH<sub>3</sub>)CH<sub>2</sub>, (f):2R=CH(CH<sub>3</sub>)CH(CH<sub>3</sub>), (g):2R=CH=CH

ref.1 (and refs. cited therein). From these compounds a number of charge transfer complexes, cation radical salts and cation deficient metal 1,2-diheterolenes have been prepared by chemical or electrochemical procedures (ref.1). Some of them were found to be conducting solids. Recently, a number of new oxygen-containing compounds have been prepared and studied. Pyrazino-ethylenedioxo-



-diselenadithiafulvalene (PEDODSDTF), (mp=202°C) for example, has been prepared (ref.2) by cross-coupling reaction of 4,5-ethylenedioxo-1,3-dithiole-2-one [(20) with O instead of Se, to avoid possible rearrangements of S and Se] (see



refs.2,3) and pyrazino-1,3-diselenole-3-one [(16) with O instead of Se] (ref.4) via triethyl phosphite. Fig.1 shows the UV-visible spectrum of PEDODSDTF and the spectra of bis(ethylenedioxo)tetrathiafulvalene (BEDO-TTF) and bis(pyrazino)tetraselenafulvalene (BPTSF), for comparison. Also, ethylenedioxo-tetrathiafulvalene (EDOTTF) (mp=92°C) has been prepared from 4,5-ethylenedioxo-1,3-dithiole-2-one and 4,5-bis(methylcarboxy)-1,3-dithiole-2-thione by a two steps sequence (:coupling via triethylphosphite and decarboxylation with LiBr in hexamethylphosphoramide) (ref.2). It has been found that PEDODSDTF and EDOTTF are  $\pi$ -donors and give with TCNQ,  $\text{Bu}_4\text{NI}_3$  and  $\text{Bu}_4\text{NIBr}_2$ , for example, black

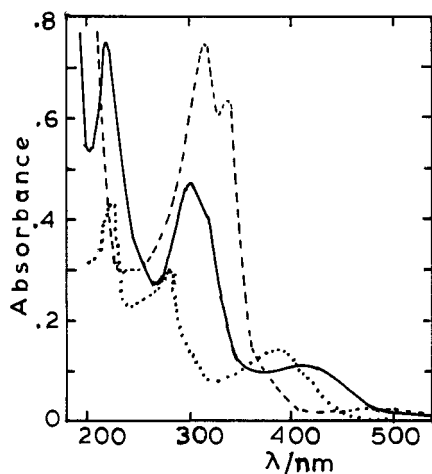


Fig. 1. UV-visible spectra of PEDODSDTF (—), BEDO-TTF(---) and BPTSF(....) in  $\text{CH}_3\text{CN}$ .

conducting needles or plates. Similar results have been obtained from a number of oxygen-,sulfur- or selenium-containing tetraheterafulvalenes. However, details on the preparation and physical properties of these solid products will be published elsewhere (refs.5,6).

## REFERENCES

- G.C.Papavassiliou "Design and Synthesis of polyheterotetraheterafulvalenes, Metal 1,2-diheterolenes and their low-Dim. cond. and supercond. salts" in "Proc. of NATO-ASI, on Lower-Dim.Systems and Mol.Electronics"Spetses Island, Greece, 12-23 June, 1989, Ed.R.M.Metzger, Plenum, in press.
- G.C.Papavassiliou,D.Lagouvardos,V.Kakoussis,G.Mousdis,to be published.
- T.Suzuki, H.Yamochi,G.Srdanov,K.Hinkelmann and F.Wudl,*J.Am.Chem.Soc.* **111**, 3109 (1989).
- G.C.Papavassiliou,S.Y.Yiannopoulos,J.S.Zambounis,K.Kobayashi,and K.Umemoto, *Chem.Lett.*, 1279(1987).
- G.C.Papavassiliou, A.Terzis, B.Hilti, and C.W.Mayer "Cond.and Supercond.Solids Based on MDTTF, EDTTF etc". in "Proc. of 1st ISSP Int.Symp.Phys.Chem. of Org.Supercond.", Tokyo, Japan, 27-30-August, 1989, Ed.G.Saito, Springer-Verlag, to be published.
- G.C.Papavassiliou et al,*Mol.Cryst.Liq.Cryst.*, to be published.