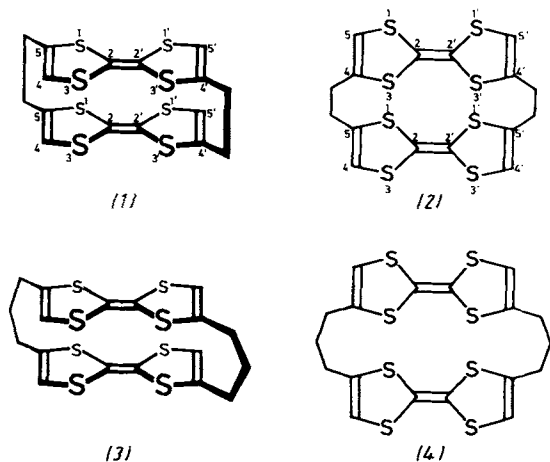


[2.2]- and [3.3]Tetrathiafulvalenophanes^[1]

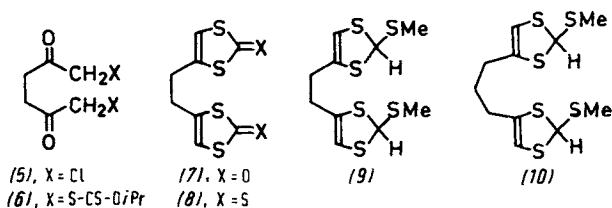
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In order to systematically vary the crystal lattice in charge transfer systems which could be of interest as electrical semiconductors or conductors by changing the molecular architecture^[1], we synthesized [2.2]- and [3.3]tetrathiafulvalenophanes ("TTF-phanes"). For these compounds the following structural and stereo-isomers are possible: 1) "paracyclophane-like" compounds with diagonal 4',4'- and 5,5-linkage, which may exist as an achiral stereoisomer with approximately parallel TTF "axes" and all corresponding C- and S-atoms of the two TTF groups [(1) and (3), respectively] in the eclipsed position as well as a chiral stereoisomer with crossed TTF axes which formally is derived from (1) and (3), respectively, by 180° rotation of one of the TTF units about the axis through the C-4'/C-5 points of linkage; 2) "metacyclophane-like" compounds with 4,5- and 4',5'-linkage [(2) and (4), respectively], whose TTF groups, as in the metacyclophanes, could be in a step-like *anti*-conformation and—less likely—in a *syn*-arrangement; 3) finally, TTF-phanes in which one TTF group is linked metacyclophane-like, the other paracyclophane-like (4,5-/4',4'-linkage). In the synthetic method employed by us, in which the central C—C double bonds of the TTF groups were formed in the last step^[1], in principle, all the structural and stereo-isomers could be formed. Although only a few of them have so far been isolated in pure form and unequivocally characterized, we should like to report some preliminary results even at this stage since representatives of this type of compounds in combination with tetracyanoquinodimethane (TCNQ) show interesting properties.

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For the synthesis of the [2.2]tetrathiafulvalenophanes (1)/(2), 1,6-bisdiazo-2,5-hexanedione was converted, in analogy to the method given in [2], into 1,6-dichloro-2,5-hexanedione (5)^[3] (m.p. 87–88 °C; 23%), which on reaction with potassium *O*-isopropylthiocarbonate (acetone, 20 °C, 3 h) gave the bis(*O*-isopropylthiocarbonate) (6)^[3] (m.p. 82–83 °C; 84%). Cyclization of (6) with conc. sulfuric acid afforded 4,4'-ethylenedi(1,3-dithiol-2-one) (7)^[3] (m.p. 135–136 °C; 87%). On boiling with phosphorus(v) sulfide (xylene, 6 h, 140 °C), (7) was converted into the bis(thione) (8)^[3] (m.p. 172–174 °C; 80%). (8) was methylated with methyl iodide



(nitromethane, 2.5 h, 50 °C) and the crude product was reduced with sodium tetrahydridoborate (tetrahydrofuran/methanol, –78 °C; overall yield 27–40%) to the bis(methylthio) derivative (9)^[3]. Analogously to the synthesis of tetrathiafulvalenoparacyclophane, the bis(thiolium ion) was then prepared from (9) by reaction with tetrafluoroboric acid in acetic anhydride. On dropwise addition of its solution in acetonitrile to a solution of triethylamine in acetonitrile under argon the bis(thiolium ion) underwent dimerization and cyclization to [2.2]tetrathiafulvalenophane.

After removal of oligomeric and polymeric reaction products, fractional crystallization from carbon disulfide afforded (2)^[3] as yellow, cubic crystals (dec. >210 °C) in 10–15% yield. Besides (2), an isomer [presumably (1)] could also be enriched, but not completely purified. The mass spectra essentially agree with those of (2)^[4].

The structure of (2) is confirmed by X-ray structure analysis^[4]. The molecule has the step-like *anti*-conformation. As in the case of [3]tetrathiafulvaleno[3]paracyclophane^[1] the TTF units deviate considerably from a planar arrangement: The S(1)–C(5)–C(4)–S(3) planes in all five-membered rings of (2) are bent at an angle of 20° to the planes through the four sulfur atoms and central double bond of the two TTF units.

The [3.3]tetrathiafulvalenophanes (3)/(4) were synthesized analogously to (1)/(2) via the homologs of (5)^[2], (6)^[3] (m.p. 98–100 °C; 74%), (7)^[3] (63–64 °C; 93%) and (8)^[3] (m.p. 101–102 °C; 52%). Methylation of the bis(dithiolthione) analogous to (8) with methyl iodide in nitromethane and

subsequent reduction of the almost quantitatively formed methylation product with sodium tetrahydridoborate (tetrahydrofuran/methanol, –78 °C) afforded 4,4'-trimethylene-di(2-methylthio-1,3-dithiol) (10)^[3] (yellow oil; 77%). Like (9), (10) can undergo dimerizing cyclization. Oligomers and polymers can be removed by extraction with carbon disulfide. After evaporating *in vacuo* (9% yield) the extract consisted essentially of one isomer^[6], which, however, has not yet been obtained free from isomers.

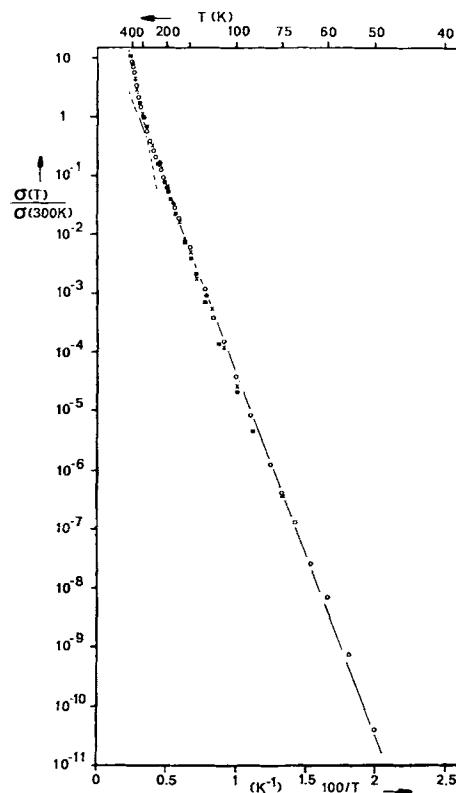


Fig. 1. Conductivities $\sigma(T)/\sigma(300 \text{ K})$ of four single crystals of the 1:4 complex of [3.3]tetrathiafulvalenophane and TCNQ as a function of temperature. $\sigma(300 \text{ K})$ of the four single crystals: $\bullet 5 \times 10^{-3}$, $\circ 5.3 \times 10^{-3}$, $\times 6 \times 10^{-3}$, $\triangle 7.5 \times 10^{-3} [\Omega \text{ cm}]^{-1}$.

Treatment of the [3.3]tetrathiafulvalenophane obtained with tetracyanoquinodimethane (TCNQ) in carbon disulfide/acetonitrile (room temperature, under argon, exclusion of light) afforded black-needles of a complex, which, according to elemental analysis, has the composition [3.3]tetrathiafulvalenophane/TCNQ = 1:4. The following crystallographic data were determined on a single crystal (0.4 × 0.1 × 0.08 mm) of this complex^[5]: triclinic, space group $P\bar{1}$, $a = 780$, $b = 1393$, $c = 2873 \text{ pm}$, $\alpha = 92.9^\circ$, $\beta = 88.9^\circ$ and $\gamma = 91.9^\circ$; $\rho_{\text{calc}} = 1.39 \text{ g} \cdot \text{cm}^{-3}$; a structure elucidation has not yet been completed. Conductivity measurements (4-contact measurements) on single crystals of this complex showed conductivities between 5×10^{-3} and $10^{-2} [\Omega \text{ cm}]^{-1}$ along the long axis of the needles at 300 K. Figure 1 shows for four different single crystals the excellent reproducibility of the conductivities measured and their temperature-dependence. Between 40 and 400 K, σ varies by more than ten orders of magnitude. Pellets of the complex (diameter 2.5 mm, thickness 0.5–1.0 mm) show a conductivity very similar to that of the single crystals at room temperature, with $\sigma = 6 \times 10^{-3} [\Omega \text{ cm}]^{-1}$.

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- [1] Electron Donor-Acceptor Compounds, Part 26.—Part 25: *H. A. Staab, J. Ippen, T. Chu, C. Krieger, B. Starker*, *Angew. Chem.* 92, 49 (1980); *Angew. Chem. Int. Ed. Engl.* 19, 66 (1980).
- [2] *E. Fahr*, *Justus Liebigs Ann. Chem.* 638, 1 (1960).
- [3] These compounds gave correct elemental analyses and characteristic spectra.
- [4] M^+ calc. 459.8705, obs. 459.8708; MS: $m/e = 462$ (35, $(M+2)^+$), 460 (100, M^+), 230 (20, M^{2+}); cf. (2): 462 (36, $(M+2)^+$), 460 (100, M^+), 230 (19, M^{2+}). (2), space group $P2_1/c$, $a = 1001.3(2)$, $b = 973.1(2)$, $c = 1118.5(2)$ pm, $\beta = 121.00(3)$, $Z = 2$, 1383 observed reflections, $R = 0.043$ [5].
- [5] *C. Krieger*, unpublished results.
- [6] $m/e = 490$ (36, $(M+2)^+$), 488 (100, M^+), 244 (16, M^{2+}); $^1\text{H-NMR}$ (80 MHz, $\text{CD}_2\text{Cl}_2/\text{CS}_2$): $\delta = 5.88$ (s, 4H), 2.25—2.80 (m, 12H).