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1,4,5,8-Tetrachalcogeno-2,3,6,7-tetramethylnaphthalenes as New Electron Donors

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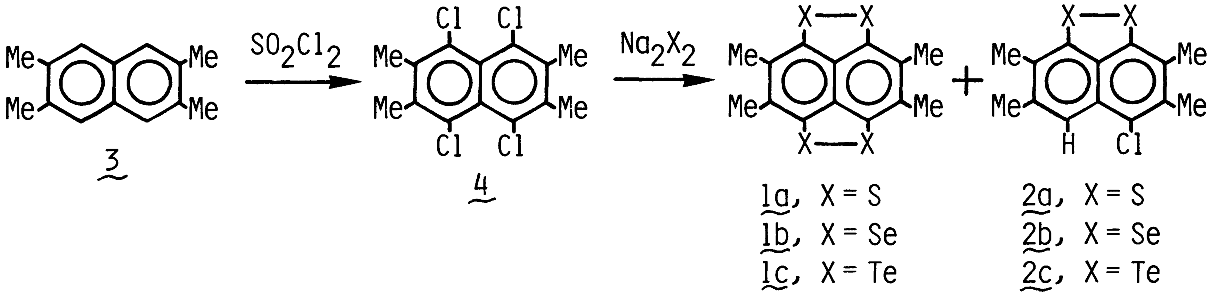
The title compounds have been prepared with a view of developing new electron donors for low-dimensional molecular complexes. They have increasing donor character in order of the chalcogen triad, i.e., S, Se, Te, and all form semi-conductive complexes with TCNQ.

Polycyclic aromatic compounds bearing peri-dichalcogen bridges, as represented by tetrathiotetracene, have been known to be good electron donors for the formation of low-dimensional molecular complexes.1) Wudl et al. reported that even 1,4,5,8-tetrathionaphthalene (TTN) as the simplest example of the doubly bridged compounds could form a conductive complex with tetracyanoquinodimethane (TCNQ).2) Substitution of heavy chalcogen for sulfur in such compounds offers advanced donors with increasing molecular polarizability and accordingly with intermolecular contact. Yamahira3) and Stark4) recently synthesized the selenium analog of TTN, which was, however, too insoluble in usual solvents to study its complexation. The tellurium analog is more interesting, but still remains unknown probably because of its extremely poor solubility. Introduction of alkyl groups at the 2,3,6,7-positions of these compounds might not only improve their solubilities but also enhance their donor character. We now like to report the syntheses of 1,4,5,8-tetrachalcogeno-2,3,6,7-tetramethylnaphthalenes **1a-c** involving all the elements of chalcogen triad.



2,3,6,7-Tetramethylnaphthalene **3** was prepared in several steps from 2,3-dimethysuccinic anhydride and o-xylene according to the method reported by Dozen and Hatta.5) It was then treated with sulfuryl chloride in the presence of a catalytic amount of ferric chloride in benzene at 60 °C, giving 1,4,5,8-tetrachloro-2,3,6,7-tetramethylnaphthalene **4** in 69% yield. Reaction of **4** with sodium disulfide, in situ prepared from an equimolar mixture of sodium and sulfur, in hexamethylphosphoric triamide at 120 °C under nitrogen gave a mixture of the desired tetrathio compound **1a** and dithio compound **2a**. After both products were separated by gradient sublimation in vacuo, 1a was obtained in 19.1% yield as brown needles with mp > 300 °C by recrystallization from benzene, and 2a in 21.1% yield as orange needles with mp 199-200.5 °C by recrystallization from hexane.[6)]

Similar reactions were also applicable to the syntheses of the selenium and tellurium analogs. However, the yields of 1b and 1c decreased and those of 2b and 2c reversely increased in the order owing to an increase in the reducing power of sodium dichalcogenides; 1b: yield 11.6%, black plates from benzene, mp >300 °C; 1c: yield 5.6%, black needles from chlorobenzene, mp >300 °C; 2b: yield 25.9%, purple scales from hexane, mp 184 °C (dec); 2c: yield 34.5%, green plates from benzene-hexane, mp 223 °C (dec).

The electronic spectra of compounds 1a-c showed two strong absorptions in the regions of 260 nm and 410 nm and additional weak, broad, and solvent-dependent absorptions at further longer wavelengths, causing deep coloration, λmax nm (log ε) in chloroform; 1a: 261(4.41), 408(4.19), 500(sh, 2.35), 700(1.75); 1b: 267(4.30), 416(4.23), 528(2.72), 855(2.22); 1c: 281(4.07), 445(4.22), 647(2.88), 1028(2.17). The former and the latter are assigned to π-π^* and π-σ^* transitions, respectively.[7)] The bathochromic shifts of both absorptions in order of chalcogen triad indicate that the energy level of the highest occupied molecular orbital is elevated by an enhanced electronic interaction between the naphthalene and the polarizable heavy chalcogen element.

The cyclic voltammograms of compounds 1a-c exhibited two reversible oxidation waves, whose half-wave potentials $E_{1/2}$ were as follows; 1a: +0.475, +0.953 V; 1b: +0.458, +0.902 V; 1c: +0.307, +0.717 V vs. Ag/AgCl in benzonitrile. The donor character is evidently strengthened by introduction of the heavy chalcogen, as described in the above electronic spectrum. It is worth noting that the oxidation potentials of tellurium compound 1c are quite same as those ($E_{1/2}$ +0.310, +0.710 V) of tetrathiafulvalene which forms a metallic complex with TCNQ.

All compounds 1a-c formed black charge-transfer complexes with TCNQ. However, their electrical conductivities, measured on compressed pellets with a two-probe method, were ca. 10^{-3} S/ cm and independent of the kind of chalcogen element; 1a·TCNQ: 5.8×10^{-3} S/cm; 1b·TCNQ: 2.4×10^{-3} S/cm; 1c·TCNQ: 3.5×10^{-3} S/cm. Further study of the other charge-transfer complexes or salts is now under way.

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