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3,4-DICHALCOGEN-BRIDGED FLUORANTHENES AS NEW ELECTRON DONORS

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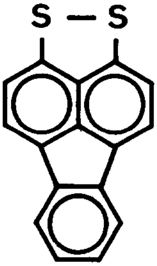
Abstract: Three 3,4-dichalcogen-bridged fluoranthenes were prepared with a view of developing new electron donors. Their donor strength was observed to increase in order of the chalcogen triad, i.e., sulfur, selenium, and tellurium.

Polycyclic aromatic compounds bearing peri-dichalcogen bridges, represented by tetrathiotetracene, have been known to be good electron donors for the formation of low-dimensional molecular complexes.$^{1)}$ Meinwald et al. reported that even simple 1,8-dichalcogen-bridged naphthalene, when the chalcogen was replaced by heavy element such as tellurium, could form a conducting charge-transfer complex with 7,7,8,8-tetracyanoquinodimethane (TCNQ).$^{2)}$ For the purpose of discovering a new effective donor, therefore, it is very promising to search potential arenes with heavy-chalcogen bridging. Fluoranthene might give rise to one of such interesting arenes because fluoranthene itself forms highly conducting radical cation salts.$^{3)}$ An electronic interaction between fluoranthene and its peri-substituted chalcogen is expected to lower its ionization potential and accordingly enhance its donor character. We now report the syntheses and some properties of fluorantheno[3,4-cd]-1,2-dithiole **1**, -diselenole **2**, and -ditellurole **3**.



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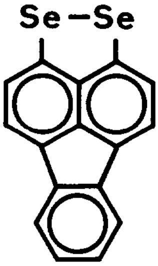

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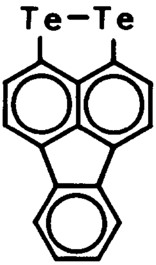

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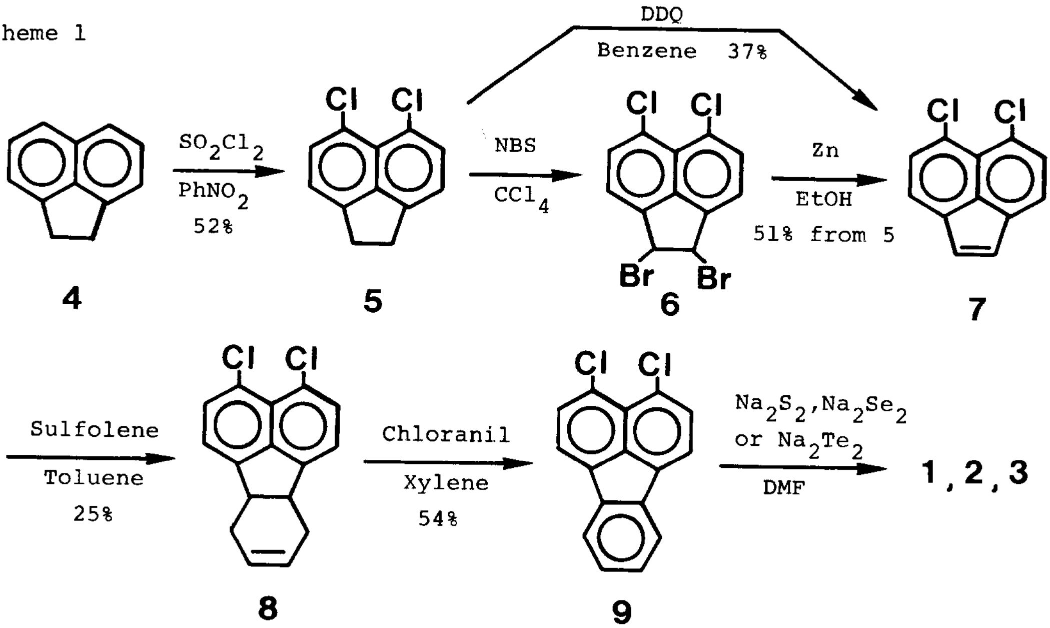
The synthetic approach to **1**, **2**, and **3** is shown in Scheme 1. Fluoranthene did not permit direct, regioselective dichlorination to 3,4-dichlorofluoranthene **9**, which served as a precursor of the target molecules. We then developed an alternative multistage pathway to **9**, starting with acenaphthene **4**. The chlorination of **4** with sulfonyl chloride in the presence of a catalytic amount of anhydrous aluminium chloride in nitrobenzene at 25-30 °C gave 5,6-

Scheme 1



dichloroacenaphthene **5** in 52% yield.4) The direct dehydrogenation of **5** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to 5,6-dichloroacenaphthylene **7** in refluxed benzene proceeded in 37% yield.5) On the other hand, the bromination of **5** with N-bromosuccinimide in refluxed carbon tetrachloride, followed by debromination of the resulting 1,2-dibromo-5,6-dichloroacenaphthene **6** with zinc dust in refluxed ethanol led to formation of **7** in 51% overall yield. A Diels-Alder reaction of **7** with butadiene, in situ generated from thermolysis of sulfolene in toluene, at 160 °C in an autoclave gave an adduct **8** in 25% yield,6) which was dehydrogenated with chloranil in refluxed xylene to afford the precursor **9** in 54% yield.7) Treatment of **9** with sodium dichalcogenides, in situ prepared from an equimolar reaction of sodium and elemental chalcogen in N,N-dimethylformamide, at 90-140 °C in a nitrogen atmosphere gave the desired 3,4-dichalcogen-bridged fluoranthenes; **1**: yield 26.2%, orange needles from hexane-benzene, mp 213-215 °C; **2**: yield 76.6%, purplish black needles from chloroform, mp 238 °C (dec.); **3**: yield 17.8%, greenish black needles from carbon disulfide, mp >300 °C.

All the structures of **1**, **2**, and **3** were characterized by elemental and spectroscopic analyses. Their ^{1}H-NMR spectra showed composite patterns of AX and AA'XX', consistent with 3,4-disubstituted fluoranthene.8) In addition, their MS spectra showed satisfactory molecular ion peaks, which consisted of typical clusters due to the chalcogen isotopes.

Fluoranthene itself has no absorption above 400 nm in the electronic spectrum. In contrast, 3,4-dichalcogen-bridged fluoranthenes strongly absorb in the region of 400-500 nm as shown in Fig. 1; **1**: λmax 461 nm (log ε 4.29) and 438 nm (log ε 4.29); **2**: λmax 466 nm (log ε 4.45) and 442 nm (log ε

4.29); 3: λmax 503 nm (log ε 4.54) in carbon disulfide. In addition, they show weak, broad, and solvent-dependent absorptions in the longer wavelength, which appear as shoulders for 1 (500 nm) and for 2 (540 nm), but as an independent peak for 3 (λmax 719 nm, log ε 2.43).10) The bathochromic shifts of these two kinds of absorptions in order of the chalcogen triad, i.e., sulfur, selenium, and tellurium are considered to reflect an enhanced electronic interaction between the fluoranthene and the heavy chalcogen.

The cyclic voltammograms of 1, 2, and 3 exhibited one reversible oxidation waves, whose half-wave potentials were situated at 1.15 V, at 0.88 V, and at 0.53 V, respectively, vs. a Ag/AgCl reference electrode in benzonitrile.11) Thus, the donor character of 3,4-dichalcogen-bridged fluoranthene is considerably strengthened by introduction of heavy chalcogen element, being correlated to the above enhanced electronic interaction.

It has become apparent from a preliminary experiment of complexation that compounds 1 and 2 formed 1:1 crystalline charge-transfer complexes with either TCNQ or its tetrafluoro derivative ($TCNQF_4$). However, the electrical conductivities of these complexes were semi-conducting or insulating,12) suggesting a mixed stacking of donor and acceptor in the crystal structures. On the other hand, 3 failed to separate such crystalline complexes in spite of its stronger donor character. This unexpected result may be attributed to very poor solubility of 3. Further study on the electrochemical crystallization of their radical cation salts is now under way.

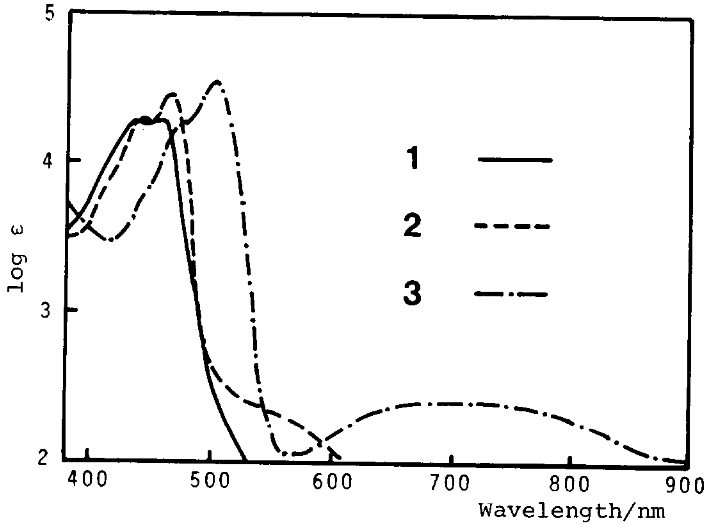


Fig. 1. The electronic spectra of 3,4-dichalcogen-bridged fluoranthenes 1, 2, and 3 in CS_2

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4) 5: colorless needles from hexane-benzene, mp 165.8-167.5 °C (lit., mp 165-167 °C); H. Okada, Y. Sato, Y. Kimura, and M. Kaneko, Japan Patent 77 08307; Chem. Abstr., 87: 134828f.

5) 7: yellow needles from hexane, mp 156.7-158.7 °C (lit., mp 163-164 °C); J. C. Koziar and D. O. Cowan, J. Am. Chem. Soc., 98, 1001 (1976).

6) 8: colorless needles from hexane, mp 119.7-120.7 °C.

7) 9: yellow plates from hexane, mp 185.0-186.9 °C.

8) ^{1}H-NMR data are as follows (CS$_2$, 360 MHz); 1: δ 7.345 and 7.880 (AA'XX' m), 7.416 and 7.908 (AX d, J=7.5 Hz); 2: δ 7.329 and 7.835 (AA'XX' m), 7.542 and 7.811 (AX d, J=7.5 Hz); 3: δ 7.321 and 7.797 (AA'XX' m), 7.632 and 7.708 (AX d, J=7.4 Hz).

9) MS data of molecular ion peaks (relative intensity); 1: m/z 264(100), 265 (19), 266(11); 2: m/z 354(22), 355(17), 356(55), 357(37), 358(92), 360 (100), 362(31); 3: m/z 450(16), 451(16), 452(37), 454(68), 456(100), 458 (90), 460(49).

10) On the basis of the spectroscopic study of naphtho[1,8-cd]-1,2-dithiole by Zweig and Hoffmann, the strong bands may be assigned to a normal π-π^* transition and the weak bands to a symmetry-forbidden π-σ^* transition associated with anti-bonding σ^* orbital of the dichalcogen bond; A. Zweig and A. K. Hoffmann, J. Org. Chem., 30, 3997 (1965).

11) Measurement conditions of cyclic voltammetry; Pt working electrode, 0.1 M Bu$_4$NClO$_4$ supporting electrolyte, 100 mVsec^{-1} scan rate, and 23 °C temperature.

12) Electrical conductivities (compressed pellet, RT); 1$\cdot$TCNQ complex 5.4×10^{-11} Ω^{-1}cm^{-1}; 1$\cdot$TCNQF$_4$ complex 5.6×10^{-6} Ω^{-1}cm^{-1}; 2$\cdot$TCNQ complex 2.6×10^{-11} Ω^{-1}cm^{-1}; 2$\cdot$TCNQF$_4$ complex 5.4×10^{-8} Ω^{-1}cm^{-1}.

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