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Synthesis of Pyrazinodithiadiselenafulvalenes. New Unsymmetrical π-Donors

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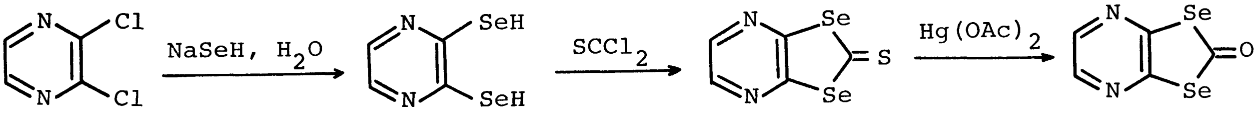
Unsymmetrical dithiadiselenafulvalenes, which are annelated on the 1,3-dithiole or 1,3-diselenole moiety to a 1,4-pyrazine ring, have been prepared by the cross coupling method and characterized as electron-donors for use in conductive charge-transfer salts.

Charge-transfer salts of dimethyl(ethylenedithio)dithiadiselenafulvalene (DMET) have been thrust to the forefront of organic metals research with the quite recent discovery of superconductivity in $(DMET)_2Au(CN)_2$,[1)] which has increased importance of the synthesis of unsymmetrical dithiadiselenafulvalene compounds for the discovery of new organic superconductors. Although a number of unsymmetrically substituted donors based on BEDT-TTF[2-5)] and TMTSF[5,7,8)] have been prepared, there have been very few reports of donor species with dithiadiselenafulvalene framework. Recent synthesis of pyrazino(ethylenedithio)-tetrathiafulvalenes and similar π-donors[3,6)] prompted us to prepare dithiadiselenafulvalenes fused to a pyrazine ring. In this paper we report the preparation and properties of six unsymmetrical pyrazinodithiadiselenafulvalenes (**1**-**6**).

The new donors were prepared by the cross coupling between the following 1,3-diselenole and 1,3-dithiole compounds in appropriate combinations: pyrazino-

1,3-diselenole-2-one, dimethylpyrazino-1,3-diselenole-2-one, pyrazino-1,3-dithiole-2-one, dimethylpyrazino-1,3-dithiole-2-one, 4,5-dimethyl-1,3-diselenole-2-selone, 4,5-methylenedithio-1,3-dithiole-2-thione, and 4,5-ethylenedithio-1,3-dithiole-2-thione. Pyrazino-1,3-diselenole-2-thione, a key precursor of **3** and **5**, was prepared as follows. To a solution of NaHSe (prepared[9]) from 6.9 g of Se and 6.9 g of $NaBH_4$) in 150 ml of water, 6 g of 2,3-dichloropyrazine was added at once. The mixture was heated at the reflux temperature for 15 min. After cooling to 10 °C, the precipitate was filtered off. The dark brown solution was treated with 30 ml of glacial acetic acid to give the precipitate, which was filtered and washed with water. Then this was combined with a solution of 4.5 g of NaOH in 450 ml of water and the mixture was warmed under stirring, during which small excess of 2,3-dichloropyrazine was removed off by evaporation with water (100 ml). The solution (350 ml) was cooled to room temperature and filtered. The filtrate was diluted with 1050 ml of water. To the solution 6 ml of thiophosgene was added dropwise within 30 min at 0-5 °C under stirring. The stirring was continued at room temperature for 1 h. The precipitate was filtered, washed with water and methanol and air-dried. Separation on silica gel column chromatography afforded 3.3 g (29%) of pyrazino-1,3-diselenole-2-thione as yellow solid of mp 205 °C.



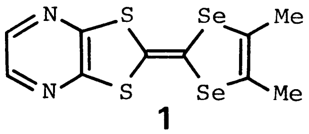
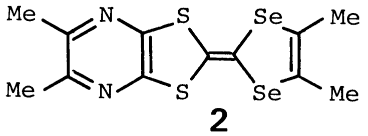
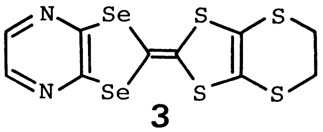
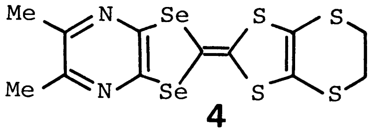
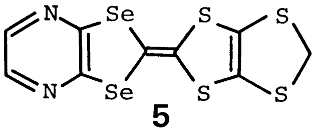
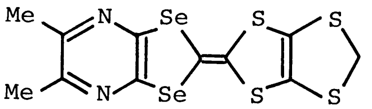
Dimethylpyrazino-1,3-diselenole-2-thione, yellow solid of mp 145 °C, was prepared by a similar reaction, except that KHSe was used, at 95-97 °C for 10 h.

Pyrazino-1,3-diselenole-2-thione and dimethylpyrazino-1,3-diselenole-2-thione were converted to the corresponding 1,3-diselenole-2-ones by treatment with $Hg(AcO)_2$ in dichloromethane-acetic acid (1:1).

The donors were prepared in the last step by cross coupling of suitable precursors in the presence of a large excess of triethylphosphite at 120 °C. In every case, the unsymmetrical products were completely separated using silica gel column chromatography (benzene-hexane or CH_2Cl_2); the mass spectrum exhibited the expected peak and no peaks due to the contamination of the symmetrical coupling products.

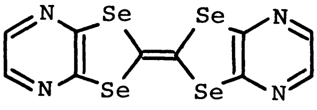
The preparative, spectral, and electrochemical data of six new donors are given in Table 1. All the donor compounds undergo two reversible one-electron

Table 1. Yields and some properties of new donor compounds

	Yield/%[a)]	Mp θ_m/°C	Mass M^+	UV λ/nm[b)]	Redox potentials[c)] $E_{1/2}[1]$/V	Redox potentials[c)] $E_{1/2}[2]$/V
 **1**	10	282	378	415	+0.69	+1.02
 **2**	1	302	406	405	+0.63	+0.93
 **3**	25	229	440	405	+0.74	+1.03
 **4**	18	238	468	386	+0.59	+0.99
 **5**	7	218	426	400	+0.69	+0.96
 **6**	10	218	454	380	+0.66	+0.92

a) Based on the corresponding 2-one. b) Peak position of the longest wavelength band (in MeCN). c) V vs. SCE (at Pt electrode, in MeCN, 0.1 M Et_4NClO_4, 50 mV/s).

oxidations in cyclic voltammetry.[10)] The first half wave potential values are higher in these donors than that of TMTSF and BEDT-TTF, but lower than that of symmetrical bis(pyrazino)TTF ($E_{1/2}[1]=+0.89$, $E_{1/2}[2]=+1.17$ V vs. SCE, CH_3CN) and bis(dimethylpyrazino)TTF ($E_{1/2}[1]=+0.99$ V, $E_{1/2}[2]=+1.28$ V vs. SCE, CH_3CN). The separations between the first and second oxidation wave of these donors are almost the same as that of TMTSF[11)] and BEDT-TTF.[12)] The electrochemical crystallization of the radical salts with inorganic anions is now underway. Compound **1** afforded, so far, black plates by treating with Bu_4NPF_6.



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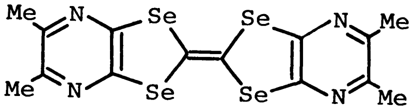

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It should be noted that synthesis of bis(pyrazino)tetraselenafulvalene (**7**) and bis(dimethylpyrazino)tetraselenafulvalene (**8**) by the self-coupling was of no practical value because of extremely low yields (0.1%). These symmetrical donors could be characterized as follows. **7**: mp >310 °C, M^+ 496, (CH_3CN) 384 nm. **8**: mp >310 °C, M^+ 552, (CH_3CN) 378 nm.

References

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