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NEW π-ELECTRON DONORS:
ETHANEDIYLIDENE-2,2'-BIS(1,3-DISELENOLE) AND ETHANEDIYLIDENE-2-(1,3-DITHIOLE)-2'-(1,3-DISELENOLE)

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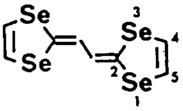
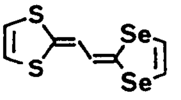
Summary: This communication describes synthesis and electrochemical properties of new type of π-donors containing 1,3-diselenole ring, ethanediylidene-2,2'-bis(1,3-diselenole)(1a) and ethanediylidene-2-(1,3-dithiole)-2'-(1,3-diselenole)(2a). The conductivities of the charge-transfer complexes of these donors with tetracyanoquinodimethane (TCNQ) are also demonstrated.

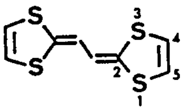
Great interest in synthesis of new donors seems to be directed toward selenium analogue of 1,3-dithiole, since tetraselenafulvalene was shown to have much higher conductivity in charge-transfer complex with TCNQ[1] compared with that of tetrathiafulvalene. In particular, it should be noted that some cation radical salts derived from tetramethyltetraselenafulvalene bring about superconductivity under an extremely limited condition (eg. low temperature and normal or high pressure).[2] In this communication we wish to report synthesis of ethanediylidene-2,2'-bis(1,3-diselenole)(1a) and ethanediylidene-2-(1,3-dithiole)-2'-(1,3-diselenole)-(2a), selenium analogues of a new type of π-donor, ethanediylidene-2,2'-bis(1,3-dithiole)(3)[3] in which two 1,3-dithiole rings are connected with two sp^2 carbons.



1a



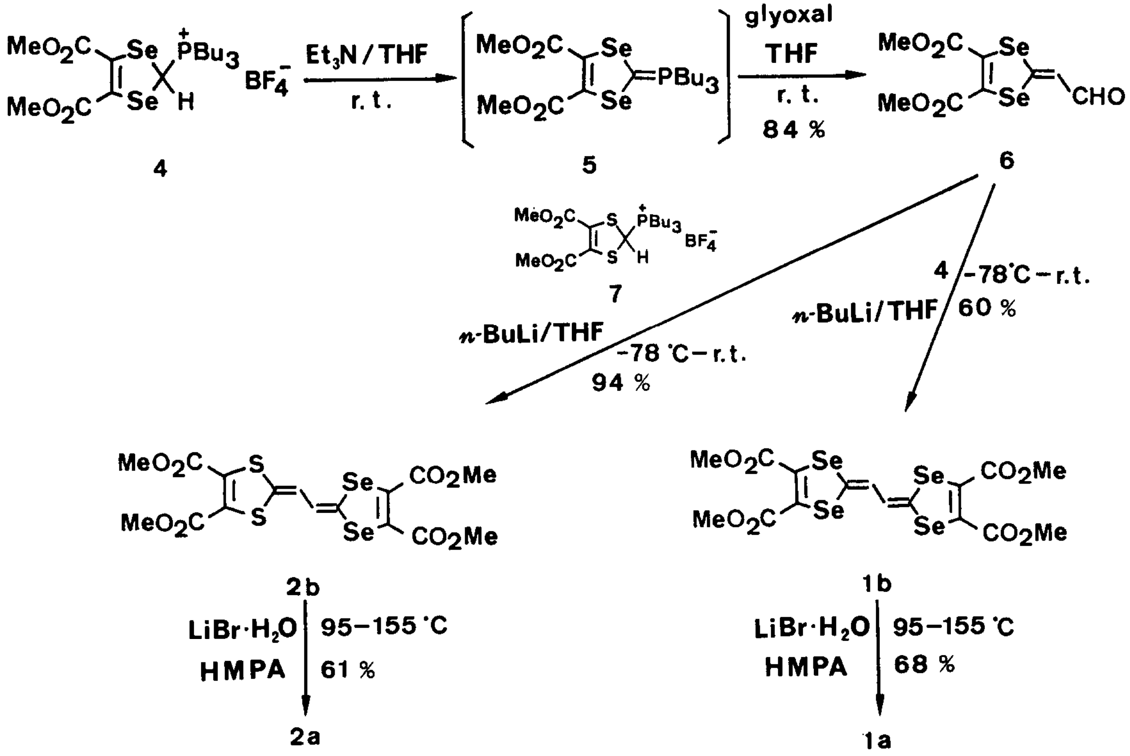
2a



3

The new donors can be obtained by the same methodology as synthesis of 3 (Scheme). Thus, treatment of (4,5-dicarbomethoxy-1,3-diselenolyl)tributylphosphonium tetrafluoroborate (4)[4] (800 mg, 1.33 mmol) with Et_3N (5 mL) in THF (20 mL) at room temperature, followed by reaction of the generated phosphorane (5) with 2 equimolar amounts of glyoxal (40% in water, 386 mg, 2.66 mmol) gave 2-formylmethylene-4,5-dicarbomethoxy-1,3-dithiole (6)[5] in 84% yield. The subsequent reaction of 6 (72 mg, 0.20 mmol) with 4 (122 mg, 0.200 mmol) in dry THF (20 mL) at -78°C under argon atomosphere in the presence of n-BuLi as base provided the tetracarbomethoxy derivative (1b) of 1a as orange crystals (mp 156-157°C) in 60% yield. Also, the reaction of 6 (397 mg, 1.12 mmol) with phosphorane (8) genarated from (4,5-dicarbomethoxy-1,3-dithiolyl)tributylphosphonium tetrafluoroborate (7)[6] (568 mg, 1.12 mmol) and n-BuLi (1.12 mmol) in THF (15ml) gave the tetracarbomethoxy derivative (2b) of 2a as purple-brown needles (175-176°C) in 94% yield. The parent compounds, 1a[7] (yellow crystals, mp 183-184°C (dec)) and 2a[7] (yellow needles, mp 162°C (dec)) were obtained by treatment of 2b and 3b with LiBr·H_2O in HMPA[8] at 95°C and then at 155°C for each 1 h in 68 and 61% yield, respectively. The ^{1}H NMR spectra of both olefinic and ring protons of 1a

Scheme



appeared at lower magnetic field by about 0.2 and 0.9 ppm, respectively, than the corresponding protons of 3.[9] Also the ^{13}C NMR spectra of both olefinic and ring carbons of 1a appeared at lower magnetic field than those of 3. On the other hand, the C-2 carbon signal of 1a was observed at the higher field by about 7 ppm than that of 3.[10] The NMR spectra of 2a shows somewhat complicated pattern because of its unsymmetrical structure. Both the ring proton and carbon (C-4, C-5) signals in the 1,3-dithiole and 1,3-diselenole rings of 2a appear at the similar magnetic field to the corresponding signals of 1a and 3, and the exo olefinic proton signals of the 1,3-dithiole and 1,3-diselenole rings shift to higher and lower magnetic fields compared with those of 3 and 1a, respectively.[11] The three donors (1a, 2a and 3) have two strong absorption bands in the visible region. Both bands shift toward longer wavelength as going 1a to 3 ($\lambda_{max}^{CHCl_3}$(log ε), 1a: 365 (4.06), 390 (4.06); 2a: 372 (4.16), 398 (4.11); 3: 387 (4.31), 406 (4.33) nm).[12]

The cyclic voltammetry of 1a and 2a in acetonitrile[13] at room temperature showed two reversible one-electron oxidation steps (E_1 +0.33, E_2 +0.47 for 1a; E_1 +0.26, E_2 +0.40 V vs. Ag/AgCl for 2a). When the E_1 and E_2 values are compared with those of 3 (+0.20 and +0.36V vs. Ag/AgCl), the both values are shown to be shifted to more positive region in the order of 3 < 2a < 1a. This means that oxidation becomes more difficult as an increasing number of replaced selenium atoms. However, the (E_2-E_1) value remains almost unchanged with selenium replacement in this series.

When each donor was mixed with an equimolar amount of TCNQ in CH_3CN at room temperature, purple-green crystals were obtained, each of which had a composition of D:A=2:3. The conductivities on their compressed pellets were measured in the temperature range of 190 to 300°K by using a four-probe method. The values at room temperature were 0.24 and 0.072 ohm^{-1} cm^{-1} for $(1a)_2$-$(TCNQ)_3$ and $(2a)_2$-$(TCNQ)_3$, respectively. In particular, it is worth noting that these complexes have very low Ea values (0.04-0.05 eV), suggesting that they might exhibit high conductivities in a single crystalline state.

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References and Notes

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2) a) Bechgaard, K.; Jacobsene, C. S.; Mortensen, K.; Pedersene, H. J.; Thorup, N. Solid State Commun., 1980, 33, 1119. b) Jerome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. J. Phys. Lett. (Paris), 1980, 41, 95. c) Jerome, D. Chem. Scr. (Swed.), 1981, 17, 13. d) Parkin, S. S. P.; Ribault, M.; Jerome, D.; Bechgaard, K. J. Phys., 1981, C14, 5305. e) Parkin, S. S. P.; Jerome, D.; Bechgaard, K. Mol. Cryst. Liq. Cryst., 1982, 79, 213. f) Bechgaard, K.; Carneiro, K.; Rasmussen, F. B.; Olsen, M.; Rindorf, G.; Jacobsen, C. S.

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3) Yoshida, Z.; Kawase, T.; Awaji, H.; Sugimoto, I.; Sugimoto, T.; Yoneda, S. Tetrahedron Lett., 1983, 3469.

4) The salt 4 was prepared by the 1,3-dipolar cycloaddition reaction of $(n\text{-Bu})_3P\text{-}CSe_2$ adduct with dimetyl acetylenedicarboxylate in the presence of fluoroboric acid etherate. Recrystallization from acetonitrile-ether gave a pure material as white needles (yield 70%): mp 141-142 °C; ^1H NMR(CD_3CN) δ 0.7-2.8 (m,27H,n-Bu), 3.86(s,6H,CO_2Me), 5.67(d,1H,J_{P-H}=2 Hz, methine); IR(KBr) 1920(C=O), 1080(BF_4^-) cm^{-1}; Anal. Calcd for $C_{19}H_{34}BO_4F_4PSe_2$:C, 37.9; H, 5.69; P, 5.14. Found: C, 37.77; H, 5.84; P, 5.21.

5) 6: yellow needles; mp 108-109°C; ^1H NMR($CDCl_3$) δ 3.91(s,3H,CO_2Me), 3.93(s,3H,CO_2Me), 7.44(d,1H,J=3 Hz,=CH-CHO), 9.78(d,1H,J=3 Hz,=CH-CHO); IR(KBr) 1725(CO_2Me), 1700(CHO), 1240(C-O) cm^{-1}; mass m/e 356(M^+, based on ^{80}Se).

6) Sato, M.; Gonnella, N. C.; Cava, M. P. J. Org. Chem., 1979, 44, 930.

7) Spectral data are as follows; 1a: ^1H NMR($CDCl_3$) δ 6.10(s,2H), 7.08(s,4H); ^{13}C NMR ($CDCl_3$) δ 119.9($J13_{C-H}$=185 Hz, Se-C=C-Se), 120.4($J13_{C-H}$=185 Hz, Se-C=C-Se), 121.2 ($J13_{C-H}$=157 Hz, olefinic), 125.3(Se-C-Se); IR(KBr) 1541, 1515, 1498, 1273, 810, 718, 645, 630 cm^{-1}; mass m/e 422 (M^+, based on ^{80}Se), 2a: ^1H NMR($CDCl_3$) δ 5.64(d,1H, J=11Hz), 6.19(s,2H), 6.29(d,1H,J=11Hz), 7.07(s,2H); ^{13}C NMR($CDCl_3$) δ 112.6($J13_{C-H}$=158 Hz, olefinic), 117.3 ($J13_{C-H}$=186 Hz, S-C=C-S), 117.9($J13_{C-H}$=186 Hz, S-C=C-S), 119.4($J13_{C-H}$=157 Hz, olefinic), 119.8($J13_{C-H}$=185 Hz, Se-C=C-Se), 120.4($J13_{C-H}$=184 Hz, Se-C=C-Se), 123.0(Se-C-Se), 134.1(S-C-S); IR(KBr) 1539, 1505, 1276, 800, 719, 656, 630 cm^{-1}; mass m/e 326 (M^+, based on ^{80}Se).

8) Yoneda, S.; Kawase, T.; Yasuda, Y.; Yoshida, Z. J. Org. Chem., 1979, 44, 1728.

9) The spectral data for 3 are as follows: ^1H NMR($CDCl_3$) δ 5.88(s,2H), 6.23(s,4H); ^{13}C NMR ($CDCl_3$) δ 110.8($J13_{C-H}$=157 Hz, olefinic), 117.1($J13_{C-H}$=185 Hz, S-C=C-S), 117.7($J13_{C-H}$=185 Hz, S-C=C-S), 131.8(S-C-S).

10) The electron density at each carbon of 3 and 1a was calculated by using PPP MO method[14]: The C-4 and C-5 and olefinic carbons are shown to have higher electron densities for 3 than for 1a, while the reverse tendency is found at the C-2 carbon.

11) Extraordinary shift of the C-2 and olefinic carbons suggests some contribution of the following polar structure (A) to the ground state of 3a.

A B

12) The PPP SCF-CI MO calculations[14] suggest that the longest and the next longest wavelength bands are due to the allowed electronic $\pi\text{-}\pi^*$ transition from HOMO to LUMO and next LUMO, respectively, and that their transition energies decrease in the order as above.

13) 0.1M $Et_4NClO_4\text{-}CH_3CN$, V vs. Ag/AgCl, Pt electrode, scan rate 43 mV/s.

14) Yoshida, Z.; Awaji, H.; Kawase, T,; Yoneda, S.; Sugimoto, T.; Kobayashi, T. to be submitted elsewhere.

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