Selenocarbonyl Analogues of Tetrathiafulvaleno-quinone(-thioquinone)-1,3-dithiolemethides as New Donor Molecules

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Diethylthiotetrathiafulvalenoselenoquinone-1,3-dithiolemethide (**1a**) and -1,3-benzodithiolemethide (**2a**) were newly prepared as a donor molecule, which was colored blue in contrast to the corresponding thiocarbonyl- (**1b** and **2b**) (green) and carbonyl-analogues (**1c** and **2c**) (red). From comparison of their first redox potentials, **1a** (**2a**) possesses almost the same electron-donating ability to **1b** (**2b**) and **1c** (**2c**). The reaction of **2a** with P(n-Bu)$_3$ afforded a coupled ylidene compound (**3**) albeit in low yield, which can be expected as another new donor molecule.

Current interest is directed toward the development of new molecular/organic π/d cooperated systems, especially radical cation salts of tetrathiafulvalene (TTF) derivatives with magnetic counter-anions, which involve such significant interaction between conducting π electrons and localized d spins as to bring about novel electrical conducting and/or magnetic properties.[1] We now report on the synthesis of diethylthiotetrathiafulvalenoselenoquinone-l,3-dithiolemethide (**1a**) and -1,3-benzodithiolemethide (**2a**), selenocarbonyl analogues of the corresponding thiocarbonyl (**1b** and **2b**) and carbonyl compounds (**1c** and **2c**), which possess electron-donating ability comparable to TTF[2] and also can bind directly several magnetic-metal (Cu and Fe etc.) salts through coordination with the thiocarbonyl or carbonyl group.[3–5] In addition, it is shown that **la** (**2a**) possesses almost the same redox property to **1b** (**2b**) and **1c** (**2c**), but very different optical property and chemical reactivity.

1a: X = Se; **1b**: X = S; **1c**: X = O   **2a**: X = Se; **2b**: X = S; **2c**: X = O
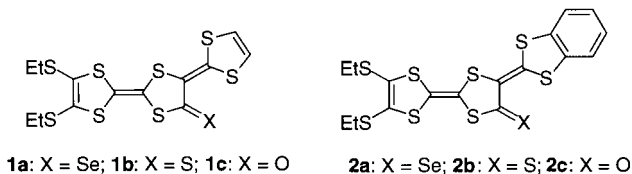
Bis(tetraethylammonium) bis(2,3-diethylthiotetrathiafulvalenyl-6,7-diselenolato)zinc complex[6] was reacted with 2 equiv. of 2-methylthio-1,3-dithiolylium or -1,3-benzodithiolylium tetrafluoroborate in THF at −70 °C under argon, followed by the separation of the reaction mixture on silica gel column chromatography with an eluent of CS$_2$ and by recrystallization from CS$_2$/ MeOH to afford **1a** (193–194 °C) and **2a** (207–208 °C) in 19 and 48% yields, respectively. In a similar manner, by using the corresponding dithiolato zinc complex,[2] **1b** (200–201 °C) and **2b** (216–218 °C) were obtained in 31 and 29% yields, respectively. Furthermore, **1b** and **2b** were converted to **1c** (176–178 °C) and **2c** (165–166 °C) in 81 and 82% yields, respectively, by treatment with 2.5 equiv of mercury(II) acetate in THF/AcOH at 20 °C and by recrystallization from CS$_2$/MeOH.

It was successful to get single crystals of **2a** suitable for the X-ray structure analysis.[7] As is obvious from the molecular structure in Figure 1, the molecular skeleton except for two ethyl groups is almost planar, because the contact distance between the selenium atom of a selenocarbonyl group and the sulfur atom of 1,3-benzodithiole ring is 3.10 Å, which is remarkably shorter than the sum of van der Waals' radii of selenium (2.00 Å) and sulfur atoms (1.85 Å). In addition, the bond distance (1.83 Å) of a selenocarbonyl group becomes considerably longer than those of acyclic and cyclic selenocarbonyl compounds known so far,[8] suggesting that aromatic delocalization due to 6π electrons is achieved in the five-membered ring composed of the selenocarbonyl bond, and the C=C bond and one sulfur atom of (1,3-dithiole)ylidene group.
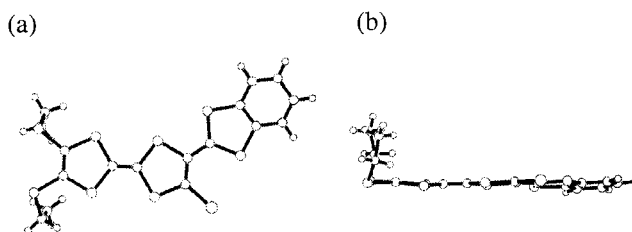
(a)   (b)

Figure 1. Molecular structure of **2a**: (a) top and (b) side views.

The redox properties of **1a** and **2a** were investigated by using cyclic voltammetry[9] and the results were compared with those of **1b**, **1c**, **2b** and **2c**. The cyclic voltammograms of **1a** and **2a** showed two pairs of waves, each of which are due to one-electron transfer. Thus, the first and second redox waves correspond to the steps of **1a** (**2a**) $\rightleftarrows$ **1a$^{+\bullet}$** (**2a$^{+\bullet}$**) (**1a$^{+\bullet}$** and **2a$^{+\bullet}$** are radical cations of **1a** and **2a**) and **1a$^{+\bullet}$** (**2a$^{+\bullet}$**) $\rightleftarrows$ **1a^{2+}** (**2a^{2+}**) (**1a^{2+}** and **2a^{2+}** are dications of **1a** and **2a**), respectively. Reversibility was very good for the first step, but slightly decreased for the second step, suggesting that **1a$^{+\bullet}$** and **2a$^{+\bullet}$** are stable species, while **1a^{2+}** and **2a^{2+}** have inferior stability. In contrast to **1a** and **2a**, both the two pairs of redox waves were entirely reversible for **1b** (**2b**) and **1c** (**2c**). Table 1 summarizes their first (E^1) and second redox potentials (E^2). The E^1 value of **1a** is +0.65 V vs Ag/AgCl, which is higher only by 0.07–0.1 V than those of **1b** and **1c**, and by 0.2 V than that (0.45 V) of tetraethylthiotetrathiafulvalene (TET-TTF). No change was observed in E^1 between **1a** and **2a**, although there was slightly increasing tendency of E^1 by benzo-substitution between **1b** and **2b**, and between **1c** and **2c**. On the other hand, the E^2 value (+0.82 V) of **1a** is reversely lower by 0.06–0.08 V than those of **1b** and **1c**. The similar tendency was also seen for a series of **2a**, **2b** and **2c**, although their E^2 values are higher by 0.05–0.08

V than those of **1a**, **lb** and **1c**. In consequence, **1a** and **2a** possess slightly inferior electron-donating ability to the corresponding thiocarbonyl- and carbonyl-analogues. Nevertheless, the Coulomb repulsion between positive charges is much more reduced for **1a** and **2a** than the thiocarbonyl- and carbonyl-analogues, as is obvious from the difference between E^1 and E^2 values.

Table 1. Redox potentials (E^1 and E^2 vs. Ag/AgCl) of **1a** - **1c** and **2a** - **2c**[a]

| Donor	E^1	E^2
1a	+0.65	+0.82[b]
1b	+0.55	+0.88
1c	+0.58	+0.90
2a	+0.65	+0.90[b]
2b	+0.60	+0.93
2c	+0.63	+0.95

[a]Measured in CH_2Cl_2 at 0 °C. [b]Pseudo-reversible.

The crystal color was markedly different between **1a** (**2a**) (blue), **1b** (**2b**) (red) and **1c** (**2c**) (orange). Now, their electronic absorption spectra were measured in CH_2Cl_2. For all cases two strong absorption bands appeared in the visible region. The longest wavelength absorptions (λ_{max}) and molar absorptivities ($\log \varepsilon_{max}$) are as follows: **1a**, 611 (4.02); **1b**, 589 (4.25); **1c**, 473 (4.16); **2a**, 623 (4.08); **2b**, 599 (4.20); **2c**, 476 (4.26). The λ_{max}'s are shifted to the longer wavelength region in the order of **1c**, **1b** and **1a**. The similar tendency can be also seen between **2a**, **2b** and **2c**, which have however larger λ_{max}'s by 3–12 nm than the corresponding **1a**, **1b** and **1c**.

The similar E^1's and very different λ_{max}'s between **1a** (**2a**), **lb** (**2b**) and **1c** (**2c**) can be well understood by MO calculations. The MOPAC/PM3 calculations of parent systems of **1a**, **1b** and **1c** substituted by hydrogen atoms for ethylthio groups (**1a'**, **1b'** and **1c'**) were performed using the molecular skeletal geometry of **1a**, **1b** and **1c** determined by X-ray structure analysis. The HOMO and LUMO energies are −8.419 and −2.699 for **1a'**, −8.402 and −2.324 for **1b'** and −8.447 and −1.694 eV for **1c'**. Accordingly, the HOMO–LUMO energy gaps of **1a'**, **1b'** and **1c'** amount to be 5.720, 6.078 and 6.753 eV, respectively. The HOMO's are in almost the same energy. In contrast, the LUMO energies are very different, which go down in the order of **1c'**, **1b'** and **1a'**. As the result, the HOMO–LUMO energy gap also becomes smaller in the order as above, suggesting that the longest wavelength absorption is due to the HOMO–LUMO transition. Of course, almost the same HOMO and very different LUMO energies are related to the distribution of their AO coefficients. Thus, for the HOMO's large AO coefficients are present at the central tetrathiaethylene part, while there is very small amount at the C=X (X=Se, S, O) group. On the other hand, the LUMO's have only AO coefficients at the C=C–C=X part.

When **2a** was reacted with an excess of P(n-Bu)$_3$ in toluene at 100 °C for 2 h, a coupled ylidene compound (**3**) was obtained as a yellow oil[10] albeit in very low yield of 4%. The similar reaction was also carried out by using **2b** or **2c**, but the starting material was only recovered. The cyclic voltammogram of **3** in CH_2Cl_2 at 0 °C showed three pairs of waves at +0.57, +0.83 and +1.03 V vs Ag/AgCl. The first pair of waves possessed much more intensity than the second and third pairs of waves. Since

3   **4**
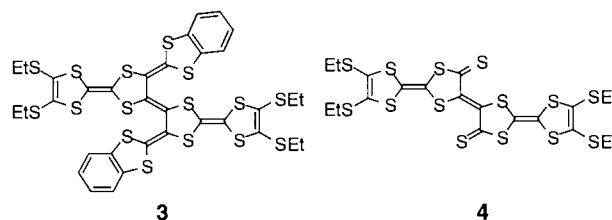
for the corresponding thiocarbonyl-anlogue previously prepared (**4**)[11] four pairs of waves were observed at + 0.40, + 0.53, + 0.88 and + 1.01 V under the same conditions, it is conceivable that the first pairs of waves involve two-electron transfer, while the second and third pairs of waves one electron transfer. In view of considerably the low first/second redox potential, **3** can be also expected as another new donor molecule. We are now preparing Cu and Fe complexes of **1a**, **2a** and **3**.

References and Notes
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7   Crystal data for **2a**: C$_{17}$H$_{14}$S$_8$Se, M =553.79, monoclinic, space group $P2_1/c$, $a = 5.22(1)$, $b = 34.14(1)$, $c = 11.95(1)$ Å, $\beta = 93.2(1)°$, $Z = 4$, $V = 2126(4)$ Å^3, $Dc = 1.830$ g/cm^3. $R = 0.143$ and $Rw = 0.181$ for 1342 observed reflections with $I > 2\sigma$ (I). The measurements were made by Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å).
8   S. Patai and Z. Rappoport, "The chemistry of organic selenium and tellurium compounds," Wiley, Chichester (1986).
9   The measurements were performed at 0 °C in CH_2Cl_2 containing 0.1 M (n-Bu)$_4$NPF$_6$ as a supporting electrolyte by using Pt wires as both working and counter electrodes.
10   MS (m/z): 949 (M$^+$); ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 7.18–6.99 (m, 8H), 2.76 (q, $J = 7.5$ Hz, 8H), 1.23 (t, $J = 7.5$ Hz, 12H); UV (CH_2Cl_2) λ_{max} ($\log \varepsilon_{max}$) 327 (4.41) and 384 (sh) nm (3.92).
11   K. Ueda, Y. Kamata, T. Kominami, M. Iwamatsu, and T. Sugimoto, *Chem. Lett.*, **1999**, 987.