SYNTHESIS AND ELECTROCHEMICAL BEHAVIOR OF 1,4-DITHIIN RING CONDENSED SYSTEMS

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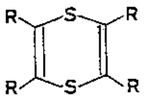
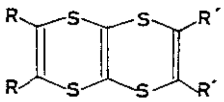
Abstract —— Alkylthio-substituted derivatives of 1,4-dithiin (1a), 1,4,5,8-tetrathianaphthalene (2a), 1,4,5,6,9,10-hexathia-anthracene (3a) and 1,4,5,6,7,10,11,12-octathianaphthacene (4a) are synthesized by Diels-Alder reaction of *cis*-1,2-dialkylthio-ethylenes or 2a with dimethyl tetrathiooxalate (6) and the successive dehydrogenation with 2,3-dichloro-5,6-dicyano-*p*-benzo-quinone (DDQ). The electrochemical behavior of the new compounds (1b, 2b, 3b and 4b) and 2a is investigated by cyclic voltammetry. The skeletal rearrangement of 2a to tetrathiafulvalene (TTF) via the dication state, is found to occur by electrochemical or chemical means.

Based on the X-ray structural analysis[1] and NMR spectroscopic study,[2] 1a, a cyclic 8π-electron system, has been shown to have a boat structure with a fold angle[3] of 137 ± 2°. However, recent experimental evidence on the conformation in solution[4] and vapor phase,[5] provides that the dithiin ring rapidly oscillates between the boat and planar structures. If it was correct, 1a and its polycondensed systems, 2a - 4a, in particular the latter should have low oxidation potentials and be expected as a donor component for organic metals. In fact, from such an expectation Mizuno et al. have synthesized 2a with an isoelectronic structure to TTF, a most promising donor among those investigated so far. However, they found the oxidation potential of 2a to be considerably high and no formation of charge-transfer complex with 7,7,8,8-tetracyanoquinodimethane. In this paper we describe the synthesis of "alkylthio-substituted" derivatives of 1a - 4a, and their electrochemical behavior by using cyclic voltammetry.

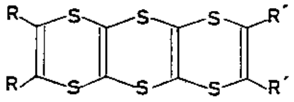
The synthesis of 2,3,5,6-tetramethylthio-1a (1b), 2,3-dimethylthio-6,7-ethylenedithio-2a (2b), 2,3-dimethylthio-3a (3b), and 2,3,8,9-tetramethylthio-4a (4b) was



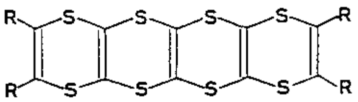
1a R=H
1b R=SCH_3



2a R=R′=H
2b R=SCH_3,R′, R′=SCH_2CH_2S



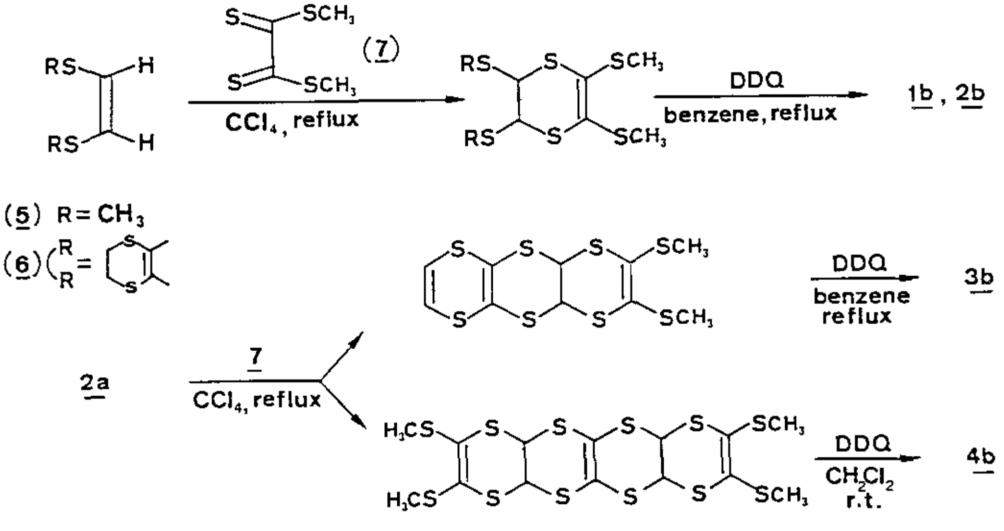
3a R=R′=H
3b R=H,R′=SCH_3



4a R=H
4b R=SCH_3

successfully achieved by Diels-Alder reaction of *cis*-1,2-dimethylthioethylene (5), 1,4,5,8-tetrathiatetralin (6)[6] and 2a with dimethyl tetrathiooxalate (7)[7] in refluxing CCl_4, and the successive dehydrogenation of the resulting mono- or bis-adducts with DDQ in refluxing benzene or CH_2Cl_2 (see Scheme): 1b (a pale yellow viscous oil, overall yield 8%); $\lambda_{max}^{CH_2Cl_2}$ (log ε) 275 nm (3.90); ^1H nmr ($CDCl_3$) δ 2.49 (s); ^{13}C nmr ($CDCl_3$) δ 18.4, 131.2; 2b (pale yellow crystals, mp 134°C, 32%); $\lambda_{max}^{CH_2Cl_2}$ (log ε) 253 (4.07), 299 nm (sh, 3.69); ^1H nmr ($CDCl_3$) δ 2.44 (s, 6H), 3.24 (s, 4H); ^{13}C nmr ($CDCl_3$) δ 18.1, 30.4, 120.5, 127.6, 131.4; 3b (yellow crystals, mp 155°C, 22%); $\lambda_{max}^{CH_2Cl_2}$ (log ε) 247 (4.37), 262 nm (4.29); ^1H nmr ($CDCl_3$) δ 2.43 (s, 6H), 6.41 (s, 4H); ^{13}C nmr ($CDCl_3$) δ 18.1, 123.4, 125.6, 127.0, 131.3; 4b (

Scheme



yellow crystals, mp 210°C, 6%); $\lambda_{max}^{CH_2Cl_2}$ (log ε) 250 (4.49), 297 nm (4.05); ^{1}H nmr ($CDCl_3$) δ 2.43 (s); ^{13}C nmr ($CDCl_3$) δ 18.1, 127.0, 128.0, 131.2.

The electrochemical behavior of newly synthesized 1b - 4b was investigated by using cyclic voltammetry. Also, the cyclic voltammogram of 2a was determined. Figure 1 shows cyclic voltammograms of 1b - 4b measured in CH_3CN containing 0.1 M *n*-Bu_4NClO_4 at room temperature. As is obvious from the Figure, for all the compounds two waves are observed at each site of oxidation and reduction in the voltage range of 0 - +1.5 V *vs.* Ag/AgCl. From comparison of peak heights in the oxidation and reduction sites these redox processes in the voltage range were shown to be electrochemically irreversible. However, for even multi-scanning in the voltage range no change in the cyclic voltammograms was observed. When the voltage was changed in the limited range of 0 - *ca.* +1.0 V, where only the first redox process occurs, the two peak heights in both sites were almost equal, indicating the electrochemical reversibility of the first process. The change of peak

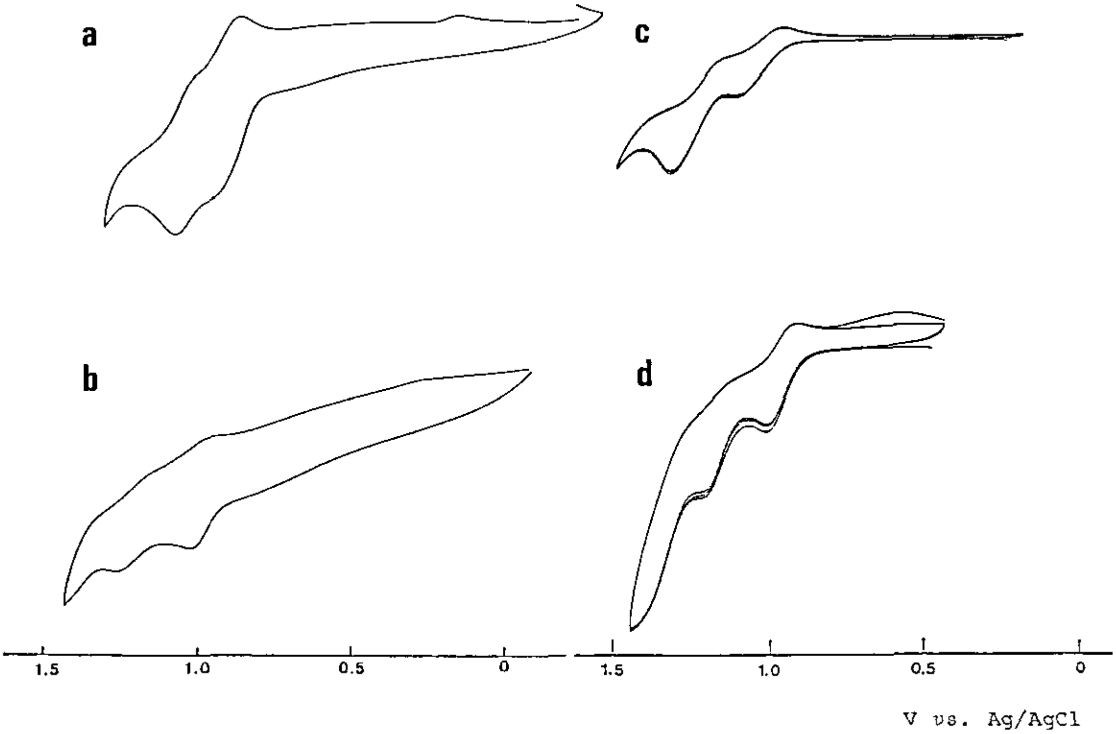
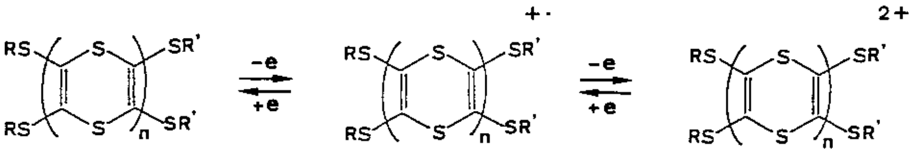


Figure 1. The cyclic voltammograms of (a) 1b, (b) 2b, (c) 3b, and 4b in CH_3CN.

current with respect to sample concentration shows that this redox process involves one-electron migration.[8] Therefore, the first redox step corresponds to a reversible redox process accompanying one-electron migration. From comparison of peak heights of two waves appearing in the oxidation site, the second wave, electrochemically irreversible, also transfers one electron. Thus, the first and second redoxes of 1b - 4b can be regarded as those between neutral and radical cation states, and between radical cation and dication states, respectively. The resulting radical cations and dications are stable and not subject to any chemical reaction in the electrochemical condition.



In Table I are summarized the oxidation potentials of the first (E_1) and second (E_2) waves. Both the E_1 and E_2 values remain almost unchanged (E_1: +0.95 - 1.05 V, E_2: +1.10 - 1.25 V). The values of oxidation potential suggest no extension of π-conjugation by increase of 1,4-dithiin rings, each of which might still have the boat structure for 1b - 4b.

In contrast to the alkylthio-substituted derivatives, the unsubstituted system, 2a showed very unique electrochemical behavior involving the skeletal

Table I. The Oxidation Potentials, E_1 and E_2 of 1b, 2a, 2b, 3b and 4b.

Compound	E_1 1)2)	E_2 1)3)	$E_2 - E_1$
1b	+0.95	+1.10	0.15
2a	+0.97	+1.41	0.44
2b	+1.02	+1.25	0.23
3b	+1.05	+1.24	0.19
4b	+0.97	+1.17	0.20

1) V *vs*. Ag/AgCl; working and counter electrodes: platinum; supporting electrolyte: n-Bu_4NClO_4; solvent: acetonitrile; room temperature; scan rate: 100 mV/sec. 2) Reversible. 3) Irreversible.

rearrangement in the dication state. The cyclic votammograms of 2a measured in CH_3CN containing 0.1 M n-Bu_4NClO_4, are shown in Figure 2. One-scanning in the voltage range of 0 - +1.5 V gave the similar cyclic voltammogram to that of the alkylthio-substituted derivative as described above. Very interestingly, as the number of scanning increases, the two pairs of waves appearing at +0.97 and +1.41 V, respectively, gradually decrease and eventually the new two pairs of waves, electrochemically reversible, were observed at +0.31 and +0.68 V. From comparison of cyclic voltammograms between some related compounds and 2a the rearranged product was determined to be TTF.[9] In the voltage range of 0 - +1.0 V, where only the radical cation is generated, there is no change in the shape of waves, indicating that the skeletal rearrangement occurs via the dication state. The same rearrangement also was accomplished by the reaction of 2a with an appropriate oxidant. For instance, 2a was allowed to react with 2 equiv. lead tetraacetate in trifluoroacetic acid at 0°C, and the successive treatment of the reaction mixture with

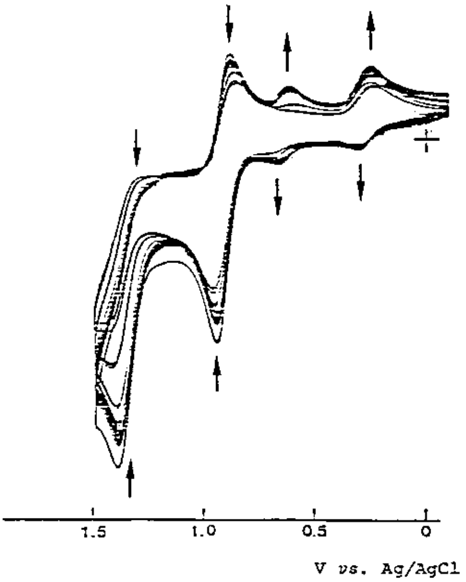
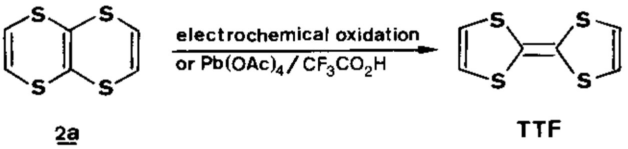


Figure 2. The cyclic voltammograms of 2a in CH_3CN (↑↓ and ↓↑ represent increase and decrease of peak currents, respectively).



saturated sodium dithionite gave TTF in 54% yield. The occurrence of the dicationic rearrangement could be explained in terms of more decreased coulombic interaction between two positive charges in the dicationic TTF than in the dicationic 2a. On the other hand, the dications of 2b, 3b and 4b are somewhat more stabilized than that of 2a, as is seen in their E_2 values (+1.41 V for 2a; +1.17 - 1.20 V for 2b, 3b and 4b). This small increase in stabilization by alkylthio substitution or by further condensation of 1,4-dithiin rings, is considered to retard the dicationic rearrangement. Very recently, Okada et al. have synthesized a 1,4,5,8-tetratelluranaphthalene derivative and found no rearrangement in the scanning range of 0 - +1.5 V *vs.* Ag/Ag$^+$.[10] Judging from the comparatively low oxidation potentials (+0.74 and +1.08 V) and the more puckered boat structure than that of 1a (the fold angle is 123.9°), it is most likely that the electron release occurs from the tellurium atoms, whose atomic orbitals contribute to a large extent to the highest occupied molecular orbital.

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