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Alkali Metal Reduction of Oligo-6-(2-thienyl)pentafulvenes. Synthesis of Oligothienylenemethines Attached with Cyclopentadienide Groups

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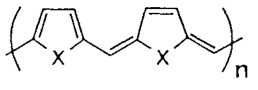
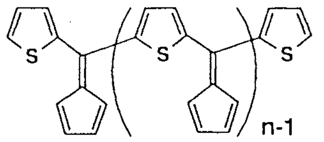
Oligo-6-(2-thienyl)pentafulvenes smoothly undergo alkali metal reduction to form novel, stable oligothienylenemethines attached with cyclopentadienide groups as confirmed by UV-Vis and NMR spectra.

Theoretical calculations predict that polyarenemethines **1** are to possess a small band gap (1 eV) suitable for highly conducting polymers.[1)] In this context, a number of attempts to synthesize **1** have been reported.[2,3)] We have recently reported the synthesis of oligo-6-(2-thienyl)pentafulvenes, i.e. dimer (difulvene) **2**, trimer (trifulvene) **3**, and tetramer (tetrafulvene) **4**, by application of our new pentafulvene synthesis.[4,5)] Compounds **2-4** show appreciably low reduction potentials on cyclic voltammetry owing to electron accepting properties of pentafulvenes to form substituted cyclopentadienyl anions.[4)] Here we report the synthesis of novel oligothienylenemethines attached with cyclopentadienide groups, **5**, **7** and **8**, by alkali metal reduction of **2-4.**



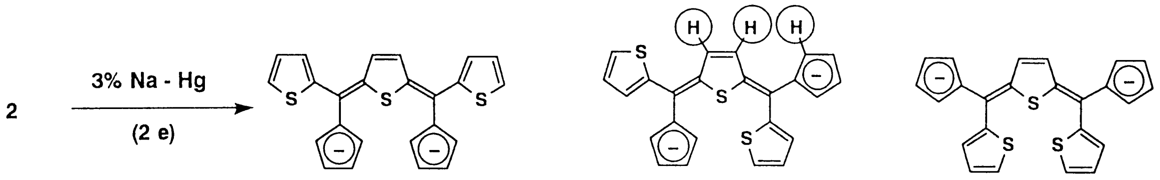
1

X = O, S, NR, CH=CH



2: n = 2; **3**: n = 3; **4**: n = 4

When dimer **2** ($^1E_{1/2}$ = -0.93 V, $^2E_{1/2}$ = -1.03 V) was reduced with 3% Na-Hg in degassed THF, its absorptions at 368 and 415 nm decreased and a new band at 551 nm cleanly grew to give a deep purple solution (Fig. 1). ^{1}H NMR spectrum of the solution shows the presence of one major product with good symmetry and one minor product with poor symmetry in a ratio of about 5 : 1 (Fig. 2). The spectrum showed little change at the temperature range of 30 to -70 °C. Lithium metal and Na-K alloy also gave a similar mixture, but they overreduced the mixture upon prolonged contact, forming radical species (broadening of NMR spectra) and then intractable substances. The products formed by the Na-Hg reduction were stable in solutions at room temperature and regenerated starting **2** (82% yield) on exposure of the solutions to air. These results and ^{13}C NMR data (Table 1) indicate the major product to be a dianion. There can be three geometrical isomers for the dianions of **2**, i.e. two syn isomers **5a** and **5c** and one anti isomer **5b**. The major product is assigned to syn isomer **5a** because NOE is observed between the singlet at δ 6.29 (assignable to the protons of the central thienoquinonoid group) and the multiplet at δ 6.88 (the protons at C-3 and C-4 of the 2-thienyl groups). The triplets at δ 5.80 and 6.17 are characteristic to monosubstituted cyclopentadienyl anion.[6)] On the other hand, ^{1}H signals of the minor product are reasonably assigned to anti dianion **5b**, where the thienoquinonoid protons are observed as a AB quartet (J = 6.3 Hz) at δ 6.57 and 7.09. The considerably low field appearance of the latter signal suggests strong anisotropy effect of the proximate cyclopentadienide group. The preferable formation of **5a** over **5b** and **5c** is presumably attributed to a steric reason. While the thienoquinonoid moiety of **5** must be nearly coplanar, the substituent cyclopentadienide and 2-thienyl groups may be twisted to some extent out of the plane of the thienoquinonoid moiety.[3)] Thus, steric interaction between the thienoquinonoid and cyclopentadienide or 2-thienyl group would be larger than that between the cyclopentadienide and 2-thienyl group. In addition, regardless of counter metal ion, cyclopentadienide group should be bulkier than 2-thienyl group because of the presence of two hydrogens at 2- and 5-position (See the structure **5b**). Accordingly, steric congestion at a conformation capable of reasonable conjugation would be smaller in the order of **5a** < **5b** < **5c**.



5a **5b** **5c**

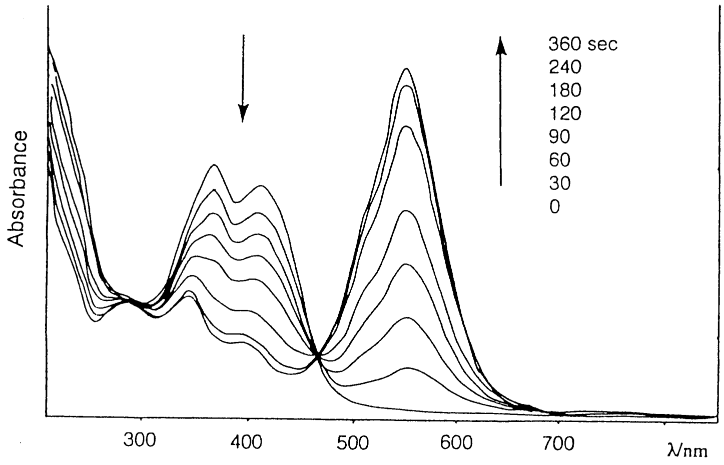


Fig. 1. UV-Vis spectral change of **2** upon reduction with 3% Na-Hg in THF.

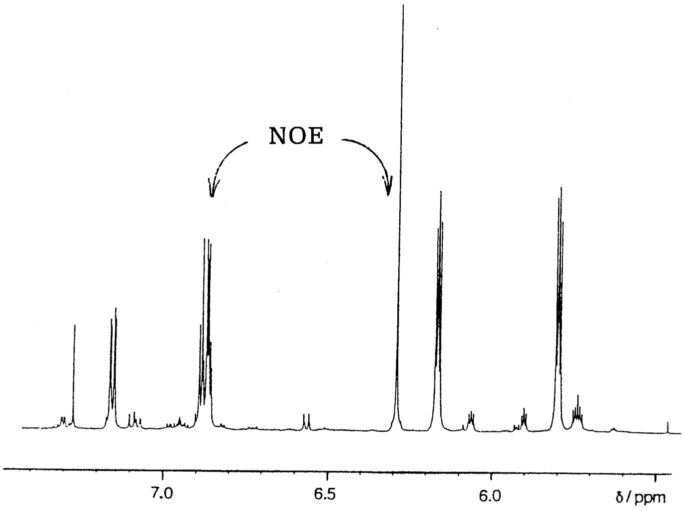
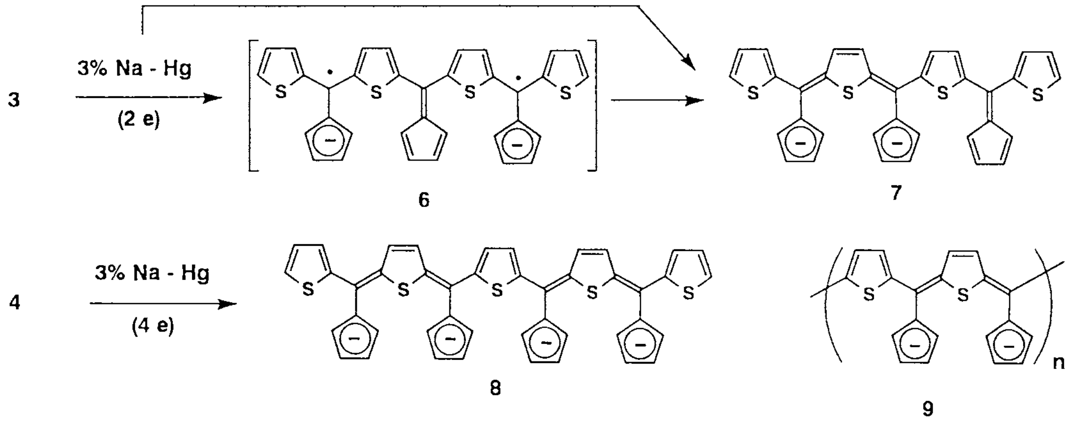


Fig. 2. ^{1}H NMR spectrum of **5** (270 MHz) at 30 °C in THF-d_8.

Upon similar reduction, trimer **3** ($^1E_{1/2}$ = -0.81 V, $^2E_{1/2}$ = -1.29 V, $^3E_{1/2}$ = -1.85 V; $^1E_{1/2}$ being of two-electron transfer) displayed almost the same final UV-Vis spectrum as dianion **5** except for intermediate appearance of a very broad absorption ranging from 600 to 1200 nm (λ_{max} = ca. 850 nm) (Table 1). No sharp ^{1}H signals were observed during this period. Therefore, radical species may be responsible for the broad absorption. ^{1}H and ^{13}C NMR spectra of the final solution are very complex because of lack of symmetry; however, careful examinations including NOE experiments lead to a conclusion that at least the major product is dianion **7**. The two-electron wave of $^1E_{1/2}$ and no appearance of broad absorption upon reduction of **2** preclude the radical species to be a monoanion radical. The NMR behaviors and rather weak reducing ability of 3% Na-Hg[7)] disfavor the formation of a trianion radical. A possibility is dianion diradical **6**. Although **6** and **7** are to be resonance forms each other at a planar conformation, **6** initially formed from conformationally labile and highly twisted **3** may be also twisted and need to pass some energy barrier to transform to **7**. This point, however, remains to be studied further.

UV-Vis spectral change of tetramer **4** ($^1E_{1/2}$ = -0.84 V, $^2E_{1/2}$ = -1.05 V; two-electron transfer each[5)]) upon reduction with the amalgam was similar to that of **3**, i.e. intermediate appearance of broad absorption at 650-1200 nm and final increase of absorption at 554 nm that is only slightly red-shifted from those of **5** and **7** (Fig. 3). ^{1}H and ^{13}C NMR spectra of the final product (Table 1) show C_2-symmetry of the molecule like **5**, indicating the formation of tetraanion **8** as the major product.



Thus, the successful alkali metal reductions of oligothienylpentafulvenes **2-4** to multi-anions **5**, **7** and **8** provide a good prospect for the synthesis of polythienylenemethines attached with cyclopentadienide groups from polythienyl-

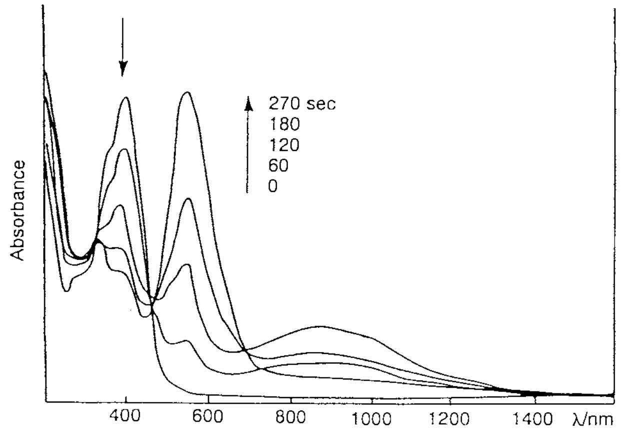


Fig. 3. UV-Vis spectral change of **4** upon reduction with 3% Na-Hg in THF.

pentafulvenes. However, the resemblance of UV-Vis spectra of dianion **5** and tetraanion **8** suggests that those polythienylenemethines are best represented as **9** where the dianion part behaves a repeating unit with rather small interaction each other.

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Table 1. Spectral data of **5a**, **7** and **8**

Compound[a)]	^{1}H-NMR[b)] δ ppm	^{13}C-NMR[c)] δ ppm	Vis. absorption[d)] λ_{max}/nm(log ε)
5a	5.80(t, J = 2.8 Hz, 4H), 6.17(t, J = 2.8 Hz, 4H) 6.17 (t, J = 2.8 Hz, 4H), 6.29 (s, 2H), 6.88(m, 4H), 7.15(dd, J = 4.8, 1.5 Hz, 2H)	106.92, 108.87, 120.99, 123.19, 123.53, 125.87, 127.22, 127.66, 133.50, 148.78	551 (4.6)
7	5.64(t, J = 2.7 Hz, 2H), 5.76 (m, 2H), 5.82(m, 4H), 6.19(t, J = 2.8 Hz, 2H), 6.21(t, J = 2.8 Hz, 1H), 6.27(t, J = 2.8 Hz, 1H), 6.32(d, J = 6.0 Hz, 1H), 6.50(d, J = 5.9 Hz, 1H), 6.62(dd, J = 3.3, 0.9 Hz, 1H), 6.69(d, J = 3.7 Hz, 1H), 6.79(m, 2H), 6.89(m, 2H), 7.02(dd, J = 5.0, 1.4 Hz, 1H), 7.19(dd, J = 5.0, 1.3 Hz, 1H),	102.69, 104.17, 106.66, 106.69, 106.95, 108.75, 108.95, 109.10, 117.17, 119.59, 120.45, 122.60, 122.89, 123.18, 123.40, 124.38, 125.90, 126.02, 126.07, 127.15, 127.46, 128.31, 129.02, 130.35, 133.37, 133.90, 146.05, 149.00, 153.06, 155.83	551 (4.9)
8	5.83(m, 8H), 6.21(t, J = 2.8 Hz, 4H), 6.33(t, J = 2.8 Hz, 4H), 6.39(d, J = 6.0 Hz, 2H), 6.60(d, J = 6.0 Hz, 2H), 6.82(s, 2H), 6.93(m, 4H), 7.19(dd, J = 3.9, 2.4 Hz, 2H)	102.69, 104.14, 106.47, 106.60, 120.49, 122.57, 122.83, 123.36, 125.85, 126.03, 127.15, 127.40. 128.51, 133.30, 134.13, 146.49, 149.10	553 (4.7)

a) Na-salts. b) In THF-d_8 at 270 MHz and 30 °C. c) In THF-d_8 at 67.8 MHz. d) In THF. The ε values are based on assumed 100% conversion.

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7) This amalgam could reduce neither benzophenone ($^1E_{1/2}$ = -1.73 V) nor 6,6-diphenylpentafulvene ($^1E_{1/2}$ = -1.44 V[6)]) under similar conditions.

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