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Preparation and Properties of 7-(1,3-Dithiol-2-ylidene)-7H-cyclopenta[1,2-b;4,3-b']dithiophenes and Their Polymers

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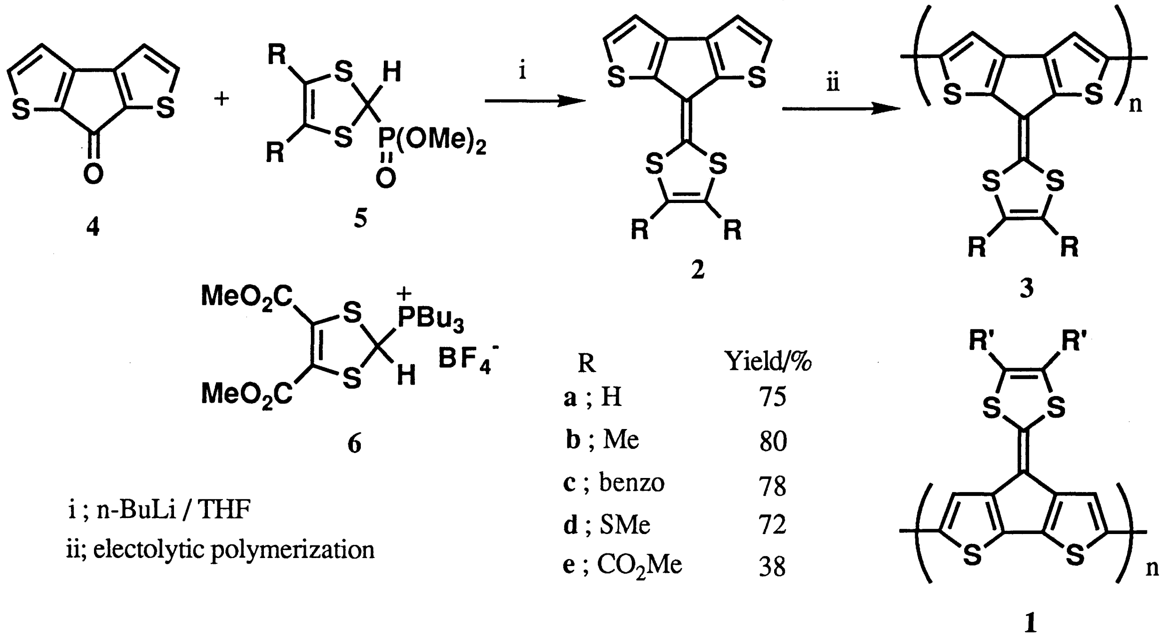
The title 1,3-dithiole compounds which were synthesized using a Wittig-Hornor reaction have a planar structure with both inter- and intramolecular short S···S contacts. Their electrochemical oxidation gave polythiophene derivatives which have lower oxidation potentials than polythiophene and the conductivity of the nonsubstituted derivative was 3.5 × 10^{-3} S cm^{-1}.

We have recently prepared poly-4-(1,3-dithiol-2-ylidene)-4H-cyclopenta[2,1-b;3,4-b']dithiophenes (**1**) which are novel polythiophene derivatives containing 1,3-dithiole rings.[1] They have relatively high conductivities. That study also showed that the introduction of 1,3-dithiole rings into polythiophene skeleton is useful to make the oxidation potentials low and the p-doping, conductive states stable. We have now synthesized 7-(1,3-dithiol-2-ylidene)-7H-cyclopenta[1,2-b;4,3-b']dithiophenes (**2**), a new type of 1,3-dithiole donors, where intramolecular S···S contacts are expected in addition to intermolecular ones. We have also succeeded in preparing the polymers **3** which are isomers of **1**, and investigated their properties.

1,3-Dithiole compounds **2a-d** were prepared by a Wittig-Hornor reaction of ketone **4**[2] with carbanions derived from the corresponding phosphonate esters **5a-d**[3] in 72-80% yields. Methoxycarbonyl derivative **2e**



R	Yield/%
a ; H	75
b ; Me	80
c ; benzo	78
d ; SMe	72
e ; CO_2Me	38

i ; n-BuLi / THF
ii; electolytic polymerization

Scheme 1.

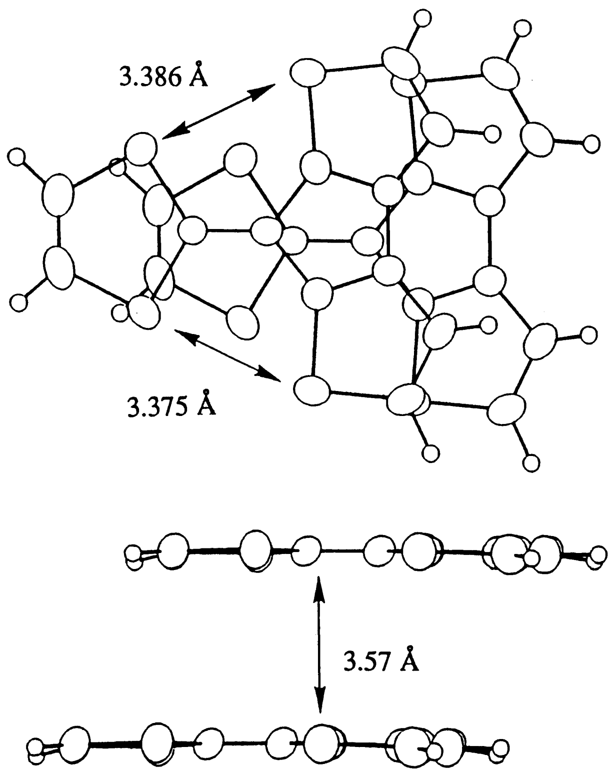


Fig. 1. Molecular structure and overlap mode of **2a**.

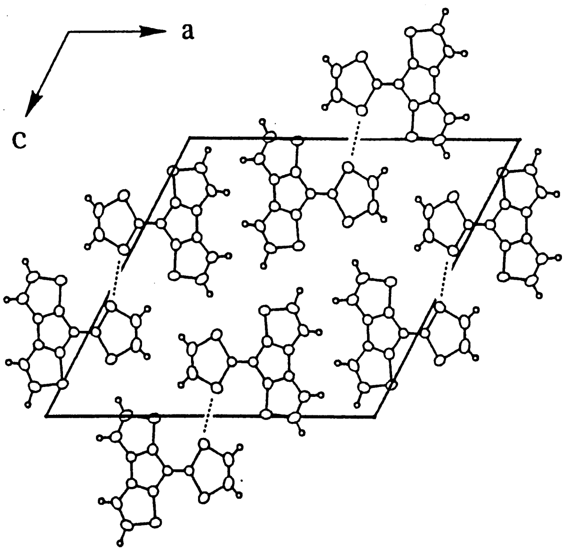


Fig. 2. Crystal structure of **2a**. Broken lines; S···S interections [3.603(2) Å].

was synthesized by a Wittig reaction of phosphonium compound **6**[4] with **4** in 38% yield (Scheme 1). They are air-stable yellow or orange solids whose absorption maxima are shown in Table 1. The absorptions containing electron-donating substituents are red-shifted, suggesting that some polarization takes place in **2**. The X-ray structural analysis of parent compound **2a** reveals that the molecule is almost planar and there are two intramolecular S···S distances (3.386 Å and 3.375 Å) which are shorter than the sum of the van der Waals radii (3.70 Å) as shown in Fig. 1.[5] The short distance may be useful for the delocalization of electrons through the S···S contacts. The crystal structure is shown in Fig. 2, where a short intermolecular S···S contact (3.603 Å) is observed. The molecules of **2a** are uniformly stacked along the b axis with good overlapping as shown in Fig. 1. A distance between molecular planes is 3.57 Å.

The cyclic voltammograms (CV) of the donors **2** showed irreversible waves. The peak oxidation potentials (E^{ox}) of **2** are summarized in Table 1. The values are significantly lower than that of bithiopene (1.44 V vs. SCE).[6] This fact is attributed to the electron-donating property of the 1,3-dithiole rings. The irreversible waves in the CV suggest the possibility of the occurrence of electrochemical polymerization.

Polymers **3** were actually prepared by electrolysis using a Pt disk as a working electrode in PhCN containing 0.1 mol $\mathrm{dm^{-3}}$ tetra-n-butylammonium perchlorate (TBAP) as a supporting electrolyte. The oxidation potentials of polymers **3** summarized in Table 1 are relatively low compared with that of polythiophene (1.03 V vs. SCE).[6] The CV of **3a** measured at various scan rates are shown in Fig. 3. The absorption spectrum of

Table 1. Oxidation potentials[a)] and absorption maxima of **2** and **3**

Monomer	$E^{ox\ b)}$	λmax/nm[c)]	Polymer	$E^{ox\ d)}$
2a	0.83	420	**3a**	0.72
2b	0.78	430	**3b**	0.73
2c	0.97	414	**3c**	0.76
2d	0.90	427	**3d**	0.77
2e	1.09	407	**3e**	0.84
bithiophene	1.44	232	polythiophene	1.03

a) 0.1 mol dm^{-3} n-Bu_4NClO_4 in PhCN, Pt electrode, V *vs*. SCE. b) Scan rate 100 mV s^{-1}. c) Scan rate 10 mV s^{-1}. d) In CH_2Cl_2.

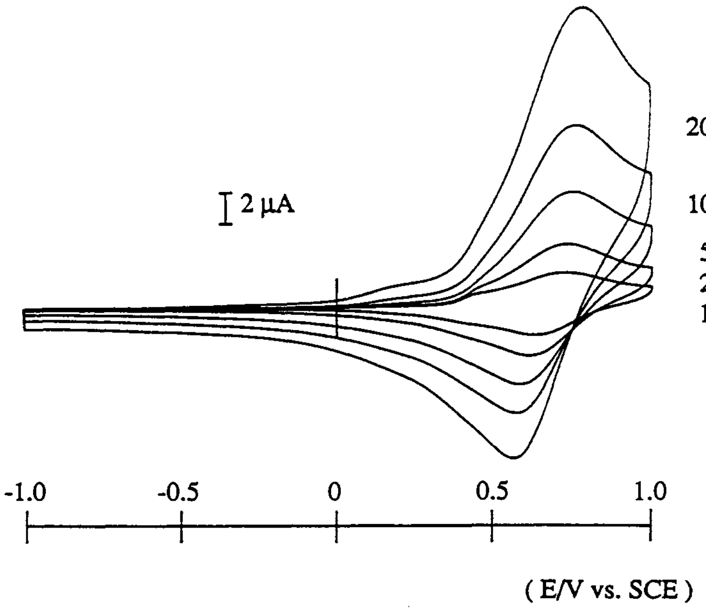


Fig. 3. Cyclic voltammograms of **3a** measured in a monomer-free PhCN / 0.1 M TBAP at various scan rates under an argon atmosphere. A platinum disk, and SCE were used as a working and a reference electrode, respectively.

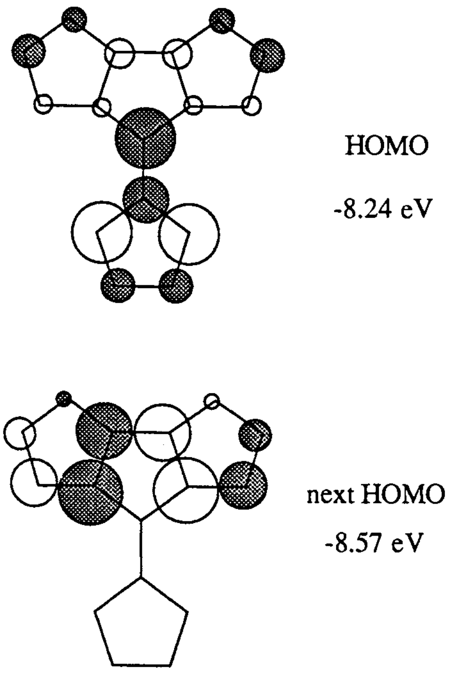


Fig. 4. HOMO and next HOMO of **2a**.

3a on an indium-tin oxide conducting glass (ITO) electrode showed a peak at 444 nm in the neutral state. A new peak could be observed around 730 nm on the oxidative film. The similar electrochromic behaviors were observed in the case of polymers **3b**-**e**.

The conductivity of **3a**[7)] measured by a four-probe method was 3.5 × 10^{-3} S cm^{-1} in the doping state. This value is lower than that of **1a** probably due to the unfavorable conjugation in **3a**. The superficial morphology of **3a** observed by a scanning electron microscope (SEM) was very smooth and flat while **1a** showed a granular appearance. MNDO calculations[8)] of **2a** show that the HOMO and next HOMO are close in energy (-8.24 and -8.57 eV, respectively) as shown in Fig. 4. Carbon atoms at the α-positions have larger AO coefficients than β-positions in both the HOMO and the next HOMO, suggesting that the polymerization selectively occurs at the former positions.

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5) Crystal data for **2a**: $C_{12}H_6S_4$, F_w = 278.42, monoclinic, space group $P2_1/n$, a = 18.297(5), b = 4.006(0), c = 17.220(0) Å, β = 118.05(1)°, V = 1113.9(4) $Å^3$, Z = 4, D_{calcd} = 1.96 g cm^{-3}. The structure was solved by the direct method using the MULTAN78 program9) and successive Fourier syntheses followed by the refinement by the block-diagonal least-square using UNICSIII10) with anisotropic temperature factors for non-H atoms and isotropic ones for H atoms. The final R value is 0.0776 for 1897 reflections with $|Fo| > 3\sigma|F|$. These calculations were carried out in the Computer Center of Institute for Molecular Science.
6) CV of bithiophene and polythiophene were measured using a Pt disk as a working electrode in PhCN containing 0.1 mol dm^{-3} TBAP as a supporting electrolyte.
7) The polymer **3a** was prepared for the conductivity measurement by the constant potential method at 0.70 V vs. SCE using an ITO electrode in PhCN containing 0.1 mol dm^{-3} tetraethylammonium p-toluenesulfonate. The thickness of the film was measured by SEM.
8) MNDO calculations11) [MOPAC program; J. J. P. Stewart, *Q. C. P. E. Bull.*, **3**, 43 (1983)] were performed by using the MNDO optimized geometry. These calculations were carried out in the Computer Center of Institute for Molecular Science.
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