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Facile Preparation and Charge-Transfer Complexes of Naphtho[1,8-*bc*:4,5-*b'c'*]dithiophene and 2,5-Dimethyl and Bis(methylthio) Derivatives

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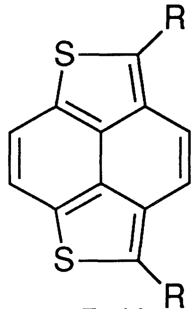
Naphtho[1,8-*bc*:4,5-*b'c'*]dithiophene was conveniently prepared via annulation of benzo[1,2-*b*:4,3-*b'*]dithiophene and converted to 2,5-dimethyl and bis(methylthio) derivatives. The parent and methylthio compounds have a herringbone type of crystal structures, and formed conductive charge-transfer complexes with iodine and with DDQ.

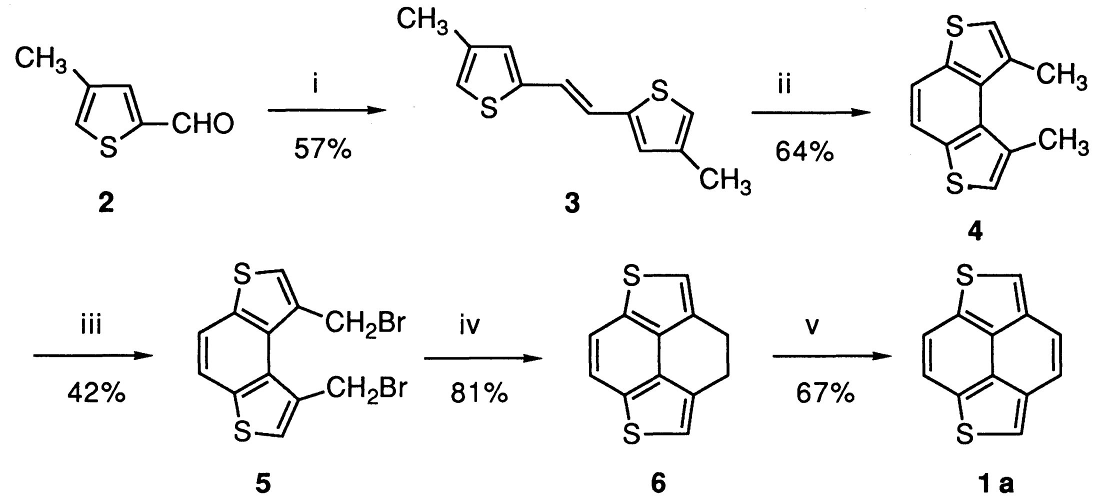
We recently reported the synthesis of naphtho[1,8-*bc*:4,5-*b'c'*]dithiophene (**1a**) as the first example of heteroarene isoelectronic with pyrene and found that it has a potentiality as a novel electron donor, though its donor character is rather weak.1) The synthetic route is based on a unique strategy via transannular dehydrogenation of [2.2](2,4)thiophenophane-1,8-diene, but has a disadvantage of requiring multisteps. In order to study the detailed properties of **1a** and to extend the research to its modified derivatives, it is necessary to develop an alternative synthetic approach. In this paper we like to report a convenient synthesis of **1a** via annulation of benzo[1,2-*b*:4,3-*b'*]dithiophene and the conversions to 2,5-dimethyl derivative **1b** and 2,5-bis(methylthio) derivative **1c**.2)

As shown in Scheme 1, the reductive coupling reaction of 4-methyl-2-thiophenecarboxaldehyde (**2**)3) with low-valent titanium gave *trans*-1,2-bis(4-methyl-2-thienyl)ethene (**3**) in 57% yield, which was subjected to photocyclization4) to 1,8-dimethylbenzo[1,2-*b*:4,3-*b'*]dithiophene (**4**) in 64% yield.5) The reaction of **4** with *N*-bromosuccinimide gave 1,8-bis(bromomethyl) derivative **5** in 42% yield, which was then treated with phenyllithium to afford 3,4-dihydronaphtho[1,8-*bc*:4,5-*b'c'*]dithiophene (**6**) in 81% yield. The dehydrogenation of **6** to **1a** was performed with DDQ in 67% yield.



1a: R=H
1b: R=Me
1c: R=SMe

The properties of **1a** were consistent in all respects with those of the sample previously obtained from [2.2](2,4)thiophenophane-1,8-diene. Recrystallization of **1a** from chloroform-hexane provided a good



Scheme 1. Reagents and conditions: i) $TiCl_4$, Zn, THF, reflux, 9 h; ii) hν, I_2, air, benzene, 8 h; iii) NBS, CCl_4, reflux, 1 h; iv) PhLi, THF, rt, 0.5 h; v) DDQ, toluene, reflux, 4 h.

single crystal which was subjected to an X-ray crystallographic analysis.[6] As shown in Fig. 1, the molecular structure is perfectly planar. Both bond lengths and bond angles are, however, strained. In the crystal structure of pyrene, the molecules are grouped in stacked pairs about the symmetry centers, and the pair units are packed so as to avoid any direct overlap.[7] On the other hand, that of **1a** consists of a herringbone type of uniform stacking columns (Fig. 2). The molecules are stacked face-to-face with van der Waals contact. There are no indications of close S-S contacts in the columns but of weak S-S interactions between the adjacent columns. This nonbonded heteroatomic interactions may possibly facilitate the herringbone type of crystal structure.

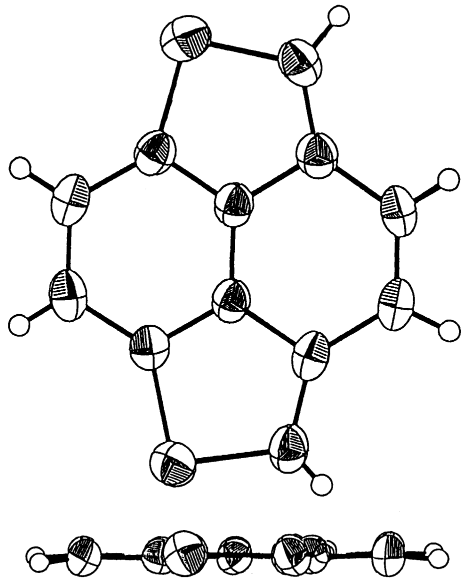


Fig. 1. ORTEP drawing of **1a**.

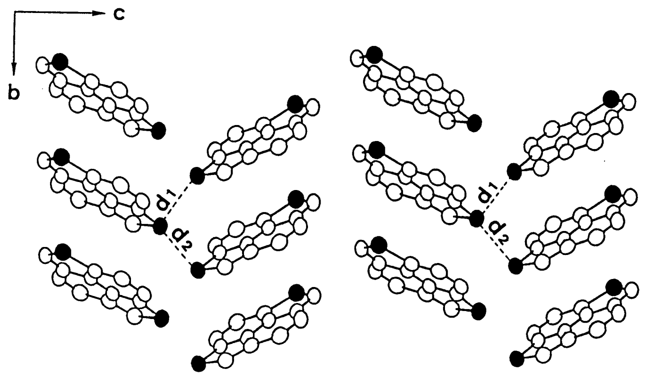
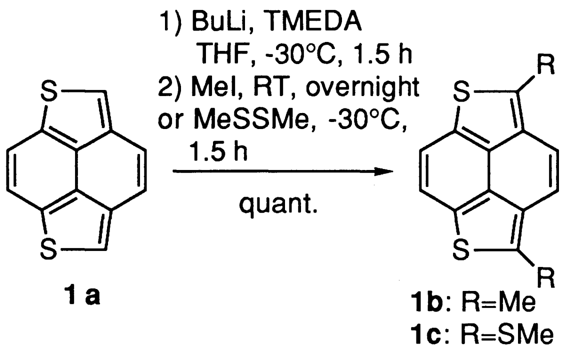


Fig. 2. Crystal structure of **1a** viwed along *a*-axis. (S-S Contacts d_1=3.767 Å, d_2=3.768 Å)



1a

1b: R=Me
1c: R=SMe

Scheme 2.

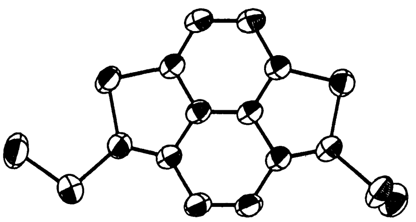


Fig. 3. Molecular structure of **1c**. (The hydrogen atoms are omitted)

A treatment of **1a** with excess butyllithium followed by methyl iodide and by dimethyl disulfide gave 2,5-dimethyl derivative (**1b**) and 2,5-bis(methylthio) derivative (**1c**), respectively, in quantitative yields. The molecular structure of **1c** revealed by an X-ray analysis has the essentially same skeleton as that of the parent **1a**, and one additional methylthio group lie parallel with the plane, but the remaining one lie perpendicular to it (Fig. 3).[8] The crystal structure of **1c** is also of a herringbone type. In this case, the intercolumnar interactions of the skeletal sulfurs are also present. On the other hand, the functional sulfurs do not participate in such heteroatomic interactions.

The cyclic voltammogram of **1a** showed one irreversible oxidation wave at +1.01 V vs. an Ag/AgCl standard electrode (Table 1). The repeated cycles induced polymerization, forming a black deposit on the working electrode. On the other hand, the two derivatives showed reversible cyclic voltammograms because of blocking the active α-sites of the thiophene rings. The oxidation potentials of these derivatives are much lower owing to conjugation of the substituent groups than that of **1a**, and **1c** shows not only the first oxidation wave but also the second one. Compound **1a** formed highly conductive complexes with DDQ and with iodine. Both complexes of methylthio derivative **1c** are also conductive, but it is not the case with those of the methyl derivative **1b**. The introduced methyl groups, though they serve to enhance the donor ability, may sterically hinder the formation of conductive complexes.

Table 1. Oxidation potentials[a] of **1** and conductivities[b] of their charge-transfer complexes

Compd	E_{ox} / V	$E_{1/2}$ / V	I_2 complex / S cm^{-1} (D:A)[c]	DDQ complex / S cm^{-1} (D:A)[c]
1a	+1.01	irreversible	0.92 (1:0.8)	2.1 (2:1)
1b	+0.92	+0.84	3.6×10^{-9} (1:0.5)	1.2×10^{-8}
1c	+0.77	+0.71, 0.97	1.3 (1:2)	5.5×10^{-2} (1:1)

a) Cyclic voltammetry was measured with an Ag/AgCl reference electrode and Pt working and counter electrodes at scan rate 100 mV/s in benzonitrile solution containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte at room temperature.
b) Conductivities were measured on compressed pellets at room temperature by a four-probe or two-probe method.
c) Compositions were calculated by elemental analyses. The D:A ratio of **1b**•DDQ complex was undecided.

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References

1) K. Watanabe, Y. Aso, T. Otsubo, and F. Ogura, *Chem. Lett.*, **1992**, 1233.

2) The authors very recently received an information from Prof. A. Moradpour that 2,5-dimethylnaphtho[1,8-*bc*:4,5-*b′c′*]dithiophene (**1b**) was formed by an acid-mediated cyclization of 2,7-dimethyl-1-benzo[1,2-*b*:4,3-*b′*]dithiophenylacetaldehyde. The authors thank him for sending them the preprint to be published in *J. Chem. Soc., Perkin Trans. 1.*

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5) All new compounds gave satisfactory elemental analyses. NMR measurements were conducted in deuteriochloroform. Selected properties and spectral data of **3** are follows: colorless prisms from hexane; mp 132 °C; ^{1}H-NMR δ 2.22 (d, J=0.8 Hz, 6H, CH_3), 6.75 (bs, 2H, ArH), 6.84 (s, 2H, ArH), 6.95 (s, 2H, olefinic H); MS m/z 220 (M^+). **4**: colorless prisms from hexane-benzene; mp 115-116.5 °C; ^{1}H-NMR δ 2.79 (s, 6H, CH_3), 7.16 (s, 2H, ArH), 7.73 (s, 2H, ArH); ^{13}C-NMR δ 21.63, 119.35, 123.56, 133.02, 134.31, 139.59; MS m/z 218 (M^+). **5**: colorless needles from chloroform; mp 130 °C (decomp); ^{1}H-NMR δ 5.36 (s, 4H, CH_2), 7.72 (s, 2H, ArH), 7.83 (s, 2H, ArH); ^{13}C-NMR δ 32.44, 120.32, 129.52; MS m/z 374, 376, 378 (M^+). **6**: colorless prisms from hexane-benzene; mp 109-109.5 °C; ^{1}H-NMR δ 3.17 (s, 4H, CH_2), 7.10 (s, 2H, ArH), 7.72 (s, 2H, ArH); ^{13}C-NMR δ 24.12, 118.37, 119.74, 129.94,132.07, 134.86; MS m/z 216 (M^+). **1a**: orange needles from hexane-chloroform; mp 187-188 °C; ^{1}H-NMR δ 7.30 (s, 2H, ArH), 7.54 (s, 2H, ArH), 7.96 (s, 2H, ArH); ^{13}C-NMR δ 119.21, 119.54, 122.30, 130.53, 132.30, 134.18; MS m/z 214 (M^+). **1b**: faint yellow needles from hexane; mp 96-97 °C; ^{1}H-NMR δ 2.74 (s, 6H, CH_3), 7.07 (s, 2H, ArH), 7.68 (s, 2H, ArH); ^{13}C-NMR δ 13.49, 118.09, 119.82, 127.49, 130.64, 133.57, 135.11; MS m/z 242 (M^+). **1c**: yellow needles from hexane; mp 80 °C; ^{1}H-NMR δ 2.61 (s, 6H, CH_3), 7.37 (s, 2H, ArH), 7.76 (s, 2H, ArH); ^{13}C-NMR δ 22.20, 119.04, 121.20, 132.47, 132.97, 133.46, 134.14; MS m/z 306 (M^+).

6) Crystal data of **1a**: M.W.=214.17, Monoclinic space group $P2_1$, a=7.837(1), b=4.128(0), c=14.035(4) Å, β=93.35(6) °, V=453.3(1) Å^3, Z=2, D_{calcd}=1.571, R=0.042 for 836 independent reflections.

7) R. Allmann, *Z. Kristallogr.*, **132**, 129 (1970).

8) Crystal data of **1c**: M.W.=306.49, Monoclinic space group $P2_1$, a=15.275(2), b=4.694(1), c=19.874(2) Å, β=111.12(8) °, V=1329.3(3) Å^3, Z=4, D_{calcd}=1.532, R=0.063 for 2081 independent reflections.

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