# SYNTHESIS OF TETRATHIENO-ACENE AND PENTATHIENO-ACENE:
UV-SPECTRAL TREND IN A HOMOLOGOUS SERIES OF THIENO-ACENES

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Summary: Tetrathieno-acene and pentathieno-acene were synthesized.   In UV-
visible spectra of a homologous series of thieno-acenes, the progressive red-
shift of the longest wavelength band exhibited an excellent linear correlation
with the number of thiophene rings.

There is new interest in the thiophene-condensed π-system because of the
possibility that it could provide new electron donors[1] or acceptors[2] for
conducting charge-transfer complexes and new monomer components for conducting
polymers.[3,4] Thieno[3,2-b]thiophene[5] **1** and dithieno[3,2-b:2',3'-d]thiophene[6] **2**
have been polymerized to form conducting polymers.[3] We have now prepared two
higher homologues of linearly condensed polythiophene, **3** and **4**, as promising
precursors for organic conductors. A homologous series of these compounds
corresponds structurally, in the sense of linear condensation, to acenes in
polynuclear aromatic compounds. Accordingly, this series of compounds should be
called **thieno-acenes**. In this communication we also demonstrate the interesting
trends observed for UV-visible spectra of the thieno-acenes in hand.
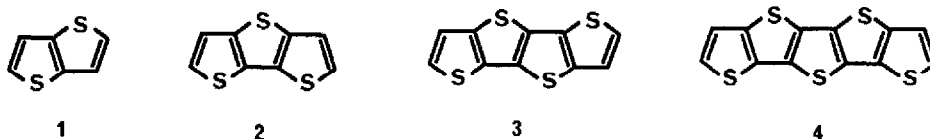
The key intermediate for the synthesis of both **3** and **4** is 3-
bromothieno[3,2-b]thiophene **5**, which could be prepared according to the route
outlined in Scheme 1. This procedure is much easier to perform and gives
improved yield over that reported by Bugge,[7] which requires the synthesis of
thieno[3,2-b]thiophene itself. Treatment of **5** with n-butyllithium and then the
dithienyldisulfide afforded **6** in 82% yield. The oxidative ring closure of **6** by
using $CuCl_2$ afforded crude **3** in 60% yield. This was purified by sublimation in
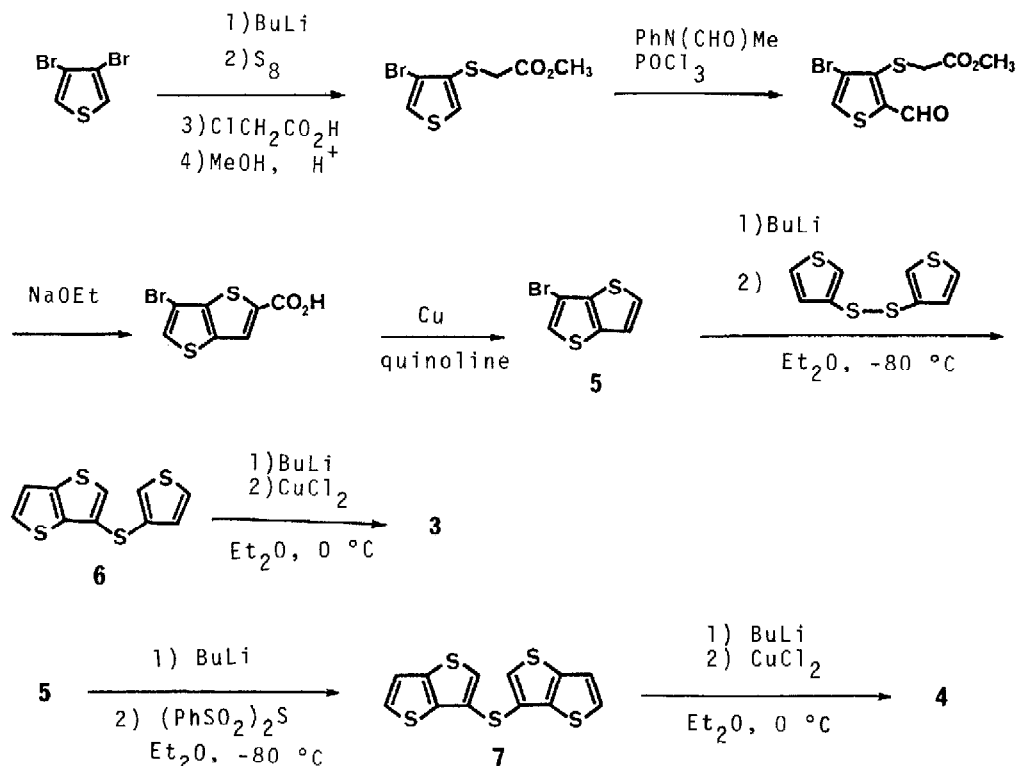
Scheme 1

vacuo to give colorless prisms. mp 220 °C. ^{1}H-NMR(CDCl$_3$); δ 7.37(d), 7.31(d),
J=5.3 Hz. ^{13}C-NMR(CDCl$_3$); δ 140.9(s), 133.2(s), 132.4(s), 126.7(d), 121.4(d).
Mass; m/e 252(M$^+$), 126(M^{2+}).

Pentathieno-acene 4 was prepared in a similar way, as illustrated in
Scheme 1. Sulfide 7 was obtained from 5 and bis(phenylsulfonyl)sulfide in 23%
yield. The yield of the oxidative ring closure of 7 was moderate (15-20%),
presumably due to the solubility problems of 7. Pure pentathieno-acene 4 was
isolated by column chromatography on silica gel as slightly yellow solids. mp
130 °C (decomp.). ^{1}H-NMR(CDCl$_3$); δ 7.39(d), 7.33(d), J=5.1 Hz. Mass; m/e
308(M$^+$), 154(M^{2+}).

Tetrathieno-acene 3 exhibited a low ionization potential of 7.52 eV as
determined from photoelectron spectroscopy[8] and formed the crystalline 1:1
charge-transfer complex with TCNQ. The conductivity measured on a single
crystal of the complex falls in the range of semiconductors (10^{-6} Scm^{-1}).

The solubility of 4 in common organic solvents was low. Solubility was
best in chloroform, where 4 decomposes gradually to give a greenish solution.
This might be ascribable to instability toward oxidation.

Figure 1 shows the ultraviolet absorption spectra for a series of thieno-acenes in CH_2Cl_2.[9] A significant trend is apparent. As the number of the thiophene rings increases, the maxima of absorption bands shift to longer wavelength. At the same time, the intensity of absorbance increases with lengthening of the thiophene annelation.[9] The longest wavelength exhibited an excellent linear correlation with the number of the thiophene rings except for one (thiophene itself), as displayed in Fig. 2. A bathochromic shift of the longest wave length band has also been known in the acene series.[10] In the thieno-acene series, however, the increase in λ_{max}, per ring added, is less than that for the acenes; pentacene is blue-colored, whereas pentathieno-acene is almost colorless.

Polythieno-acenes have an isoelectronic structure with angularly condensed polynuclear aromatics, i.e., the naphthalene-phenanthrene-chrysene-picene series. The longest wavelength bands[11] of these hydrocarbon series are also plotted in Fig. 2 , exhibiting no linear correlations with the number of the benzene rings. Additional investigation is necessary for full understanding of the basis for the electronic state of a homologous series of thienoacenes. Work from such approach is currently underway.
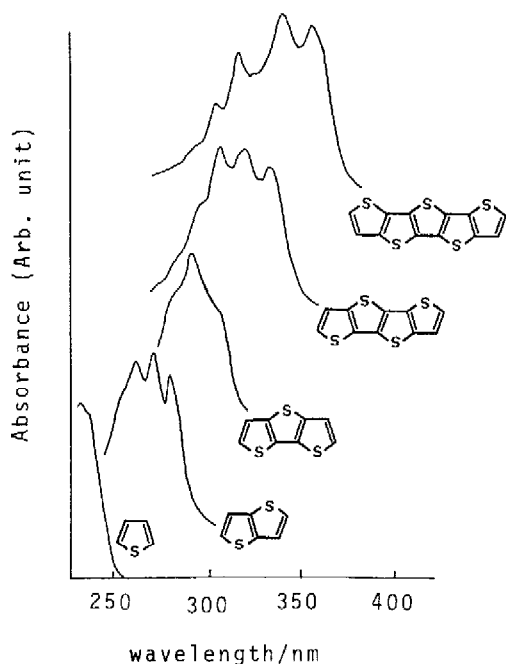

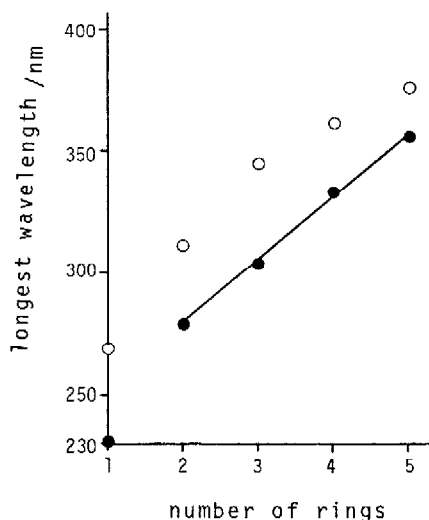Figure 1. Stacked plot of UV absorption spectra (CH_2Cl_2) of thieno-acenes.

Figure 2. The longest wavelength vs. the number of the rings in thieno-acene series (●) and in angularly condensed polynuclear aromatics (○).

References and Notes

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9   The λ_{max} and $\log \varepsilon$ in CH_2Cl_2 are as follow.
    1: 253(sh 3.93), 261(4.03), 270(4.05), 2.80(3.99).
    2: 282(sh 4.22), 292(4.34), 304(sh 4.17).
    3: 283(sh 3.91), 296(sh 4.27), 306(4.47), 320(4.46), 333(4.41).
    4: 296(sh 3.85), 305(4.16), 317(4.38), 327(4.31), 342(4.49), 357(4.46).

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11 The UV absorption data plotted in Fig. 2 for polynuclear aromatics of angular annelation are cited from, W. Schmidt, J. Chem. Phys., **66**, 828 (1977).