

Preparation of Thienyl-substituted Fulvalene and Tetrathiafulvalene Vinylogues as Electron Donors and Conductive Complexes derived from One of Them

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The thia-analogue **2** of the sixfold Hückel HOMO-degenerate tetrakis(cyclopentadienylidene)xylene biradical **3** and electron-donating tetrathiafulvalene analogues **9** and **13** have been prepared; **13** forms conductive charge-transfer complexes.

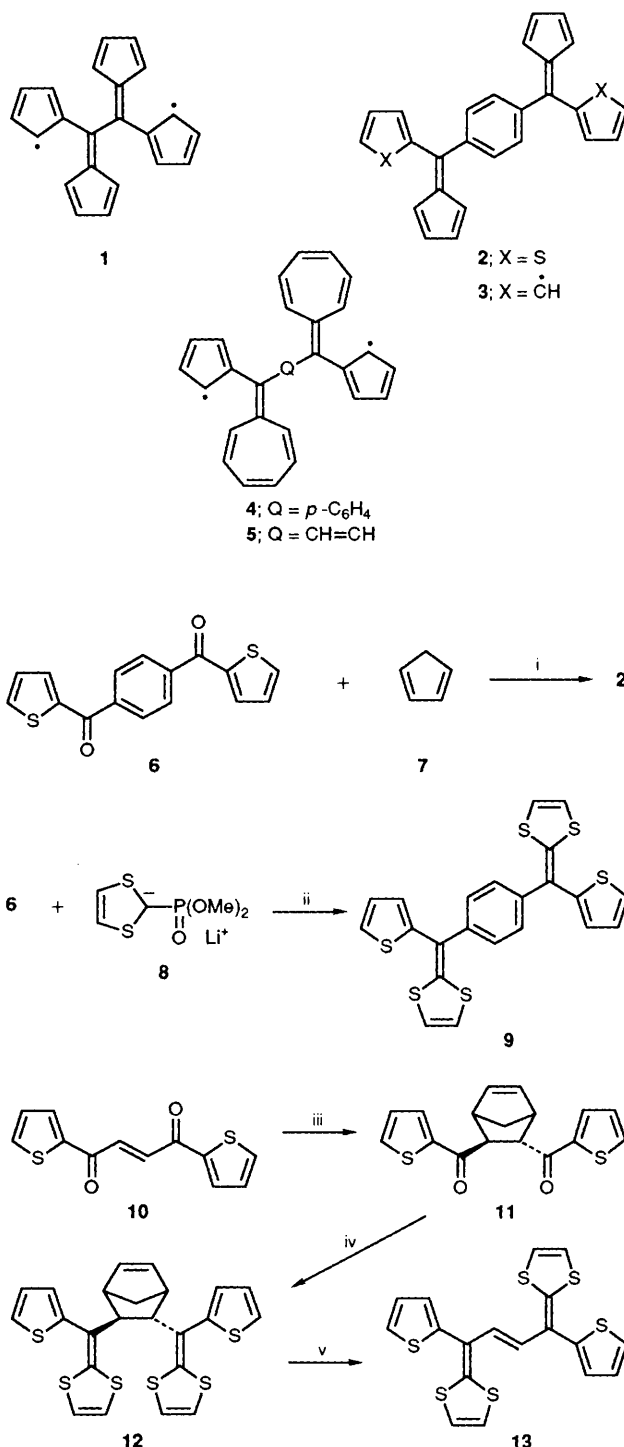
Highly degenerate Hückel systems are of current interest^{1,2} and as such, the study of the properties of stable hetero-analogues of the recently suggested sixfold HOMO-degenerate biradical **1** seemed worthwhile.¹ We report here the preparation of a dithiaphenylene analogue **2** and the structurally related electron-donating dithienyltetrathiafulvalene analogues **9** and **13**.

The base-catalysed condensation of cyclopentadiene **7** with 1,4-dithienylbenzene **6** gave the dithienyldicyclopentadienyldienylene† **2** (43% yield). The sixfold Hückel degeneracy is still retained with the corresponding hydrocarbon biradical **3**. Compound **2** is reversibly reduced by a two-electron process to the dianion at a half-wave potential of -1.63 V (vs. Ag/Ag⁺; DMF, dimethylformamide). However, oxidation to the dication corresponding to the biradical **3** could not be observed.

We next turned our attention to the closely related tetrathiafulvalene (TTF) analogues **9** and **13**, because the HOMO levels of these systems, as calculated by PM3-MNDO, are raised considerably (-8.32 and -7.95 eV) when compared with the fulvalene analogue **2** (-9.15 eV). They may be regarded as isoelectronic with the dianions derived from the heptafulvalene analogues **4** and **5**. The Wittig-Horner condensation of the dithiolyphosphonate anion³ **8** with 1,4-dithienylbenzene **6** gave the TTF phenylene analogue **9** (86% yield). Dithienylbutenedione **10** was converted to the cyclopentadiene cycloadduct **11** (90%), and the adduct was condensed with the phosphonate **8** to give **12** (67%). Pyrolysis of **12** gave the desired dithienyl-TTF vinylogue **13** (73%).

The TTF analogues **9** and **13** were found to be good electron donors: compound **9** undergoes a reversible and an irreversible single-electron oxidation at half-wave potential of 0.04 and peak potential of 0.23 V, respectively (vs. Ag/Ag⁺; DMF), while **13** is oxidised reversibly by a two-electron process to the dication at a half-wave potential of 0.02 V (vs. Ag/Ag⁺; MeCN). Compound **13** formed conductive charge-transfer (CT) complexes with tetracyanoquinodimethane (TCNQ) (*ca.* 1 : 2, 51% yield) and iodine (*ca.* 1 : 1; 97% yield). Two-probe conductivity measurements on a compressed powder pellet showed conductivities of 1.6×10^{-2} and 3.1×10^{-2} S cm⁻¹, respectively. The TCNQ complex shows an IR absorption of the nitrile group at 2205 cm⁻¹, which shows that charge transfer is 50% complete.⁴ The TCNQ complex is moderately soluble in organic solvents. Although the phenylene analogue **9** also formed a complex with TCNQ, it could not be isolated in a pure form.

Until recently, it was generally considered that only planar donor-acceptor pairs would show good electrical conductivity.⁵ Several planar extended TTF analogues, devoid of substituent(s) α to the dithiole rings, with a variety of 'spacer'



Scheme 1 Reagents and conditions: i, Bu^tOK in tetrahydrofuran (THF), 23 h at room temp.; ii, in THF, 1 h at -78°C , then 6.5 h at room temp.; iii, **7**, reflux 1.5 h in PhH; iv, **8**, in THF, 1.5 h at -78°C , then 13 h at room temp.; v, 180°C , 0.5 h

† All new compounds gave satisfactory spectral (UV, IR, ¹H and ¹³C NMR and mass) and combustion analytical data. ¹H NMR of **2**: δ 6.08–6.18 (2 H, m), 6.50–6.69 (4 H, m), 6.75–6.85 (2 H, m), 7.06–7.18 (4 H, m), 7.42 (4 H, s) and 7.55 (2 H, dd, *J* 4.5 and 1.9 Hz); **9**: δ 6.30 (2 H, d, *J* 6.7 Hz), 6.41 (2 H, d, *J* 6.7 Hz), 6.83 (2 H, dd, *J* 3.7 and 1.3 Hz), 7.02 (2 H, dd, *J* 5.0 and 3.7 Hz), 7.25 (2 H, dd, *J* 5.0 and 1.3 Hz) and 7.40 (4 H, s); **13**: δ 6.03 (2 H, s), 6.66 (2 H, d, *J* 6.6 Hz), 6.68 (2 H, d, *J* 6.6 Hz), 7.05 (2 H, dd, *J* 3.5 and 1.3 Hz), 7.16 (2 H, dd, *J* 5.0 and 3.5 Hz) and 7.65 (2 H, dd, *J* 5.0 and 1.3 Hz).

groups have been prepared.^{5a,6} They are generally good electron donors, and some of them form complexes showing conductivities comparable with those described here. Among analogues of **13**, the α,α' -unsubstituted compound formed only a transient unstable complex with TCNQ.^{6a} The α,α' -diphenyl analogue has been prepared, but it appears that it did not form a CT-complex with TCNQ.^{6a} This suggests a special role of the thiophene substituents of **13** in complex formation. A PM3-MNDO calculation on the neutral molecule of **13** shows that the thiophene plane is almost orthogonal (87°) to the dithiole plane, with the dihedral angle of 20° between the ethylene and the dithiole plane. It is noteworthy that nonplanar molecules such as **13** can form complexes with fairly high conductivities. Formation of conductive CT-complexes from nonplanar donors were reported recently.^{7,8} These reports as well as the findings described above would suggest that planarity may not be an important factor in designing components for conductive complexes.

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