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Cisoid conjugated dithienylene compounds as precursors for electropolymerisation

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Abstract

New conjugated dithienyl polyenes bearing an ethylene or butadiene linkage rigidified in a *cisoid* configuration are synthesised and their electrochemical and optical data studied.

Keywords: thiophenes; thiocarbonyl compound; disufide; ultraviolet spectra–use electronic spectra.

Terthienyls (3Ts) have led to a sustained interest related to their biological activities[1] and especially to their use as building blocks for the preparation of π-conjugated oligomers and polymers.[2] Whereas it is generally acknowledged that due to the limited reactivity of their cation radicals terthienyls are not the most appropriate precursors for electrochemical synthesis of poly(thiophene)s, they represent interesting compounds for the modelling of the relationships between the structure and electronic properties of the related oligomers and polymers. Recently, it has been shown that rigidification of the 3T or dithienyl polyenes systems by covalent bridging led to a significant enhancement of the effective conjugation in the precursors and in the resulting electrogenerated polymers.[3] As a further step in this direction, we describe here synthetic routes to precursors **3**, **4** and **5** in which the ethylene or butadiene linkage is rigidified in a *cisoid* configuration.

Dithienyl-1,4-diketone **1** was prepared according to a known procedure.[4] When treated with dibromomethane and potassium *tert*-butoxide in anhydrous DMSO this substrate undergoes a double *C*-alkylation affording the diketocyclopropane **2** (44% yield). Treatment of **1** with dichloromethane under the same conditions leads mainly to a double *O*-alkylation to yield dioxepine **3** (39%)[5] (Scheme 1).

A McMurry reaction performed on diketocyclopropane **2** leads to compound **4** in 44% yield,[6] while thionation with Lawesson's reagent affords disulfide **5** in 30% yield (Scheme 2). The structure of compound **5** was elucidated on the basis of its spectral properties (2D NMR COSY experiments, etc.) and elemental analysis.[7]

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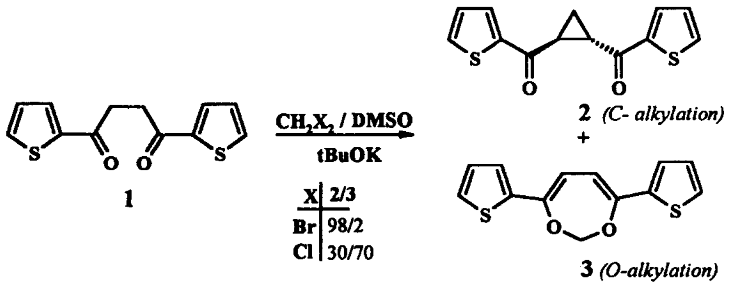
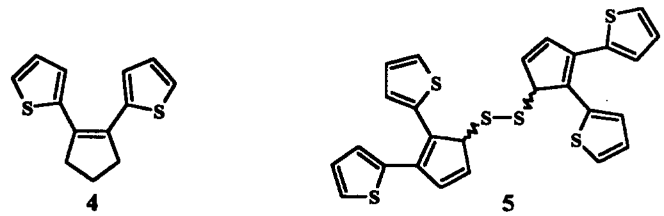
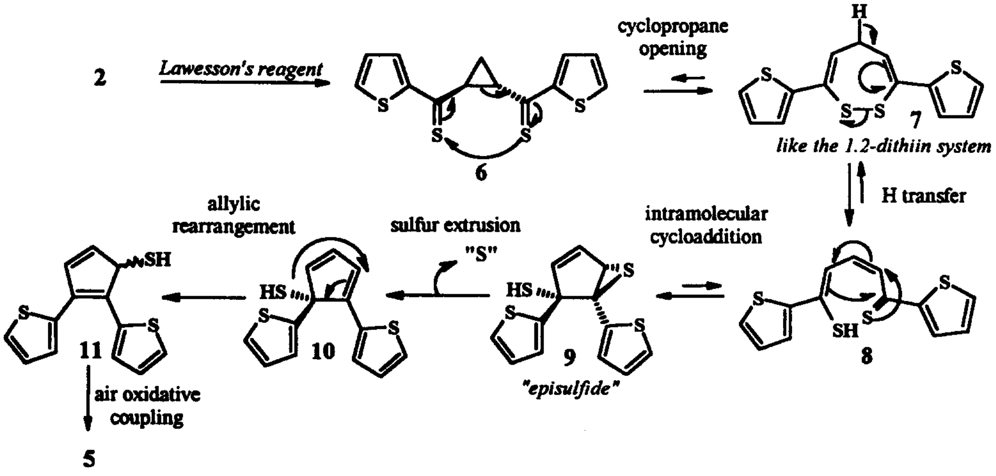


Scheme 1.



Scheme 2.

A plausible mechanism for this unexpected formation could involve the pathway depicted in Scheme 3. Initial thionation of the diketone **2** with Lawesson's reagent leads to the corresponding dithioketone **6**. This compound undergoes a cyclopropane ring opening leading to **7** with a structure like the 1,2-dithiin system recently described by Schroth.[8] A subsequent proton transfer followed by an intramolecular cycloaddition leads via the thiol **8** to the episulfide **9**. Sulfur removal to afford **10** is a familiar process in episulfide chemistry.[9] Finally, the disulfide **5** is supplied from an allylic rearrangement allowing a better conjugation in the thiol **11** followed by air oxidative coupling. Due to the presence of two asymmetric carbons, compound **5** is obtained as a mixture of two diastereomers as confirmed by ^{13}C NMR.[7]



Scheme 3.

Table 1 lists the values of the anodic peak potentials and UV–vis absorption maxima of the various *cisoid* compounds compared to those of their respective open chain *transoid* analogues, namely dithienylbutadiene (DBT) and dithienylethylene (DTE).

As could be expected, all *cisoid* compounds absorb at shorter wavelengths than their respective

Table 1
Electrochemical and UV–vis data for compounds 3–5

Compound	Epa (V vs SCE)	λmax (nm)
3	0.93	360
DTB	1.02	380
4	1.18	300
5	1.32	318
DTE	1.10	340

transoid analogues. While this result corresponds to the well-known shorter effective conjugation of *cisoid* conjugated systems,[10] steric hindrance to conjugation in the bridged systems probably contributes to a further shortening of the effective conjugation. Similar reasons can account for the higher oxidation potentials of the bridged compounds **4** and **5** compared to DTE. In contrast, the Epa value for compound **3** reveals a 90 mV negative shift of Epa which can be attributed to the electron-releasing effect of the two oxygen atoms in the bridging system.

Attempts to electropolymerise compounds **3** and **4** in potentiodynamic conditions remained unsuccessful. In the case of compound **5**, applications of recurrent potential scans between 0.0 and +1.32 V led to the electrodeposition of an electroactive material. However, the resulting deposit exhibits a rather ill-defined voltammogram with an anodic wave around 1.25 V. This is ca. 0.30 V higher than that of poly(DTE) suggesting a rather limited degree of polymerisation for poly(**5**).

To summarise, new conjugated precursors rigidified in a *cisoid* configuration have been synthesised. Electrochemical and optical data show that these compounds exhibit a shorter conjugation than their *transoid* analogues and are less convenient precursors for electropolymerisation.

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5. Cyclopropane-1,2-dicarbonyl-2,2′-bisthiophene **2** and 1,3-dioxepine-4,7-diyl-2,2′-bisthiophene **3**: A mixture of diketone **1** (0.25 g, 1 mmol) and potassium *tert*-butoxide (0.224 g, 2 mmol) in anhydrous DMSO (10 mL) under a nitrogen atmosphere was stirred for 10 min. Dibromo- or dichloromethane (3 mmol) was then slowly added and the mixture was stirred at room temperature for 30 min. After quenching with distilled water, the solution was extracted with CH_2Cl_2 (3×40 mL). The combined organic layers were successively washed with a saturated solution of NH_4Cl and brine, dried over Na_2SO_4, and evaporated in vacuo. The crude product was chromatographed (silica gel, cyclohexane:ethyl acetate, 9:1) to give cyclopropane **2** (0.115 g, 44% yield) with dibromomethane as reactant or dioxepine **3** (0.102 g, 39% yield) with dichloromethane as reactant. Selected data for products **2**: Pale yellow solid, mp 110°C; IR (KBr): 3080, 1630 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.80 (dd, ^3J=7.0 and 7.3 Hz, 2H), 3.28 (dd, ^3J=7.0 and 7.3 Hz, 2H), 7.17 (dd, ^3J=3.8 and 4.9 Hz, 2H), 7.70 (dd, ^3J=4.9 Hz, ^4J=1.1 Hz, 2H), 7.89 (dd, ^3J=3.8 Hz, ^4J=1.1 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 19.5, 28.9, 128.3, 132.6, 134.3, 144.0, 189.7; MS (EI, 70 eV) *m/z*: 262 (M^+, 31), 178 (4), 151 (20), 123 (7), 111 (100), 83 (9); **3**: dark

yellow solid, mp 120°C; IR (KBr): 2900, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.61 (s, 1H), 5.75 (s, 2H), 7.01 (dd, ^3J=4.0 and 4.8 Hz, 2H), 7.23 (dd, ^3J=4.8 Hz, ^4J=1.1 Hz, 2H), 7.23 (dd, ^3J=4.0 Hz, ^4J=1.1 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 93.5, 99.2, 123.2, 125.1, 127.6, 139.6, 152.8; MS (EI, 70 eV) *m/z*: 262 (M$^+$, 83), 232 (100), 203 (27), 171 (24), 121 (21), 116 (12), 111 (34), 83 (6).

6. Cyclopent-1-ene-1,2-diyl-2,2′-bisthiophene **4**: In a round bottomed flask, dry THF (7 mL) and zinc dust (0.261 g, 4 mmol) were introduced under a nitrogen atmosphere. After cooling to 0°C, $TiCl_4$ (0.2 mL, 2 mmol) was slowly added, and the mixture was refluxed for 1 h. After cooling to 0°C, a solution of diketone **2** (0.131 g, 0.5 mmoL) in dry THF (4 mL) was added dropwise and the mixture was refluxed for at least 3 h. The cooled mixture was hydrolysed with distilled water, and extracted with diethyl ether (3×40 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The crude product was chromatographed (silica gel, heptane:ethyl acetate, 95:5) to give the title compound **4** 0.051 g (44% yield) as a pale yellow oil. IR (KBr): 2920, 2840, 1680, 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.07 (m, 2H), 2.91 (t, ^3J=7.3 Hz, 2H), 7.00 (dd, ^3J=3.6 and 4.8 Hz, 2H), 7.04 (dd, ^3J=3.6 Hz, ^4J=1.1 Hz, 2H), 7.24 (dd, ^3J=4.8 Hz, ^4J=1.1 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 22.3, 40.1, 125.5, 126.3, 127.0, 132.2, 140.0; MS (EI, 70 eV) *m/z*: 232 (M$^+$, 100), 217 (10), 203 (11), 199 (10), 184 (12), 147 (12), 97 (10).
7. Bis[1,2-di(2-thienyl)]-5,5′-dithiobiscyclopenta-1,3-diene **5**: A mixture of diketone **2** (0.639 g, 2.44 mmol), Lawesson's reagent (1.18 g, 2.92 mmol) and dry toluene (20 mL) was slowly heated to reflux and maintained under reflux for ca. 1 h, until H_2S formation ceased. The mixture was allowed to cool to room temperature and the solvent removed. The crude product was chromatographed (silica gel, petroleum ether:CH_2Cl_2, 9:1) to give disulfide **5** 0.193 g (30% yield) as a white solid, mp 165°C (from diethyl ether/CH_2Cl_2); IR (KBr): 3060, 2840, 1600, 1430, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.13 (s, 2H), 6.72 (d, ^3J=13.6 Hz, 2H), 6.84–6.91 (m, 4H), 6.88 (d, ^3J=13.6 Hz, 2H), 6.97 (dd, ^3J=3.7 and 5.1 Hz, 2H), 7.08 (m, 2H), 7.15 (m, 4H); ^{13}C NMR ($CDCl_3$, a lot of ^{13}C signals occur as pairs due to the presence of two diastereomers): δ 49.92 (122.85, 122.95), (123.25, 123.90), (123.95, 123.97), (124.32, 124.36), (125.70, 125.75), (126.30, 126.37), (126.40, 126.45), 127.54 (136.28, 136.31), 137.32 (144.54, 144.60), (144.98, 145.05); MS (CI): 540 (M+NH_4^+). Anal. calcd: C (59.77) 59.93; H (3.83) 3.73; S (36.78) 37.06.
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