1,6-Bis(5,2′: 5′,2″-terthiophene-2-yl)spiro[4.4]nona-1,6-diene: a Molecule having Two Orthogonally Bisected α-Terthiophene Systems through a Spiro Carbon

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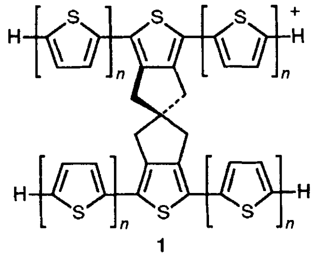
The title compound **11**, a molecule having two orthogonally bisected α-terthiophene systems through a spiro carbon, has been synthesized starting from spiro[4.4]nona-1,6-dione and 5,2′ : 5′,2″-terthiophene-2-ylcerium reagent.

Aviram has suggested that molecules that contain a proconducting (nondoped or nonoxidised, hence insulating) polymer that is fixed at a 90° angle *via* a nonconjugated σ-bonded network to a conducting (doped or oxidised system) should exhibit properties that would make it suitable for interconnection into future molecular electronic devices.[1] Molecule **1** (in doped form) is an example of this proconducting–σ–conducting type of molecule. In this connection, very recently, Tour



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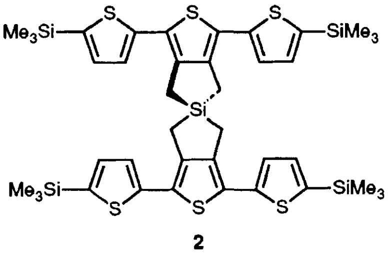

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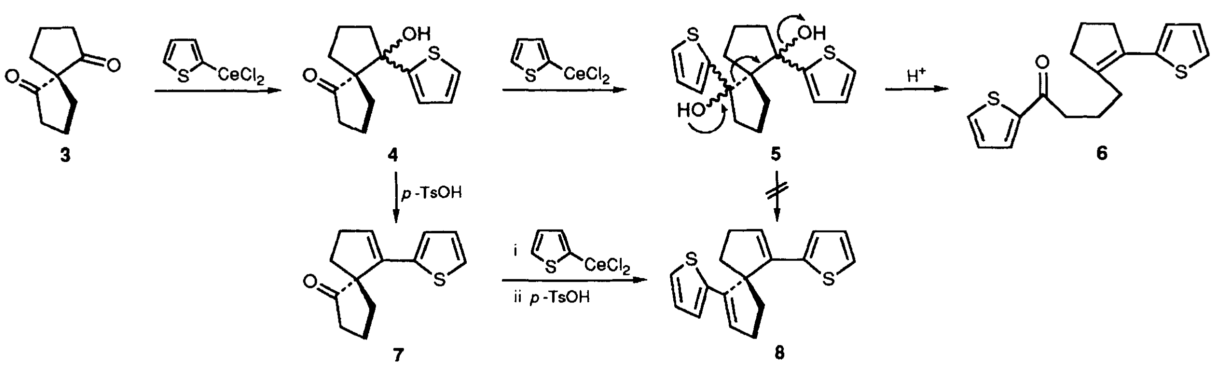

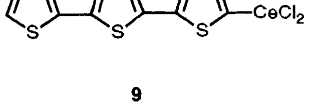

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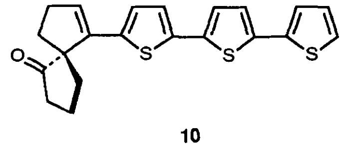

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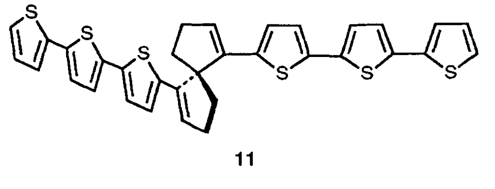

11

et al. have reported the preparation of compound **2** and related compounds.[2] We report the preparation of another type of compound **11** that contains two α-terthiophene systems bisected orthogonally through a spiro carbon.†

Prior to the preparation of the target molecule **11**, we have examined the synthesis of a simpler spiro compound **8** as a model of **11** using the spiro diketone **3**[3] as the starting material. The reaction of **3** with 2 equiv. of 2-thienylcerium reagent [prepared from 2-thienyllithium and cerium(III) chloride][4] in tetrahydrofuran (THF) afforded the expected diol **5** in 66% yield. The diol **5** is highly sensitive to acids and undergoes a facile fragmentation to give the ring-opened product **6** quantitatively on treatment with *p*-toluenesulphonic acid (TsOH).[5] Unfortunately no dehydration leading to **8** occurred. We therefore prepared the alcohol **4** by reaction of **3** with 1 equiv. of the 2-thienylcerium reagent. The resulting alcohol **4**, which is thermally labile and also acid-sensitive, was immediately converted to the ketone **7** (46%) by treatment with TsOH. The same ketone was also obtained by reaction of **3** with excess 2-thienylmagnesium bromide‡ followed by treatment with TsOH. Finally the reaction of **7** with the 2-thienylcerium reagent followed by acidic work-up (TsOH) afforded the expected spiro compound **8**§ in 30% yield.

On the basis of these results, we have succeeded in the synthesis of the target compound **11**. Thus, the reaction of **3** with the cerium reagent **9**, prepared from the corresponding lithium reagent (obtained by treatment of 2,2′:5′,2″-terthiophene with 1 equiv. of n-butyllithium at −78 °C) and cerium(III) chloride, in THF and treatment of the resulting alcohol with TsOH gave the ketone **10**§ in 28% yield. Finally the reaction of **10** with **9** (excess) in THF and the acid-catalysed dehydration of the resulting alcohol afforded the desired spiro compound **11**§ in 24% yield.¶ Both compounds **10** and **11** have an absorption maximum at 380 nm, although the molar absorptivity of **11** is nearly double that of **10**,§ thus indicating the absence of interaction between the two terthiophene units.

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† All new compounds gave satisfactory elemental analysis results or high-resolution mass spectrometric results.

‡ 2-Theinyllithium fails to give the diol **4** on reaction with **3**.

§ *Selected data* for **8**: m.p. 73.5–74.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* 5.0 Hz, 2H), 6.99 (d, *J* 3.5 Hz, 2H), 6.62 (dd, *J* 5.0 and 3.5 Hz, 2H), 6.15 (t, *J* 2.7 Hz, 2H), 2.58–2.44 (m, 4H), 2.26–2.17 (m, 2H), 2.08–2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.01 (s), 139.49 (s), 128.23 (d), 127.29 (d), 123.61 (d), 123.60 (d), 65.32 (s), 36.40 (t), 30.42 (t); *m/z* [electron impact (EI)] 284 (M^+). For **10**: m.p. 132–132.5 °C; IR ν_{max}/cm^{-1} (KBr) 1732 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* 4.4 and 0.7 Hz, 1H), 7.13 (dd, *J* 3.6 and 0.7 Hz, 1H), 7.03 (d, *J* 3.8 Hz, 1H), 6.99–6.97 (m, 2H), 6.95 (d, *J* 3.8 Hz, 1H), 6.57 (d, *J* 3.8 Hz, 1H), 6.19 (t, *J* 2.6 Hz, 1H), 2.58–1.64 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 221.78 (s), 138.05 (s), 137.58 (s), 137.07 (s), 136.14 (s), 136.01 (s), 135.55 (s), 131.70 (d), 127.65 (d), 124.61 (d), 124.45 (d), 124.30 (d), 124.18 (d), 123.72 (d), 123.65 (d), 64.58 (s), 37.94 (t), 37.34 (t), 34.35 (t), 30.86 (t), 20.10 (t); *m/z* (EI) 382 (M^+); UV–VIS ($CHCl_3$) λ_{max}/nm 380 (ε 29 500). For **11**: m.p. 181.5–182.5 °C; IR ν_{max}/cm^{-1} (KBr) 3064, 2924, 1501, 1426, 787, 688; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* 5.2 and 0.9 Hz, 2H), 7.14 (dd, *J* 3.7 and 0.8 Hz, 2H), 7.04 (d, *J* 3.8 Hz, 2H), 7.01–6.99 (m, 4H), 6.90 (d, *J* 3.8 Hz, 2H), 6.18 (t, *J* 2.6 Hz, 2H), 2.58–2.54 (m, 4H), 2.29–2.22 (m, 2H), 2.11–2.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.75 (s), 138.66 (s), 137.25 (s), 136.45 (s), 135.99 (s), 135.17 (s), 128.74 (d), 127.86 (d), 124.84 (d), 124.39 (d), 124.34 (d), 124.10 (d), 124.06 (d), 123.63 (d), 65.17 (s), 36.46 (t), 30.57 (t); *m/z* (EI) 612 (M^+), 354, 325, 306 (M^{2+}), 252, 235, 209, 185, 169; UV–VIS ($CHCl_3$) λ_{max}/nm 380 (ε 50 300).

¶ Although we attempted the reaction of **10** with **9** under a variety of conditions, we were unable to improve the yield of **11**.