Synthesis and Properties of 2,5-Dimethylnaphtho[1,8-*bc*:4,5-*b'c'*]dithiophene as a New Electron Donor

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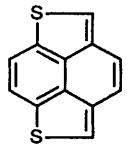
A new synthesis of 2,5-dimethylnaphtho[1,8-*bc*:4,5-*b'c'*]dithiophene **12** and its redox properties are reported.

The present very active studies into conducting molecular solids, were initiated, almost forty years ago, by a report on the halogen complexes of perylene.[1] Due to the rather high ionisation potentials of such planar polynuclear arenes, the stability of conducting materials produced therefrom are limited. A simple approach to the lowering of these oxidation potentials, resulting in far better stabilities, has been appropriate alkyl substitution of the arenes.[2] Of course, another possibility is the introduction of heteroatoms to reach this goal.[3–5] In this area, an interesting synthesis of the heterocycle **1**, an isoelectronic analogue of perylene has recently appeared,[5] but the proposed procedure failed to give the isomeric heteroarene **2**. Herein a new, versatile, synthesis of the nucleus **1**, namely 2,5-dimethylnaphtho[1,8-*bc*:4,5-*b'c'*]dithiophene **12** is reported.



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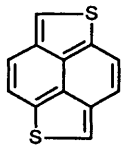

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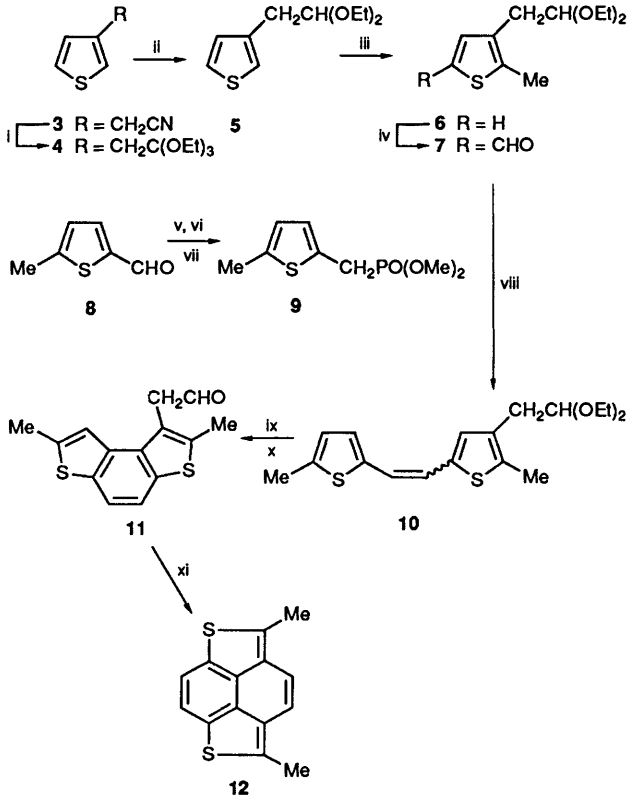
The synthesis was achieved starting from 3-thienylacetonitrile **3** and 5-methylthiophene-2-carbaldehyde **8** (Scheme 1). The thiophene **3** was first converted[6] into the orthoester **4*** (35%; b.p. 93–95 °C/1 mmHg) which was reduced to give the acetal **5**, with diisobutylaluminium hydride (DIBAH) in toluene (64%; b.p. 87–91 °C/1.2 mmHg).

The acetal **5** was metalated with butyllithium (BuLi) in ether at 20 °C and treated with dimethyl sulfate to give the methylated analogue **6** (40%; b.p. 70–72 °C/0.2 mmHg); the aldehyde **7** was obtained from compound **6** by a subsequent metalation of the unprotected C-5 position of the ring, under the same conditions, and reaction with *N*,*N*-dimethylformamide (DMF)[7] (71%; b.p. 123–124 °C/0.2 mmHg). On the other hand, the phosphonate **9** was obtained from the aldehyde **8** (overall yield 25%; b.p. 144–145 °C/2 mmHg) by successive $NaBH_4$ reduction to (5-methyl-2-thienyl)methanol (95%; b.p. 65–66 °C/0.3 mmHg), conversion into 2-chloromethyl-5-methylthiophene by $SOCl_2$ in CH_2Cl_2 (50%; b.p. 54–55 °C/0.5 mmHg) and finally by an Arbuzov reaction with neat trimethylphosphite. The di(thienyl)ethene **10** (stereochemistry not determined) was prepared from the aldehyde **7** and the phosphonate **9**† by a modified Wittig process in boiling dimethoxyethane (DME), using NaH as a base[8] (50%, yellow oil isolated by column chromatography on silica gel, eluting with toluene). The di(thienyl)ethene **10** was photocyclised in cyclohexane in the presence of iodine,[8] and compound **11** was isolated, after deprotection of the aldehyde, by column chromatography (silica gel, eluting with toluene) (yield 75%; yellow oil still containing a few percent of the unchanged acetal). The last step to 2,5-dimethylnaphtho[1,8-*bc*:4,5-*b'c'*]dithiophene **12** was a toluene-*p*-sulfonic acid (PTSA) mediated cyclisation in boiling toluene; the desired compound was also isolated by chromatography (silica gel eluting with toluene–hexane 50:50 v/v) [78%; yellow crystals, m.p. 98–98.5 °C (pentane)].



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Scheme 1 *Reagents and conditions:* i, HCl, EtOH; EtOH; ii, DIBAH, toluene, 30–35 °C; iii, BuLi–ether, room temp., $(CH_3O)_2SO_2$; iv, BuLi–ether, room temp., DMF; v, $NaBH_4$–iced H_2O; vi, NEt_3, $SOCl_2$ in CH_2Cl_2, 0 °C→reflux; vii, $P(OMe)_3$, reflux; viii, NaH, DME reflux; ix, *hv*, medium pressure Hg lamp, through pyrex; x, THF, H_3O^+; xi, PTSA, refluxing toluene

* All isolated new compounds were characterised by ^1H NMR spectroscopy (90 MHz; CCl_4; *J* in Hz) and by microanalysis. Selected data: **4**: δ_H 1.15 (9 H, t, *J* 7), 3.0 (2 H, s), 3.50 (6 H, q, *J* 7) and 6.90–7.15 (5 H, m); **5**: δ_H 2.85 (1 H, d, *J* 6), 4.55 (2 H, t, *J* 6) and 6.85–7.05 (5 H, m); **6**: δ_H 1.10 (6 H, t, *J* 7), 2.35 (3 H, s), 2.72 (2 H, d, *J* 5), 3.20–3.80 (4 H, m), 4.45 (1 H, t, *J* 5) and 6.75–6.90 (2 H, q); **9**: δ_H 2.40 (3 H, s); 3.15 (2 H, d, $^2J_{PH}$ 21) and 3.60 (6 H, d, $^3J_{PH}$ 11); **10**: δ_H 2.35 (3 H, s), 2.45 (3 H, s), 6.60 (1 H, br s), 6.65–6.95 (3 H, m) and 7.15 (1 H, s); **11**: δ_H ($CDCl_3$) 2.40 (3 H, s), 2.57 (3 H, s), 3.78 (2 H, d, *J* 2.5), 7.28 (1 H, s), 7.45 (2 H, s) and 9.48 (1 H, t, *J* 2.5); **12**: δ_H 2.64 (6 H, s), 6.81 (2 H, s) and 7.53 (2 H, s).

† At this point, if the isomeric [(2-methyl-3-thienyl)methyl]phosphonate is used in place of the phosphonate **9**, the same reaction sequence will lead to the type-**2** nucleus.

The cyclic voltammogram of compound **12** (CH_2Cl_2 in the presence of activated Al_2O_3) showed a quasi-reversible oxidation wave at +0.80 V *vs.* SCE. This value is much lower than that of perylene (+1.03 V *vs.* SCE[2]) and might be compared to the oxidation potential of 3,4,9,10-tetramethylperylene[2] (+0.80 V *vs.* SCE).

Work is presently in progress to extend this procedure to the synthesis of the type-**2** isomer, as well as to test the potentials of **12** as an electron donor for conducting solids.

Experimental

Photocyclisation of Compound **10**.—A stirred solution of **10** (3.20 g, 9.5 mmol) in cyclohexane (2.3 dm^3) containing iodine (50 mg) was irradiated with a 450 W Hanovia medium pressure mercury lamp equipped with a pyrex jacket. The progress of the reaction was followed by TLC, and the irradiation was stopped after all the starting material has been consumed (14 h). The solvent was evaporated and the residue, dissolved in a mixture of tetrahydrofuran (THF) (100 cm^3) and HCl (1 mol dm^{-3}; 30 cm^3), was stirred overnight. The THF was evaporated under vacuum, the product was extracted with ether, and the extracts were washed with water and dried ($MgSO_4$). Evaporation of ether and column chromatography over silica gel, eluting with toluene, afforded the photocyclised compound **11** (1.85 g, 75%) as a yellow oil, which was used without further purification in the next step.

References

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