Cyclobuta[1,2-*c*: 3,4-*c*′]dithiophene

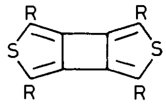
Michael K. Shepherd

Department of Pharmacology, University of Bristol, Bristol BS8 1TD, U.K.

Dithieno[3,4-*c*: 3′,4′-*e*]pyridazine *N*-oxide (7) has been synthesised in five steps from 3-iodothiophene-2-carbaldehyde; flash vacuum thermolysis of (7) gave the stable title compound (1).

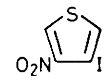
Cyclobuta[1,2-*c*: 3,4-*c*′]dithiophene (**1**) is predicted to be the most stable of the four isomeric dithia-analogues of biphenylene.[1] Despite numerous attempts to prepare (**1**) and its derivatives,[1—4] only one successful approach to this strained system has been reported.[5] Garratt and Neoh isolated the tetraphenyl derivative (**2**) from the reaction of *cis,trans,cis*-tetrabenzoylcyclobutane with P_2S_5. The phenyl substituents prevented an assessment of the paramagnetic contribution from the cyclobutadienoid ring, but the u.v. spectrum suggested some interaction between the two heterocyclic rings. Benzo[3,4]cyclobuta[1,2-*b*]thiophene[6] and a derivative[7] have recently been prepared by flash vacuum thermolysis; this method is here extended to the synthesis of the title compound (**1**).

Nitration of 3-iodothiophene-2-carbaldehyde (H_2SO_4, HNO_3, CH_2Cl_2; 0 °C) gave the 4-nitro derivative (**3**),† m.p. 120—121 °C (37%); δ_H ($CDCl_3$) 8.76 (5-H, d) and 9.94 (CHO, d), *J* 1.5 Hz. Oxidation of (**3**) (CrO_3, HOAc; 75 °C) gave the corresponding acid (**4**), m.p. 204—205 °C (73%); δ_H (CD_3COCD_3) 8.91 (5-H, s) and 11.2 (CO_2H, br.). Treatment of (**4**) with mercury(II) acetate (HgO, HOAc; 100 °C) followed by hydrolysis (H_2O, HCl, NaCl; 100 °C) gave 3-iodo-4-nitrothiophene (**5**), m.p. 65—67 °C (79%); δ_H ($CDCl_3$) 7.59 (2-H, d) and 8.33 (5-H, d), *J* 3.8 Hz. A conventional Ullmann coupling of (**5**) was unsuccessful, but under the conditions of Cornforth *et al.*[8] (MeCN, Me_2CO, aq. NH_3, Cu, $CuSO_4$; 25 °C) (**5**) formed 4,4′-dinitro-3,3′-bithienyl (**6**), m.p. 224—225 °C (86%); δ_H ($CDCl_3$) 7.30 (2-,2′-H, d) and 8.45 (5-, 5′-H,d), *J* 3.9 Hz. Cyclisation of (**6**) (C_6H_6, H_2O, Li_2S, 12-crown-4) gave dithieno[3,4-*c*:3′,4′-*e*]pyridazine *N*-oxide (**7**) as yellow crystals which decomposed sharply at 180 °C (sublimed >130 °C) (25%); δ_H ($CDCl_3$) 7.76 (1-H, d), 7.81 (8-H, d), 7.83 (3-H, d), and 8.44 (6-H, d), $J_{1,3}$ 3.2, $J_{6,8}$ 3.3 Hz. Attempted chemical reduction of either (**6**) or the *N*-oxide (**7**) to the dithienopyridazine (**8**) failed, but thermolysis‡ of (**7**) at 800 °C gave (**8**) as an air-sensitive yellow solid which decomposed above 140 °C (sublimed >110 °C) (22%); δ_H ($CDCl_3$) 7.79 (1-, 8-H, d) and 8.63 (3-, 6-H, d), *J* 3.1 Hz. Isolation of (**8**) is unnecessary, and thermolysis of (**7**) at 850 °C gave cyclobuta[1,2-*c*: 3,4-*c*′]dithiophene (**1**) as colourless



(1) R = H

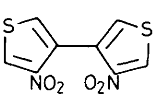
(2) R = Ph



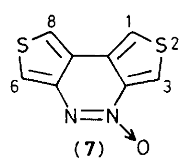
(3) R = CHO

(4) R = CO_2H

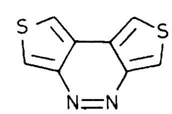
(5) R = H



(6)



(7)



(8)

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† New compounds gave satisfactory microanalytical and/or spectroscopic data.

‡ Extrusion reactions were performed using a 1 metre silica tube at 0.005 mmHg. The apparatus was kindly made available by Dr. J. W. Barton, Department of Chemistry, University of Bristol.

crystals, m.p. 120—121 °C (4%); δ_H ($CDCl_3$) 6.65, (C_6D_6) 6.10, δ_C ($CDCl_3$) 111.7 and 141.9 (quaternary); $\lambda_{max.}$ (EtOH) 231 (log ε 4.42), 318 (4.40), and 334 nm (4.41); *m/z* (%): 164 (M^+, 100) and 120 (M^+ − CS, 50).

The u.v. spectrum of (**1**) resembles that of biphenylene, but shows a pronounced hypsochromic shift. A smaller effect has been observed in the spectrum of benzo[3,4]cyclobuta-[1,2-*c*]thiophene.[9] This, in conjunction with the high-field shift of the ^1H n.m.r. spectrum, provides convincing evidence for conjugation between the two thiophene rings, and the associated presence of a paramagnetic current in the central cyclobutadienoid ring.

Received, 12th March 1985; Com. 326

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