

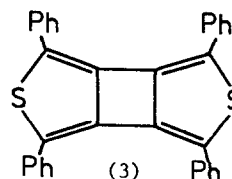
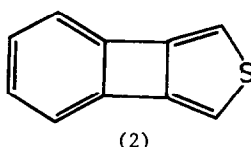
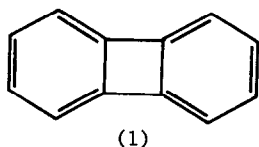
BENZO[3,4]CYCLOBUTA[1,2-b]THIOPHENE

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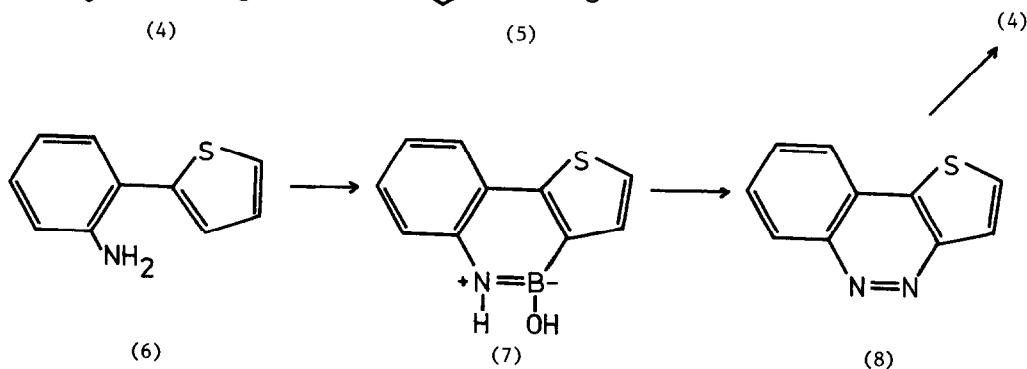
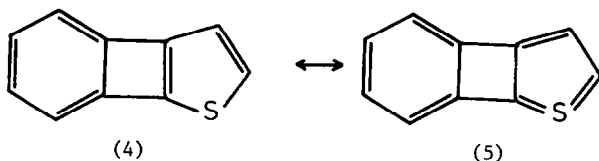
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Abstract: The synthesis of thieno[3,2-c]cinnoline is described; vapour phase thermolysis of this compound gives benzo[3,4]cyclobuta[1,2-b]thiophene.

The considerable stability of biphenylene, a system containing fused $4n$ and $(4n+2)$ π -electron rings, is associated with the fact that its structure corresponds closely to the canonical form (1),¹ which has a low total bond order, i.e. little cyclobutadiene character, in the four-membered ring.

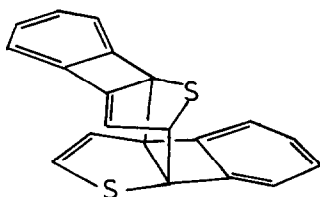


The same situation apparently exists in the thiophene analogues (2)² and (3)³, the synthesis and some chemistry of which have been described. It is therefore of interest to compare (2) with its isomer (4), which might be expected to have a much higher bond order in the four-membered ring than (2), even allowing for some contribution from forms such as (5) and the corresponding dipolar contributors. We now report the formation of (4) by thermal extrusion of dinitrogen from the cinnoline derivative (8), using a method similar to those previously employed for the synthesis of azabiphenylenes.⁴



Aprotic diazotisation of 2-nitroaniline dissolved in thiophene gave 2-(2-nitrophenyl) thiophene, which was reduced to the amine (6) with sodium hydrosulphide.⁵ Cyclisation of (6) with boron trichloride in refluxing xylene gave, after hydrolysis, the benzo[e]thieno[3,2-c]azaborine (7) (77%), which, on treatment with nitrous acid (c.f.⁶), was converted into thieno[3,2-c]cinnoline (8), m.p. 133-134°C, in 34% yield. Prominent peaks at 158.018 and 114.045 mass units in the mass spectrum of (8) indicated an initial loss of dinitrogen from the parent ion (M^+ 186.023; base peak), followed by the loss of a C-S fragment. Passage of the compound through a 50 cm silica tube at 830-840°C/0.005 Torr gave, after preparative T.L.C. on silica in benzene, benzo[3,4]cyclobuta[1,2-b]thiophene (4) (14%) as a pale yellow, air and heat sensitive oil; M^+ 158.019; λ_{\max} EtOH 207 (log ϵ 3.80), 226(3.90), 272(3.53), 283(3.55), 301(3.40), 327 nm (3.08).⁷ The ^1H N.M.R. spectrum of (4) in carbon tetrachloride shows the benzenoid protons as an AA'BB' system centred at τ 2.70 (H_4-H_7) and the thiophene-ring protons as doublets at τ 2.40 (H_2) and τ 2.72 (H_3); $J_{2,3} = 5$ Hz. In this case all the protons show normal benzenoid chemical shifts whereas they resonate at considerably higher field in biphenylene (1) (τ 3.3 - 3.4)⁸ and in (2) (τ 3.1 - 3.5).² This upfield shift has been attributed to a paramagnetic shielding effect⁸ which is obviously absent in (4), also the ultraviolet spectrum of (4) indicates less conjugation in the system than in (1) or (2).² The mass spectrum of (4) shows the initial loss of a C-S fragment and is almost identical with that of (8) after its first loss of dinitrogen.

Benzo[3,4]cyclobuta[1,2-b]thiophene undergoes extensive decomposition within a few hours at room temperature. A sample, kept under nitrogen for 1 week at 0°C, gave, after T.L.C. on silica in benzene, no recovered (4) but a low yield of dimeric product as a yellow oil. The ^1H N.M.R. spectrum of this product shows resonances centred at τ 5.95(1H), τ 4.77(1H), τ 3.98(2H) and τ 2.87 (8H), the multiple form of the peaks suggesting the presence of a mixture of isomeric (4+2) π dimers of (4), such as (9).



(9)

This is supported by the mass spectrum of the product, which shows reversion from a parent ion (M^+ 316.040) to monomer (M^+ 158.020; base peak).

REFERENCES

1. T.C.W.Mak and J.Trotter, *J.Chem.Soc.*, 1962, 1; J.K.Fawcett and J.Trotter, *Acta Cryst.* 1966, 20, 87
2. P.J. Garratt and K.P.C. Vollhardt, *J.C.S.Chem.Comm.*, 1970, 109; *J.Amer.Chem.Soc.*, 1972, 94, 7087.
3. P.J. Garratt and Soon Bin Neoh, *J.Org.Chem.*, 1975, 40, 970.
4. J.A.H.MacBride, *J.C.S.Chem.Comm.*, 1974, 359; J.W.Barton and R.B.Walker, *Tetrahedron Letters*, 1975, 569; S.Kanoktanaporn and J.A.H.MacBride, *Tetrahedron Letters*, 1977, 1817.
5. P.A.S. Smith and J.H. Boyer, *J.Amer.Chem.Soc.*, 1951, 73, 2626.
6. M.J.S. Dewar and W.E. Poesche, *J.Chem.Soc.*, 1963, 2201.
7. The log ϵ values are approximate owing to the instability of (4) in solution at room temp.; they serve only to indicate the relative intensities of the major peaks in the spectrum.
8. H.P. Figeys, *J.C.S. Chem. Comm.*, 1967, 495.

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