Benzo[3,4]cyclobuta[1,2-*c*]thiophen (2-Thianorbiphenylene)

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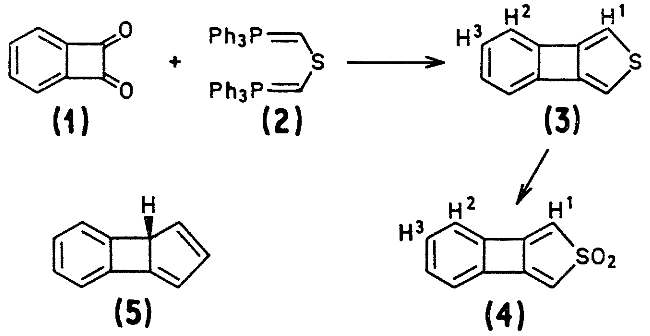
Summary The preparation of benzo[3,4]cyclobuta[1,2-*c*]thiophen (**3**) and benzo[3,4]cyclobuta[1,2-*c*]thiophen 2,2-dioxide (**4**) is described, and the occurrence of a paramagnetic ring current effect in (**3**) is discussed.

BIPHENYLENE is of considerable interest as one of the few examples of a compound derived from fused 4*n* and (4*n* + 2) π-electron rings.[1] We now report the synthesis and some properties of the first known heterocyclic analogue of biphenylene, benzo[3,4]cyclobuta[1,2-*c*]thiophen (**3**).[2]

A Wittig reaction between 1,2-benzocyclobutadienequinone (**1**)[3] and the bis-ylide (**2**)[4] (prepared by treatment of the corresponding bisphosphonium dichloride with n-butyl-lithium) in dry ether under nitrogen gave (**3**), m.p. 98—98·5°, in 14% yield.† The spectroscopic properties are in accord with the assigned structure. The mass spectrum showed the parent peak at *m/e* 158; the n.m.r. spectrum ($CDCl_3$) has absorptions at τ 3·14 (bs, 4H, H^2, H^3) and 3·51 (s, 2H, H^1). The u.v. spectrum [(EtOH) 242sh (ϵ 41,800) 245 (43,500), 281sh (1150), 294sh (1450), 300sh (1940), 307sh (2660), 316sh (4400), 322sh (5300), 330 (8700), and 347 nm (10,200)] is similar in the long wavelength region to biphenylene except that the absorptions show a small hypsochromic shift. Desulphurisation of (**3**) with Raney nickel gave 1,2-dimethylbenzocyclobutene[1] and *o*-diethylbenzene.

Oxidation of (**3**) with 6% H_2O_2 in acetic acid proceeded smoothly to give a quantitative yield of benzo[3,4]cyclobuta[1,2-*c*]thiophen 2,2-dioxide (**4**), m.p. 213—215°. The spectral properties [mass spectrum, *m/e* 190, 126 ($-SO_2$) base peak; n.m.r. ($CDCl_3$) τ 2·37 (s, 4H, H^2, H^3), 3·60 (s, 2H, H^1); u.v. (EtOH) 236 (ϵ 66,000), 272sh (3700), 300sh (3130), 308 (4650), 315 (4770), 321 (7950), 328sh (4700), and 336 nm (10,100)] are in accord with the assigned structure. Comparison between the n.m.r. proton chemical shift positions in (**3**) and (**4**) dramatically demonstrates the paramagnetic ring current shielding effect of the 4*n* cyclobutadienyl ring in (**3**).‡ The compound (**4**), unlike the hydrocarbon (**5**),[2] shows no tendency to dimerise, indicating that the reactivity of the trisubstituted double bond in (**5**) arises from the strain induced by the tetrahedral ring junction.[7]



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† Satisfactory elemental analyses were obtained for all new compounds.

‡ An estimate of the magnitude of the paramagnetic ring current effect of the cyclobutadienyl ring has been made (ref. 5). We have suggested elsewhere that this estimate is probably too low (ref. 6).

[1] For a review of biphenylene and related compounds, see M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, 1967.

[2] The norbiphenylene anion has recently been prepared: M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich, and M. D. Glick, *J. Amer. Chem. Soc.*, 1969, **91**, 2378.

[3] M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Amer. Chem. Soc.*, 1963, **85**, 2076.

[4] K. Dimroth, H. Follmann, and G. Pohl, *Chem. Ber.*, 1966, **99**, 642.

[5] H. P. Figeys, *Chem. Comm.*, 1967, 495; *Angew. Chem. Internat. Edn.*, 1968, **7**, 642.

[6] C. S. Baxter, P. J. Garratt, and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, in the press.

[7] For a closely related finding, see M. B. D'Amore and R. G. Bergmann, *J. Amer. Chem. Soc.*, 1969, **91**, 5694.