Naphthocarborane

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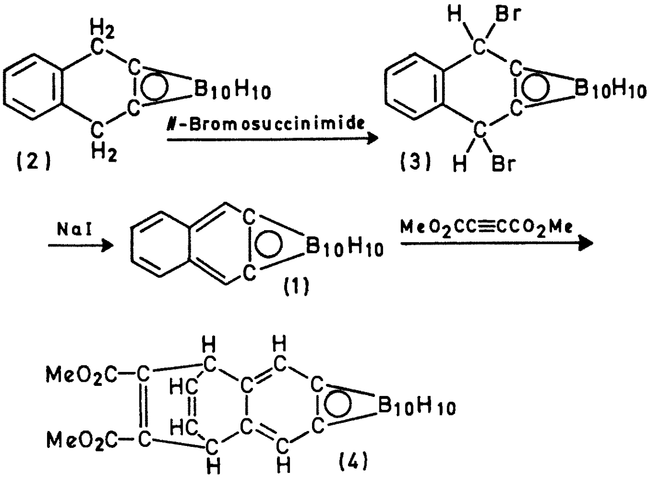
Summary Naphthocarborane has little aromatic character in the carbocyclic rings but is stabilised by unusual steric hindrance.

NAPHTHO[2,3,*a*]-*o*-CARBORANE (**1**) could have an aromatic outer benzenoid ring only if the inner ring were also aromatic, with substantial π-bond-order at the ring-cage junction. Benzocarborane, synthesised previously,[1] is very stable and appears aromatic by superficial criteria. However, we have now found that (**1**) resembles an *o*-xylylene with remarkable steric shielding by the carborane cage.

$\alpha\alpha'$-Dibromo-*o*-xylene and dilithio-*o*-carborane[1] yielded dihydronaphthocarborane (**2**), m.p. 186—187°, n.m.r. (CCl_4) δ 3·75 (s, 4, CH_2) and 7·17 (m, 4, C_6H_4).† *N*-Bromosuccinimide attacked (**2**) sluggishly in the presence of benzoyl peroxide and unexpectedly yielded only dibrominated product (**3**), m.p. 196—197°; n.m.r. ($CDCl_3$) δ 5·82 (s, 2, CHBr), 7·30 (s, 4, C_6H_4).

A solution of 3·5 g of dibromo-compound (**3**) and 35 g of sodium iodide in 50 ml of acetone was refluxed under argon 4 h. Naphthocarborane (**1**) was precipitated with 100 ml of deaerated water and was sublimed at 0·1 mm; 1·2 g (58%); fluorescent yellow crystals; m.p. 152—159° (sealed capillary); *m/e* 244 ($C_{10}H_{16}{}^{10}B_2{}^{11}B_8$); u.v. (2,2,4-trimethylpentane) λ_{max} 414 (ϵ 2400) 393 (3140), 377 (2420), 355 (1360), 335 (400), 280 nm ($3{\cdot}5 \times 10^4$); fluorescence (2,2,4-trimethylpentane) λ_{max} 447 nm; n.m.r. (CCl_4) δ 6·50 (s, 4, C_6H_4), 6·65 (s, 2, inner-ring CH). For comparison, the



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† Satisfactory analyses were obtained on compounds (**1**)–(**4**).

ring protons of *p*-xylylene appear at δ 6·49 in the n.m.r., but the terminal protons are considerably upfield, δ 5·10.[2] Thus, the inner ring of (**1**) appears to have some aromatic character, even though the double bonds are predominantly localised and disrupt the aromaticity of the outer ring.

Naphthocarborane reacts at the inner ring with relatively small oxidising agents. Bromine adds to form (**3**). Atmospheric oxygen reacts with (**1**) (0·2% in 2,2,4-trimethylpentane) overnight to precipitate a polymeric peroxide; *M* (osmometric in $CHCl_3$) 1700; n.m.r. ($CDCl_3$) δ 7·35 (broad s, 4, C_6H_4) and 5·5 (broad s, 2, O–C*H*); *m/e* 276, suggesting the presence of or breakdown to $C_{10}H_{16}B_{10}O_2$. *p*-Xylylene forms an analogous peroxide much more rapidly.[3]

Dienophiles are sterically prevented from attacking the inner ring but do add to the outer ring of (**1**). Dimethyl acetylenedicarboxylate (0·14 g) and (**1**) (0·24 g) in a sealed tube at 110° 16 h yielded 0·35 g (90%) of adduct (**4**); m.p. 214—215°; n.m.r. ($CDCl_3$) δ 3·76 (s, 6, OC*H*$_3$), 4·62 (m, 2, bridgehead C*H*), 6·28 (*s*, 2, inner-ring C*H*), and 6·59 (m, 2, *H*C=C*H*).[3] Maleic anhydride and (**1**) under similar conditions form an adduct analogous to (**4**); n.m.r. [$(CD_3)_2SO$] δ 3·43 (m, 2, *H*C–CO), 4·07 (m, 2, bridgehead C*H*), 6·48 (m, 2, *H*C=C*H*), and 6·85 (s, 2, inner-ring C*H*). The chemical shifts and splittings correlate well with other bicyclo-octenes[4] and are clearly inconsistent with addition at the inner ring, which would have made the outer ring aromatic as it is in (**3**).

Naphthocarborane (**1**) surprisingly failed to react with tetracyanoethylene in 48 h at 110° in a sealed tube. Models suggest that the carborane cage could interfere with π-complex formation even at the outer ring of (**1**), provided that the rings are very rigid and perhaps drawn toward the carborane cage by short bond distances in the inner ring.

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