624. *New Heteroaromatic Compounds. Part I. 9-Aza-10-boraphenanthrene.*

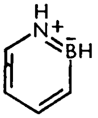
By M. J. S. Dewar, Ved P. Kubba, and R. Pettit.

Replacement of one carbon atom in an aromatic hydrocarbon by nitrogen gives rise to an isoconjugate positive ion; *e.g.*, the pyridinium ion is related in this way to benzene. Replacement by boron should give an analogous negative ion. Replacement of a pair of carbon atoms, one by nitrogen and one by boron, should therefore give a neutral aromatic system. Borazole is the only hitherto known compound of this type; we now describe a similar analogue of phenanthrene with the 9 : 10-carbon atoms so replaced. The parent compound, and derivatives with chlorine, hydroxy, methyl, ethyl, and phenyl attached to boron, have been prepared; they have the expected aromatic properties.

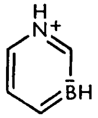
If one carbon atom in an aromatic hydrocarbon is replaced by nitrogen, an isoconjugate positive ion is obtained; for example, the pyridinium ion $C_5NH_6^+$ is related in this way to benzene, C_6H_6. Replacement of one carbon atom by boron should likewise give rise to an isoconjugate negative ion, *e.g.*, $C_5BH_6^-$, but no compounds of this type are known. It follows that replacement of a pair of carbon atoms, one by nitrogen and one by boron, should give rise to a neutral aromatic system; thus three such molecules (I), (II), and (III) should be capable of existence, all isoconjugate with benzene. It has long been recognised that borazole (IV) is of this type, being derived from benzene by replacement of all three pairs of carbon atoms; the chemical and spectroscopic properties of borazole indicate that it is aromatic. However, no other such aromatic boron compounds have yet been prepared (unless boron nitride is regarded as such an analogue of graphite), and we have therefore undertaken a general study of this new class of aromatic system. In this preliminary paper we describe the preparation and properties of compounds derived from phenanthrene by replacing the 9-carbon atom by nitrogen and the 10-carbon atom by boron.

2-Aminodiphenyl with boron trichloride in hot benzene gave hydrogen chloride and a product which could not be purified but was probably 2-diphenylylaminoboron dichloride (V); this on heating with aluminium chloride gave in good yield a compound $C_{12}H_9BNCl$ which, for reasons given below, we believe to be 10-chloro-9-aza-10-boraphenanthrene (VI; R = Cl).

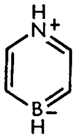
The chloro-compound was hydrolysed with extreme ease, even when kept in air for a day, to the corresponding hydroxide (VI; R = OH), which was unchanged by prolonged boiling with alkali; this indicates that the boron atom must be attached to carbon, since the B–N bond is readily broken by alkaline hydrolysis. Reduction of the chloro-compound by lithium aluminium hydride gave the parent substance (VI; R = H); this was quite stable and its spectrum (Fig. 1) resembled that of phenanthrene. The mode of formation of these compounds, their spectral resemblance to phenanthrene, and their stability, leave little doubt that they are indeed derivatives of 9-aza-10-boraphenanthrene (VI; R = H), and are therefore representatives of a new class of aromatic compound. The spectra of the hydroxide in neutral and alkaline conditions (Fig. 2) are very similar, and quite different from those of simple diphenyl derivatives; the B–N bond is therefore clearly much stronger than it is in simple amides of boric acid, implying that the compounds behave as aromatic analogues of phenanthrene (VI) rather than as cyclic boron amides * (VII). The stability of the parent compound (VI; R = H), a boron hydride, also supports this formulation.



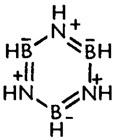
(I)



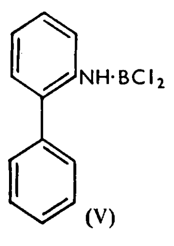
(II)



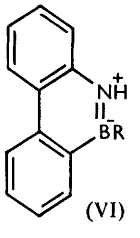
(III)



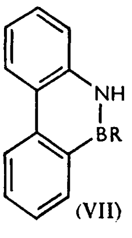
(IV)



(V)



(VI)



(VII)

FIG. 1. *Ultraviolet spectra of* 9-*aza*-10-*boraphenanthrene* (——), *and phenanthrene* (– – –).

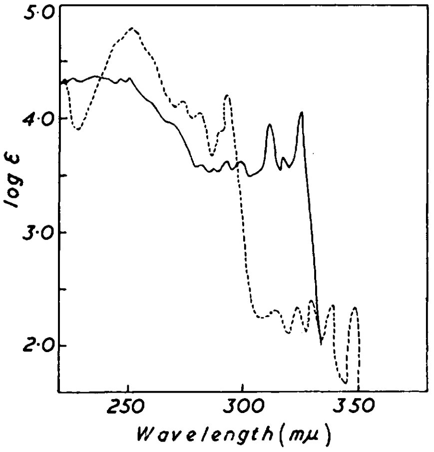
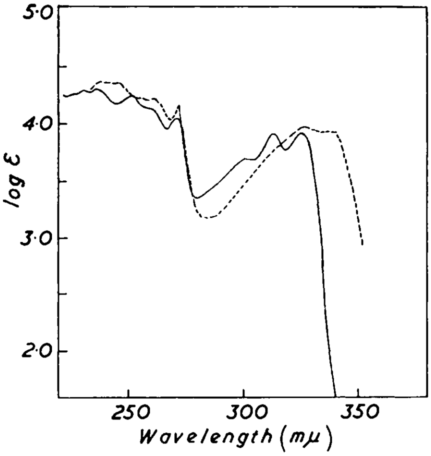


FIG. 2. *Ultraviolet spectra of* 10-*hydroxy*-9-*aza*-10-*boraphenanthrene in* cyclo*hexane or alcohol* (——), *and* 10% *aqueous alkali* (– – –).



Confirmation of these structures has been provided by two independent syntheses of 10-phenyl-9-aza-10-boraphenanthrene (VI; R = Ph). This could be obtained either by a Grignard reaction between the chloro-compound (VI; R = Cl) and phenylmagnesium bromide, or by condensing 2-aminodiphenyl with phenylboron dichloride in presence of aluminium chloride. The methyl and the ethyl analogue (VI; R = Me and Et) were also prepared by Grignard reactions from the chloro-compound (VI; R = Cl). The spectra of all these derivatives (VI) were very similar (cf. Table and Fig. 1).

The spectrum of 9-aza-10-boraphenanthrene (VI; R = H) itself is interesting (Fig. 1). It resembles very closely that of phenanthrene in the position of the main absorption bands, but the intensity of the α-band (275 mμ region) is very much greater. This would

---

* Of course the compounds are mesomeric, (VI) and (VII) being contributing structures; writing them as (VI) is intended to emphasise their aromatic nature.

be expected on the basis of a theory of hydrocarbon spectra proposed by Dewar and Longuet-Higgins[1] and by Moffitt.[2] According to these authors the α- and the β-band of alternant hydrocarbons arise from the second and the third transition respectively which are degenerate in simple molecular-orbital theory; configuration interaction splits the degenerate excited states into a lower and an upper one. Transition to the lower level from the ground state is forbidden, corresponding to the weak α-band. Introduction of heteroatoms into an alternant hydrocarbon should have no first-order effect on the wavelengths of the absorption bands[3] but should remove the degeneracy to which the weakness of the α-bands is due. This effect is well known for simple nitrogen heterocycles; for example, introduction of nitrogen atoms into naphthalene gives rise to compounds (quinoline, quinazoline, etc.) in which the positions of the main absorption bands change little, but in which the intensity of the α-band is greatly increased.

Ultraviolet absorption spectra of 10-*substituted* 9-*aza*-10-*boraphenanthrenes*: *wavelengths* (mμ) *and, in parentheses*, $\log_{10} \varepsilon$.

	10-Methyl-9-aza-10-boraphenanthrene
$\lambda_{max.}$	220(4·203), 224(4·195), 230(4·191), 236(4·191), 240(4·203), 246(4·211), 250(4·205), 298(3·725), 312(3·944), 324(3·995)
$\lambda_{min.}$	222(4·167), 228(4·171), 234(4·178), 238(4·188), 244(4·191), 248(4·198), 280(3·496), 304(3·612), 318(3·694), 334(2·413)
	10-Ethyl-9-aza-10-boraphenanthrene
$\lambda_{max.}$	220(4·332), 230(4·295), 238(4·312), 250(4·325), 298(3·747), 313(3·928), 325(4·046)
$\lambda_{min.}$	222(4·243), 234(4·286), 242(4·286), 280(3·520), 303(3·625), 319(3·698), 336(2·073)
	10-Phenyl-9-aza-10-boraphenanthrene
$\lambda_{max.}$	224(4·320), 238(4·350), 256(4·389), 300(3·789), 314(3·964), 328(4·047)
$\lambda_{min.}$	220(4·300), 226(4·316), 240(4·342), 281(3·653), 308(3·690), 322(3·750), 340(2·300)

EXPERIMENTAL

Some analyses for elements other than boron were kindly carried out by the microanalytical laboratory of the Imperial College of Science and Technology, London; boron was determined by the volumetric method developed by Leigh, Fowler, and Kraus.[4] M. p.s are corrected. Molecular weights were determined by freezing-point depression of camphor.

10-*Chloro*-9-*aza*-10-*boraphenanthrene*.—A solution of boron trichloride (12 g.) in benzene (50 ml.) was added slowly to one of 2-aminodiphenyl (17·4 g.) in benzene (350 ml.), and the mixture then boiled under reflux for 10 hr. The benzene was distilled off under reduced pressure, leaving crystalline 2-diphenylaminoboron dichloride (15 g.). This crude dichloride (6 g.) was heated with aluminium chloride (0·5 g.) to 175° for 7 hr. The resulting 10-*chloro*-9-*aza*-10-*boraphenanthrene* sublimed at 160—70°/0·05 mm., forming needles (2·8 g., 55%), m. p. 93—94° (Found: C, 67·7; H, 4·3; N, 6·8; Cl, 15·0. $C_{12}H_9NClB$ requires C, 67·5; H, 4·2; N, 6·6; Cl, 16·6%) (Repeated chlorine analyses showed a wide variation between 0·5% and 15·0%, clearly due to atmospheric hydrolysis. The figure quoted was the highest value, obtained when the analyst had been warned to take special precautions. Partial hydrolysis is also indicated by the fact that the analyses for C, H, and N are all slightly high, whereas carbon analyses on boron compounds are usually low.)

10-*Hydroxy*-9-*aza*-10-*boraphenanthrene*.—The chloro-compound, on storage in air for 24 hr., on crystallisation from moist light petroleum (b. p. 60—80°), or on treatment with water, gave almost theoretical yields of 10-*hydroxy*-9-*aza*-10-*boraphenanthrene*, which crystallised from light petroleum (b. p. 60—80°) in colourless needles, m. p. 169—170° (Found: C, 73·5; H, 5·5; N, 7·2; B, 5·6. $C_{12}H_{10}ONB$ requires C, 73·9; H, 5·1; N, 7·2; B, 5·6%). Its *picrate* was prepared from benzene solution, as orange crystals, m. p. 158—160° (Found: C, 50·8; H, 3·2; N, 13·3. $C_{18}H_{13}O_8N_4B$ requires C, 50·9; H, 3·1; N, 13·2%).

9-*Aza*-10-*boraphenanthrene*.—A solution of lithium aluminium hydride (0·8 g.) in dry ether

---

[1] Dewar and Longuet-Higgins, *Proc. Phys. Soc.*, 1954, **67**, 795.

[2] Moffitt, *J. Chem. Phys.*, 1954, **22**, 1820.

[3] Dewar, *J.*, 1950, 2329.

[4] Leigh, Fowler, and Kraus, *J. Amer. Chem. Soc.*, 1940, **62**, 1143.

(100 ml.) was added slowly with stirring and cooling (ice) to a solution of crude 10-chloro-9-aza-10-boraphenanthrene (12 g.) in dry ether (200 ml.), and the whole then boiled for 1 hr. Ethyl acetate (10 ml.) was added and the solution was then filtered and evaporated to dryness. The residue crystallised from light petroleum (b. p. 40—60°), giving 9-*aza*-10-*boraphenanthrene* (7 g., 70%) as colourless plates, m. p. 69—70° (Found: C, 80·0; H, 5·6; N, 7·8; B, 5·9%; *M*, 180. $C_{12}H_{10}NB$ requires C, 80·5; H, 5·6; N, 7·8; B, 6·0%; *M*, 179).

10-*Phenyl*-9-*aza*-10-*boraphenanthrene*.—(a) *From phenylboron dichloride.* Phenylboron dichloride [5] (4·5 g.) and 2-aminodiphenyl (5 g.) in benzene (400 ml.) were boiled for 8 hr., then evaporated to dryness under reduced pressure. The residue was heated with anhydrous aluminium chloride (0·5 g.) for 15 hr. at 170—180°, cooled, and crystallised first from benzene and then from light petroleum (b. p. 40—60°), giving 10-*phenyl*-9-*aza*-10-*boraphenanthrene* as light brown prisms (4·0 g., 66%), m. p. 110—111·5° (Found: C, 84·5; H, 5·4; N, 5·7; B, 4·1. $C_{18}H_{14}NB$ requires C, 84·8; H, 5·5; N, 5·5; B, 4·2%). (b) *By a Grignard reaction.* To a solution of crude 10-chloro-9-aza-10-boraphenanthrene (10 g.) in dry benzene (75 ml.) was added slowly a solution of phenylmagnesium bromide prepared from magnesium (1·1 g.) and bromobenzene (7 g.), and the solution then boiled under reflux for ¾ hr. Water was added and the benzene layer separated, dried, and evaporated; the residue after recrystallisation from light petroleum had m. p. and mixed m. p. 110° (6·9 g., 59%).

10-*Methyl*-9-*aza*-10-*boraphenanthrene*.—Prepared by a Grignard reaction in the same way as the phenyl analogue, in 67% yield, 10-*methyl*-9-*aza*-10-*boraphenanthrene* crystallised from ethanol in colourless needles, m. p. 103—104° (Found: C, 80·7; H, 6·4; N, 7·2; B, 5·4. $C_{13}H_{12}NB$ requires C, 80·9; H, 6·2; N, 7·3; B, 5·6%).

10-*Ethyl*-9-*aza*-10-*boraphenanthrene*.—Prepared in the same way, in 72% yield, 10-*ethyl*-9-*aza*-10-*boraphenanthrene* crystallised from ethanol in colourless needles, m. p. 77—78° (Found: C, 80·8; H, 6·7; N, 7·0; B, 5·2. $C_{14}H_{14}NB$ requires C, 81·2; H, 6·8; N, 6·8; B, 5·2%).

Spectroscopic Data.—The spectra were determined for *cyclo*hexane solutions by using a Unicam S.P. 500 spectrophotometer.

We thank the University of London for the award of an I.C.I. Research Fellowship (to R. P.), and for a grant for the purchase of apparatus.

QUEEN MARY COLLEGE, (UNIVERSITY OF LONDON),
MILE END ROAD, LONDON, E.1.
[Present address (R. P.): UNIVERSITY OF TEXAS,
AUSTIN 12, TEXAS, U.S.A.]

[*Received, December 23rd,* 1957.]

---

[5] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.