

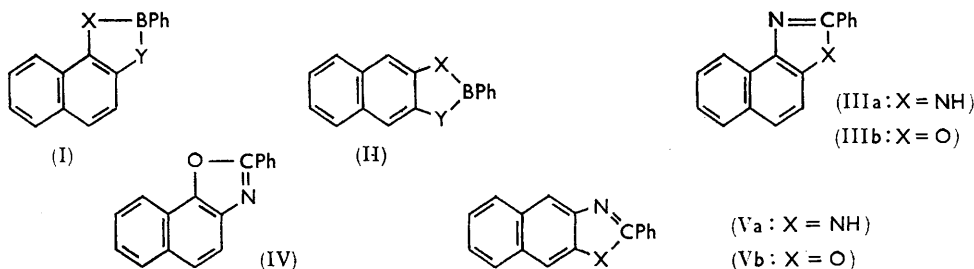
83. Heterocyclic Organoboron Compounds. Part I. Five-membered Ring Systems from Amino- and Hydroxy-naphthalenes.

By R. HEMMING and D. G. JOHNSTON.

Some heterocyclic boron compounds, all sensitive to moisture, have been prepared from phenylboronic anhydride and 1,2- and 2,3-diamino-, -dihydroxy-, and -aminohydroxy-naphthalenes. Their infrared spectra are described and their ultraviolet spectra are compared with those of analogous heterocyclic compounds not containing boron, and those of the substituted naphthalenes from which they were prepared.

VARIOUS compounds in which a boron atom forms part of a potentially aromatic five-membered ring have been synthesised from *o*-disubstituted aromatic compounds¹⁻⁵ and acylloins.⁶⁻⁸ Since the vacant p_z -orbital of the boron atom can in theory overlap with the full p_z -orbital of nitrogen or oxygen also contained in these heterocyclic rings, an aromatic system of six π -electrons is possible in the boron-containing ring. Such compounds are analogous with imidazoles and oxazoles. That the heterocyclic ring in these compounds has an aromatic system of π -electrons has been indicated by ultraviolet^{1,3,6,7} and infrared⁴ spectral investigations. Further, aromatic stabilisation has been indicated by the unusual stability of certain of the compounds towards hydrolysis in aqueous-alcoholic solution,^{1,3,6} in spite of the fact that these compounds are cyclic esters or amides of boronic acids, which normally are readily hydrolysed.

The resistance to oxidation and hydrolysis of these ring systems is very variable, so we have begun a systematic examination of the isomeric angular and linear heterocycles derived from 1,2- and 2,3-disubstituted amino- and -hydroxy-naphthalenes. The compounds were prepared by refluxing the *o*-disubstituted naphthalenes with phenylboronic anhydride in toluene or benzene and removing the water formed by azeotropic distillation, which afforded the compounds (I) and (II) where X = Y = NH or O, and X = NH, Y = O, and (I) where X = O, Y = NH.



These compounds were sufficiently stable to heat to be sublimed at about 0.2 mm. Sublimation was a better method than crystallisation for their final purification, since hydrolysis and oxidation were more easily avoided. The compounds (I) soon developed a violet colour in air, but series (II) was not affected by dry air.

Rupture of the heterocyclic ring occurred rapidly in alcoholic solution; thus the ultraviolet spectrum of 2-phenylnaphtho[2,3-*d*]-1,3,2-diazaboroline (II; X = Y = NH) in

¹ Dewar, Kubba, and Pettit, *J.*, 1958, 3076.

² Letsinger and Hamilton, *J. Amer. Chem. Soc.*, 1958, **80**, 5411.

³ Nyilas and Soloway, *J. Amer. Chem. Soc.*, 1959, **81**, 2681.

⁴ Blau, Gerrard, Lappert, Mountfield, and Pyszora, *J.*, 1960, 380.

⁵ Pailer and Fenzl, *Monatsh.*, 1961, **92**, 1294.

⁶ Letsinger and Hamilton, *J. Org. Chem.*, 1960, **25**, 592.

⁷ Smolinsky, *J. Org. Chem.*, 1961, **26**, 4915.

⁸ Jensen and Pedersen, *Acta Chem. Scand.*, 1961, **15**, 1780.

alcohol proved virtually identical with that of an equimolar mixture of the diamionaphthalene and phenylboronic acid.

FIGS. 1—4. Ultraviolet spectra.

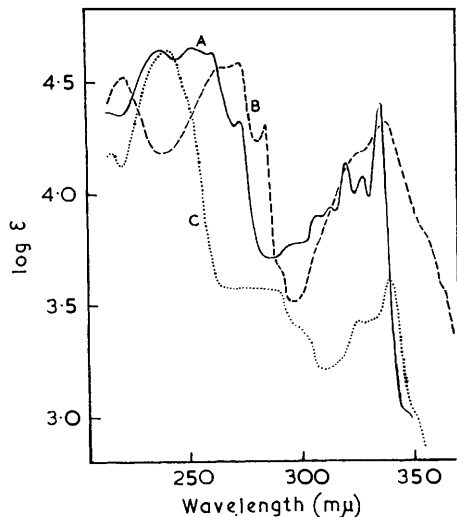


FIG. 1 (A) 2-Phenylnaphtho[2,3-*d*]-1,3,2-diazaboroline (II; X = Y = NH), (B) 2-phenylnaphth[2,3-*d*]imidazole (Va), and (C) naphthalene-2,3-diamine.

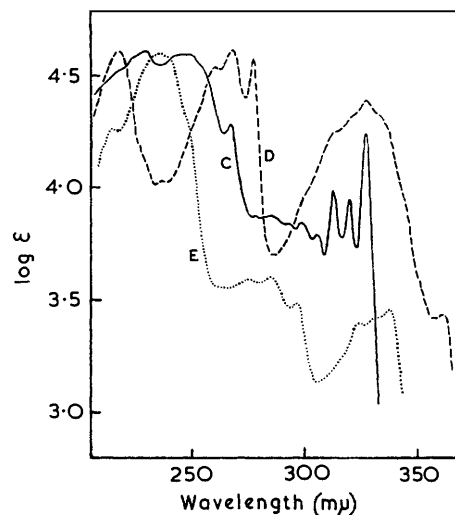


FIG. 2. (C) 2-Phenylnaphth[2,3-*d*]-1,3,2-oxazaboroline (II; X = NH, Y = O), (D) 2-phenylnaphth[2,3-*d*]imidazole (Va), and (E) 2-amino-3-naphthol.

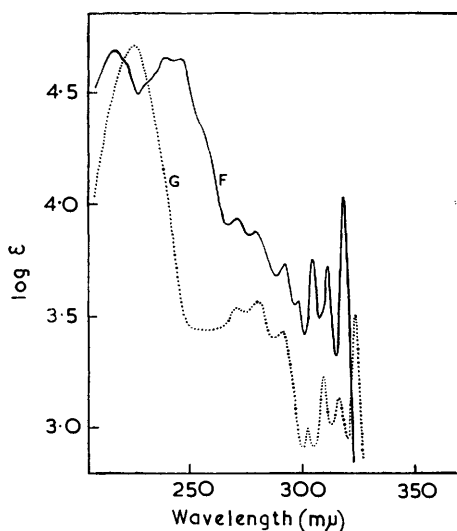


FIG. 3. (F) 2-Phenylnaphtho[2,3-*d*]-1,3,2-dioxaboroline (II; X = Y = O) and (G) naphthalene-2,3-diol.

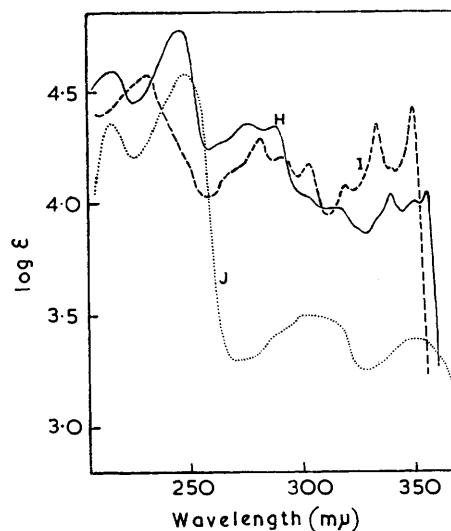


FIG. 4. (H) 2-Phenylnaphtho[1,2-*d*]-1,3,2-diazaboroline (I; X = Y = NH), (I) 2-phenylnaphth[1,2-*d*]imidazole (IIIa), and (J) naphthalene-1,2-diamine.

Ultraviolet Spectra.—The degree of aromatic character of potentially aromatic boron heterocycles may be assessed by comparing the ultraviolet spectra of the boron compounds with those of carbon compounds in which the linkage C=N replaces B-NH. Similar band shifts and intensity changes should occur on passing from a disubstituted naphthalene

starting material to the boron heterocycle and to the carbon analogue if the heterocyclic ring in both types of compound allows the π -electrons of the 2-phenyl group to interact with those of the naphthalene system. Thus close similarity of the spectra of a boron heterocycle and the analogous carbon compound indicates that the bond between boron

FIGS. 5—7. Ultraviolet Spectra.

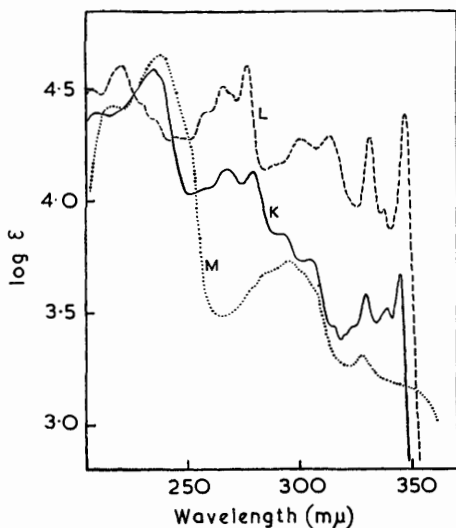


FIG. 5. (K) 2-Phenyl-naphth[2,1-*d*]-1,3,2-oxazaboroline (I; X = NH, Y = O), (L) 2-phenyl-naphth[2,1-*d*]oxazole (IIIa), and (M) 2-amino-1-naphthol.

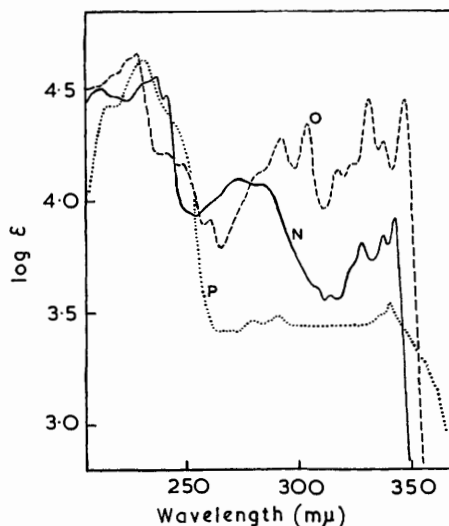


FIG. 6. (N) 2-Phenyl-naphth[1,2-*d*]-1,3,2-oxazaboroline (I; X = O, Y = NH), (O) 2-phenyl-naphth[1,2-*d*]oxazole (IV), and (P) 1-amino-2-naphthol.

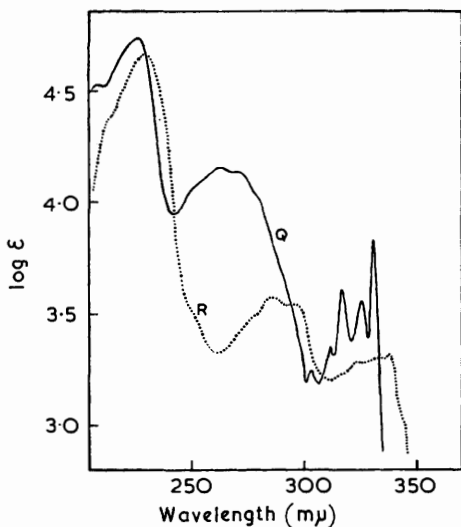


FIG. 7. (Q) 2-Phenyl-naphtho[1,2-*d*]-1,3,2-dioxaboroline (I; X = Y = O) and (R) naphthalene-1,2-diol.

and nitrogen has some double-bond character ($-B=NH^+$) and is comparable with the $C=N$ double bond. The carbon compounds (III—V) were prepared, and their ultraviolet spectra, together with those of the boron heterocycles and starting materials, were determined. Carbon analogues of the two naphthodioxaborolines are unknown. The Figures show that the spectra of the boron compounds and carbon analogues are closely

similar, more so for the linear than for the angular series, and more so for the diazaborolines than for the oxazaborolines. Thus the B-O double-bond character is less than that of the B-N bond.

The absorption intensities of the bands in the spectrum of an equimolar mixture of starting materials, *e.g.*, 2,3-diaminonaphthalene and phenylboronic acid, were much weaker than those in the spectrum of the boron heterocycle, and showed that the overall increase in intensity with the boron heterocycle (II; X = Y = NH) could not be ascribed simply to the additive effect of the separate naphthalene and phenyl chromophores within the molecule.

Infrared Spectra.—The spectra of the boron heterocycles derived from the dihydroxynaphthalenes contained no bands attributable to the O-H stretching vibration (3570—3125 cm^{-1}), and those from aminonaphthalenes all had a single, strong, sharp peak at 3472—3425 cm^{-1} attributable to an imino N-H stretching vibration, providing evidence that the required cyclisations had occurred.

Compounds containing B-N or B-O bonds with some double-bond character have strong characteristic bands in the region 1540—1280 cm^{-1} , and the stretching frequencies of aromatic C-O or C-N bonds lie in the region 1330—1200 cm^{-1} . The positions and intensities of bands occurring in the 1540—1200 cm^{-1} region of the spectra of the boron compounds are given in Table 1.

TABLE 1.

The infrared spectra (cm^{-1}) of boron heterocycles.

I; X = Y = NH	II; X = Y = NH	II; X = Y = O	I; X = Y = O	I; X = O, Y = NH	I; X = NH, Y = O	II; X = O, Y = NH
1530w	1520w	1515m	1527w	1527m	1530m	1513m
1507m	1504w	1458s	1504w	1504m	1504w	1470s
1440vs	1477m	1440s	1465w	1456m	1453s	1445m
1412m	1440vs	1385s	1440w	1440m	1440m	1434sb
1387vsb	1400vs	1350sb	1415w	1424m	1420sb	1413sb
1365vsb	1333w	1320 *	1380s	1410s	1404sb	1382 *
1332w	1318m	1292 *	1350vsb	1403s	1380s	1346s
1318m	1303w	1272w	1313w	1380sb	1366s	1320m
1300w	1275s	1242s	1276vs	1365sb	1350s	1300m
1280w	1205m		1250 *	1348 *	1316w	1277m
1210w			1227m	1316s	1282s	1266s
			1212m	1288m	1266m	1242m
				1267m	1202m	1225m
				1235s		
				1215m		

* Shoulder.

Some assignments are now possible which correspond with those made for other similar boron heterocycles.^{3,4} They are listed in Table 2.

TABLE 2.

Assignments (cm^{-1}) in infrared spectra.

Compound	B-N	C-N	B-O	C-O	B-Ph
I; X = Y = NH	1387, 1365 ¹	1280 ²	—	—	1440
II; X = Y = NH	1400 ³	1275 ⁴	—	—	1440 ³
I; X = Y = O	—	—	1350 ⁵	1276 ⁶	1440 ⁷
II; X = Y = O	—	—	1350 ⁵	1242 ⁶	1440 ⁷

Notes: (1) Doublet; the separation and relative intensities of the peaks are not consistent with isotopic splitting. (2) The strong absorption at 1290 cm^{-1} for naphthalene-1,2-diamine due to the C-N stretching vibration is diminished to a weak band for both the boron heterocycle and carbon analogue. (3) Strong absorptions absent from the spectrum of naphthalene-2,3-diamine. (4) A similar, strong absorption occurs at 1270 cm^{-1} for the carbon analogue and at 1275 cm^{-1} for naphthalene-2,3-diamine. (5) This strong band occurs in the same position in phenylboronic acid. (6) Several bands occur in this region for the naphthalenediol starting materials. (7) This band is much weaker than that found in the corresponding nitrogen heterocycle.

EXPERIMENTAL

Except where stated otherwise, ultraviolet spectra were determined for cyclohexane solutions on a Perkin-Elmer model 137 ultraviolet spectrophotometer. Infrared spectra were determined on samples dispersed in a potassium bromide disc, by using a Grubb-Parsons G.S.3 infrared spectrometer.

The boron heterocycles were prepared by refluxing the appropriate 1,2- or 2,3-disubstituted naphthalene with phenylboronic anhydride in benzene or toluene. After azeotropic removal of the water the impure heterocycle was deposited and then purified by crystallisation from benzene or toluene, followed by vacuum-sublimation. All the purified *products* (see Table 3) were colourless.

TABLE 3.
Boron heterocycles.

Compound	M. p.	Yield (%)	Found (%)				Formula	Required (%)			
			C	H	B	N		C	H	B	N
I; X = Y = NH ...	210—211°*	89	78.2	5.5	4.4	11.2	C ₁₆ H ₁₃ BN ₃	78.7	5.4	4.4	11.5
II; X = Y = NH ...	328—330†	74	—	—	—	—	—	—	—	—	—
I; X = NH, Y = O	159—160	82	78.9	5.0	4.4	5.8	C ₁₆ H ₁₂ BNO	78.4	4.9	4.4	5.7
I; X = O, Y = NH	117—118	95	78.2	5.1	4.5	5.8	"	"	"	"	"
II; X = O, Y = NH	229—230	86	79.0	4.7	4.4	5.9	"	"	"	"	"
I; X = Y = O	125—126	78	78.2	4.7	4.4	—	C ₁₆ H ₁₁ BO ₂	78.1	4.5	4.4	—
II; X = Y = O	225	95	78.9	4.6	4.4	—	"	"	"	"	—

* Ref. 5 gives 217°. † Ref. 3 gives 327—328°.

Established methods were used to prepare 2-phenylnaphth-[1,2]- (IIIa)⁹ and -[2,3]-imidazole (Va).¹⁰ However, some modification of the reported methods was necessary in the preparation of the oxazoles.

2-Phenylnaphth[1,2-d]oxazole (IV).—2-Amino-1-naphthol hydrochloride (0.98 g.) was heated with an excess of benzaldehyde (2.0 c.c.) according to Osman and Bassiouni's method,¹¹ and the reaction mixture, diluted with benzene and cyclohexane, was passed through a column of alumina. Removal of the solvent yielded a colourless solid (0.77 g., 63%), m. p. 87—88°, that sublimed as needles, m. p. 91—93° (lit.,¹² 122°) (Found: C, 83.4; H, 4.6; N, 5.5. Calc. for C₁₇H₁₁NO: C, 83.2; H, 4.5; N, 5.7%). The *picrate* separated from toluene as plates, m. p. 125—126° (Found: C, 58.2; H, 2.8; N, 11.7. C₂₃H₁₄N₄O₈ requires C, 58.2; H, 3.0; N, 11.8%).

2-Phenylnaphth[2,1-d]oxazole (IIIb).—This was prepared by an adaptation of Stephens and Bower's method.¹³ A solution of 1-amino-2-naphthol (1.59 g.) and benzaldehyde (1.05 c.c.) in benzene (30 c.c.) was slowly distilled azeotropically to remove the water formed. The volume of solvent was kept constant by addition of benzene. The yellow-brown solution obtained was allowed to cool and lead tetra-acetate (4.5 g.) was added. In a short time the solution became hot. It was then refluxed for 5 min. and, after cooling, the lead acetate was filtered off, and the filtrate run through a column of alumina to remove the bulk of the brown impurity. When the fluorescent eluate was reduced to a small volume a grey solid (1.89 g., 77%), m. p. 133°, was deposited. Vacuum-sublimation gave a colourless solid, m. p. 134—135° (lit.,¹¹ 130—131°).

2-Phenylnaphth[2,3-d]oxazole (Vb).—This *naphthoxazole* was prepared from 2-amino-3-naphthol by the method used above. It was obtained as a pale yellow solid (27%), m. p. 200°, that gave a colourless solid, m. p. 207—208°, on vacuum-sublimation (Found: C, 83.5; H, 4.8; N, 5.8. C₁₇H₁₁NO requires: C, 83.2; H, 4.5; N, 5.7%).

We thank R. Hindson and K. Lytollis for technical assistance, and one of us (D. G. J.) acknowledges a research studentship awarded by Newcastle upon Tyne Education Committee.

DEPARTMENT OF CHEMISTRY AND METALLURGY, RUTHERFORD COLLEGE OF TECHNOLOGY,
NEWCASTLE UPON TYNE 1. [Received, December 6th, 1962.]

⁹ Hodgson and Kilner, *J.*, 1924, 807; Hunter, *J.*, 1945, 809.

¹⁰ SabanJeff, *Z. anorg. Chem.*, 1899, **20**, 23; Franzen, *J. prakt. Chem.*, 1907, **76**, 213, 229; 1906, **73**, 557, 563, 567.

¹¹ Osman and Bassiouni, *J. Org. Chem.*, 1962, **27**, 558.

¹² Worms, *Ber.*, 1882, **15**, 1815.

¹³ Stephens and Bower, *J.*, 1949, 2971.