625. *New Heteroaromatic Compounds. Part II.*[1] *Boron Compounds Isoconjugate with Indole,* 2 : 3-*Benzofuran, and Thionaphthen.*

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

Boron analogues of three aromatic compounds containing five-membered rings have been prepared. Their ultraviolet spectra indicate varying degrees of aromatic behaviour; the spectrum of 2-phenylbenzo-1 : 3-diaza-2-borole (I) resembles that of 2-phenylbenziminazole very closely, indicating that (I) has a similar aromatic system of π-electrons; that of the dioxaborole (II) differs little from that of catechol.

In the preceding paper [1] we pointed out that a wide range of new heteroaromatic systems should exist, derived from normal aromatic compounds by replacing pairs of carbon atoms, one by boron and one by nitrogen. We there recorded 9-aza-10-boraphenanthrene (the second known compound of this type) whose stability and ultraviolet spectrum indicated that it was isoconjugate with phenanthrene. We now report compounds containing boron atoms in five-membered rings, isoconjugate with indole, 2 : 3-benzofuran, and thionaphthen.

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[1] Part I, preceding paper.

Our compounds were obtained by heating a solution of an appropriate *ortho*-disubstituted benzene derivative in benzene with phenylboron dichloride, hydrogen chloride being evolved. The yields were good, except in the case of the benzofuran analogue (III); the reaction of *o*-phenylenediamine with phenylboron dichloride led to extensive polymerisation. Addition of triethylamine to assist in the elimination of hydrogen chloride seemed to have little effect. These compounds are all crystalline, and soluble in benzene, ether, and chloroform. *o*-Phenylenediamine gave 2-phenylbenzo-1 : 3-diaza-2-borole (I), and catechol gave the corresponding dioxaborole (II). Analogous reactions of *o*-aminophenol, dithiocatechol, and *o*-aminothiophenol gave the corresponding oxa-azaborole (III), dithiaborole (IV), and thia-azaborole (IV). The structures of these compounds follow from their method of preparation, elementary analysis, and molecular-weight determination; moreover they were all hydrolysed by acid to the parent *ortho*-disubstituted benzene derivative and phenylboronic acid.

FIG. 1. *Ultraviolet spectra of 2-phenylbenzo-*1 : 3-*diaza-2-borole* (—), *2-phenylbenziminazole* (. . .) *and* o-*phenylenediamine* (– – –).

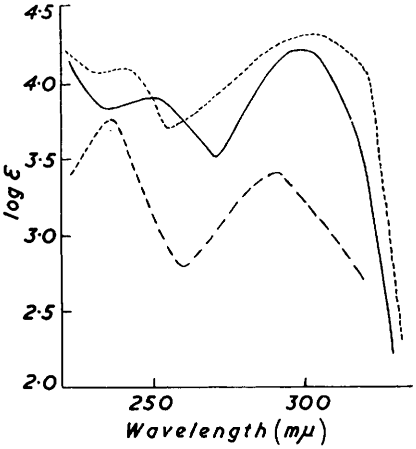


FIG. 2. *Ultraviolet spectra of 2-phenylbenzo-*1 : 3 : 2-*dioxaborole* (. . .), *catechol* (—·—·—), *2-phenylbenzo-*1 : 3 : 2-*dithiaborole* (——) *and dithiocatechol* (– – –).

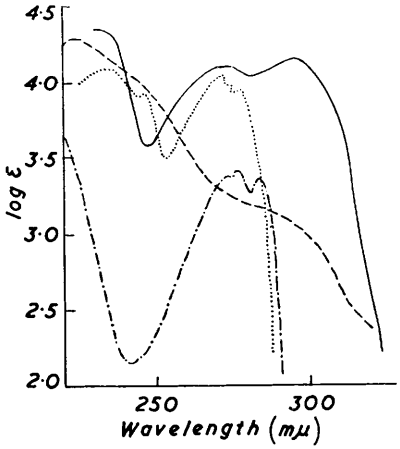


FIG. 3. *Ultraviolet spectra of 2-phenylbenzo-*1 : 3 : 2-*thiazaborole* (——), *2-phenylbenzothiazole* (. . .), *and* o-*aminothiophenol* (– – –).

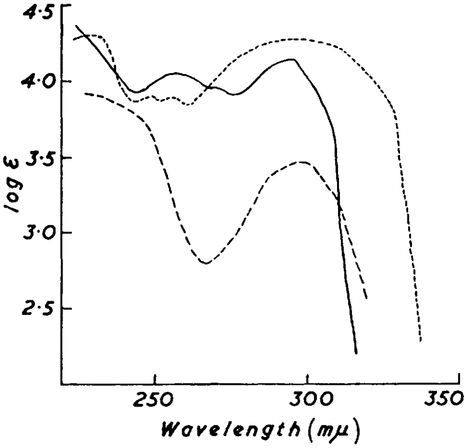
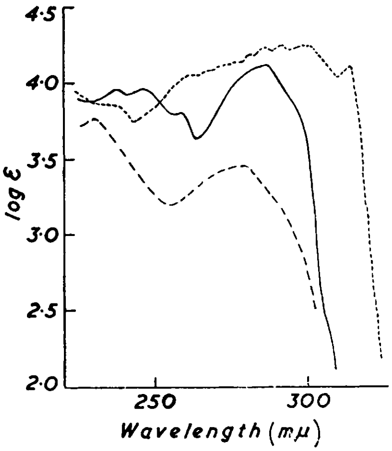
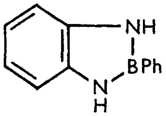


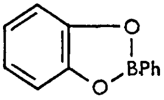
FIG. 4. *Ultraviolet spectra of 2-phenylbenzo-*1 : 3 : 2-*oxazaborole* (——), *2-phenylbenzoxazole* (. . .), *and* o-*aminophenol* (– – –).



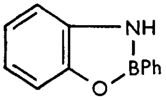
The ultraviolet spectra, together with those of various reference substances, are shown in Figs. 1—4. Those of compounds (I), (III), and (V) resemble closely those of 2-phenylbenziminazole, 2-phenylbenzoxazole, and 2-phenylbenzothiazole respectively, and differ markedly from those of the parent disubstituted benzene derivatives. This not only provides further evidence for the formulation of the boron compounds but also suggests that they are isoconjugate with conventional aromatic compounds of the indole type. If so, they should exhibit aromatic stability; compounds (I) and (V) certainly seem unusually stable to hydrolysis, compared with simple amides of boronic acids. We are investigating the stabilities of these compounds in detail. A structure determination by *X*-ray diffraction would be of great interest in this connection; for example the B–N bond lengths in compound (I) would indicate clearly the importance of conjugation in the five-membered ring.



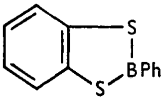
(I)



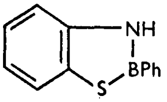
(II)



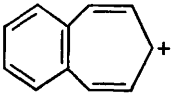
(III)



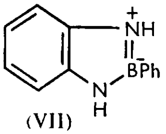
(IV)



(V)



(VI)



(VII)

No aromatic analogues of the dioxaborole (II) or dithiaborole (IV) are known, but the spectra differ markedly from those of catechol or *o*-dimercaptobenzene. The difference is particularly marked in the case of compound (IV), probably because it can be regarded as a hetero-analogue of benzotropylium (VI) (the formula of which has been written in such a way as to emphasise the resemblance). Examination of Figs. 1—4 suggests that the difference between the boroles and the parent *ortho*-disubstituted benzene derivatives is greater for the nitrogen and the sulphur compounds; this is what one would expect, for conjugation leads to a transfer of charge from the heteroatoms in the 1 : 3-positions to boron and this should occur less readily with oxygen than with nitrogen or sulphur (which are less electronegative). The spectrum of the diazaborole (I) suggests that it has a structure closely approximating to that of the corresponding benziminazole; this resemblance can be emphasised by writing (I) in the zwitterionic form (VII).

EXPERIMENTAL

The boron analyses for the following compounds were determined by the volumetric method developed by Leigh, Fowler, and Kraus.[2] Although the compounds were rigorously purified by crystallisation, the carbon values were rarely obtained with as close agreement with the calculated as is usual for organic compounds. Molecular weights were determined by freezing-point depression of camphor.

2-*Phenylbenzo*-1 : 3-*diaza*-2-*borole*.—Phenylboronic acid was obtained from phenylmagnesium bromide and tri-*n*-butyl borate[3] and converted through the anhydride into phenylboron dichloride.[4]

Phenylboron dichloride (4·0 g.) in dry benzene (50 ml.) was added dropwise and with constant stirring to *o*-phenylenediamine (3·0 g.) in dry benzene (350 ml.) at room temperature, moisture being excluded. The mixture was then boiled under reflux with stirring until evolution of hydrogen chloride had ceased (8 hr.), cooled, filtered, and evaporated under reduced pressure. The brown crystalline residue (1·8 g.) of 2-*phenylbenzo*-1 : 3-*diaza*-2-*borole* crystallised from

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[2] Leigh, Fowler, and Kraus, *J. Amer. Chem. Soc.*, 1940, **62**, 1143.
[3] Bean and Johnson, *ibid.*, 1932, **54**, 4415.
[4] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.

benzene or light petroleum (b. p. 60—80°) in white plates, m. p. 204—206° (Found: C, 73·9; H, 5·9; N, 14·3; B, 5·6%; *M*, 188. $C_{12}H_{11}N_2B$ requires C, 74·3; H, 5·7; N, 14·4; B, 5·6%; *M*, 194). When warmed with mineral acids or sodium hydroxide solution it gave phenylboronic acid and *o*-phenylenediamine.

2-*Phenylbenzo*-1 : 3-*dioxa*-2-*borole*.—Phenylboron dichloride (5 g.) in dry benzene (50 ml.) was added dropwise to catechol (3·5 g.) in benzene (600 ml.) and the mixture stirred under reflux for 6 hr. The benzene was then distilled off, leaving a quantitative yield of 2-*phenylbenzo*-1 : 3-*dioxa*-2-*borole*, which formed white plates, m. p. 109—110°, from benzene or light petroleum (Found: C, 73·0; H, 4·7; B, 5·5. $C_{12}H_9O_2B$ requires C, 73·5; H, 4·6; B, 5·5%).

2-*Phenylbenzo*-1 : 3-*dithia*-2-*borole*.—This compound was prepared in excellent yield in the usual way from dithiocatechol and phenylboron dichloride (7 hours' refluxing were required and no polymeric material was formed). The *dithiaborole* crystallised from light petroleum in white plates, m. p. 130—131° (Found: C, 61·3; H, 3·7; B, 5·1; S, 27·5. $C_{12}H_9S_2B$ requires C, 63·1; H, 3·9; B, 4·8; S, 28·1%).

2-*Phenylbenzo*-1 : 3-*thiaza*-2-*borole*.—Prepared as above from *o*-aminothiophenol and phenylboron dichloride the *thiazaborole* formed white needles (which after several recrystallisations from dry benzene had m. p. 154—156°) (Found: C, 68·3; H, 4·7; N, 6·7; S, 15·1; B, 5·0%; *M*, 220. $C_{12}H_{10}NSB$ requires C, 68·3; H, 4·7; N, 6·6; S, 15·2; B, 5·1%; *M*, 211).

2-*Phenylbenzo*-1-*oxa*-3-*aza*-2-*borole*.—Prepared (with a small amount of polymer) by heating *o*-aminophenol and phenylboron dichloride as before, the *oxa-azaborole* crystallised from benzene in white plates, m. p. 105—106° (Found: C, 72·1; H, 4·8; N, 6·9; B, 5·3. $C_{12}H_{10}ONB$ requires C, 73·9; H, 5·1; N, 7·2; B, 5·5%).

Spectra.—For the determination of their spectra 2-phenylbenziminazole,[5] 2-phenylbenzoxazole,[6] and 2-phenylbenzothiazole [7] were prepared by established procedures.

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[5] Jerchel, Fisher, and Kracht, *Annalen*, 1952, **575**, 162.
[6] Desai, Hunter, and Khalidi, *J.*, 1934, 1186.
[7] Bogert and Snell, *J. Amer. Chem. Soc.*, 1924, **46**, 1308.