Heterocyclic Organoboron Compounds. Part II.[1] Some 2-Aryl-benzo- and -naphtho-1,3,2-di-azaborolines and -oxaborolens*

By R. Hemming and D. G. Johnston

Some heterocyclic boron compounds have been prepared by reacting *o*-phenylenediamine, catechol, naphthalene-2,3-diamine and -2,3-diol with some nitro- and chloro-phenylboronic acids or anhydrides. Comparison of their ultraviolet spectra with those of 2-phenyl-benzo- and -naphtho-1,3,2-diheteroboro-compounds and some analogous benzimidazoles indicates that intramolecular bonding occurs between an *o*-nitro-group in the 2-phenyl ring and the boron atom of the heterocyclic ring.

In the preceding Part[1] we described the properties of the 2-phenylnaphtho-1,3,2-diheteroboro-compounds obtained on reacting some *o*-disubsituted amino- and hydroxy-naphthalenes with phenylboronic anhydride. Several new compounds (I), (II) have now been prepared by treating *o*-phenylenediamine, catechol, naphthalene-2,3-diamine and -2,3-diol with *o*-, *m*-, and *p*-nitro- and -chloro-phenylboronic acids or anhydrides in refluxing toluene or benzene, and removing the water formed by azeotropic distillation.

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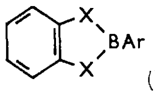
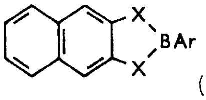
* Benzo- and naphtho-dioxaboroles were incorrectly named as derivatives of dioxaboroline in Part I.—Ed.

[1] Part I, R. Hemming and D. G. Johnston, *J. Chem. Soc.*, 1964, 466.

All the compounds are sensitive to moisture, and rupture of the heterocyclic ring occurs rapidly in alcoholic solution.



(I)



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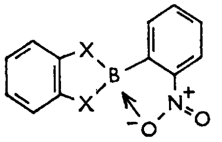
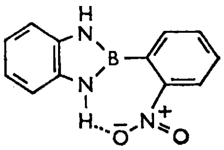


(III)



(IV)

The *o*-nitrophenyl compounds are much more soluble than the corresponding *m*- and *p*-nitrophenyl isomers in a given hydrocarbon solvent, and in a series of phenyl- and *o*-, *m*-, and *p*-nitrophenyl-boron compounds melting-points are in the order *o*- $<$ phenyl $<$ *m*- $<$ *p*- (Table 7; Table 3 in ref. 1). The exceptional properties of the *o*-nitrophenyl compounds indicate that in the solid state intramolecular bonding occurs between the nitro-group and boron atom of the heterocyclic ring (as shown in III), and support the deductions from ultraviolet spectral data. Other examples of intramolecular chelation between a boron atom and *o*-nitro-aryl group have been described elsewhere.[2]

Ultraviolet Spectra.—In the *o*-nitrophenyl boron compounds intramolecular bonding would result in a non-coplanar arrangement of the 2-phenyl and benz-hetero-rings; conjugative interactions between these chromophoric groups would be inhibited, and one could expect[3] a marked diminution in the intensity of absorption of the longest-wavelength band in the ultraviolet spectra. This hypochromic effect is observed in the spectra of the *o*-nitrophenyl boron compounds (see Figures 1—4 and Table 1); it shows that an intramolecularly hydrogen-bonded structure (IV) is unlikely, since the configuration

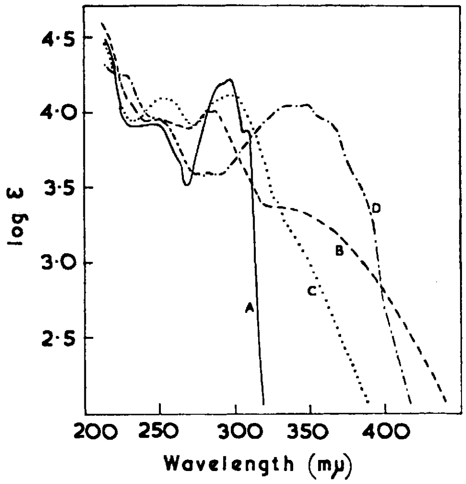


FIGURE 1 Ultraviolet spectra: 2-phenylbenzo-1,3,2-diazaboroline (A) and the 2-*o*-, *m*-, and *p*-nitrophenylbenzodiazacompounds (B, C, and D, respectively)

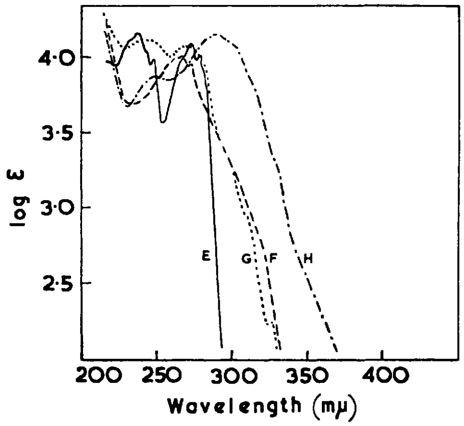


FIGURE 2 Ultraviolet spectra: 2-phenylbenzo-1,3,2-dioxaborole (E) and the 2-*o*-, *m*-, and *p*-nitrophenylbenzodioxacompounds (F, G, and H, respectively)

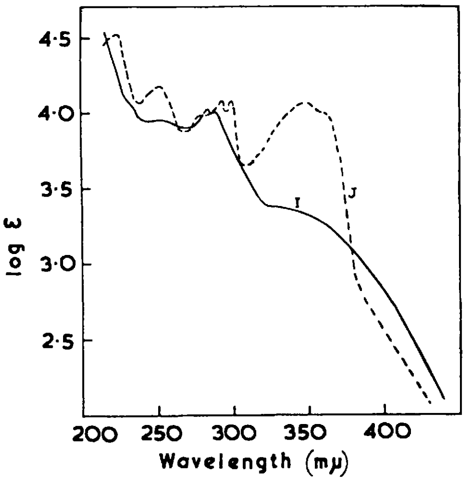


FIGURE 3 Ultraviolet spectra: 2-*o*-nitrophenylbenzo-1,3,2-diazaboroline (I) and 2-*o*-nitrophenylbenzimidazole (J)

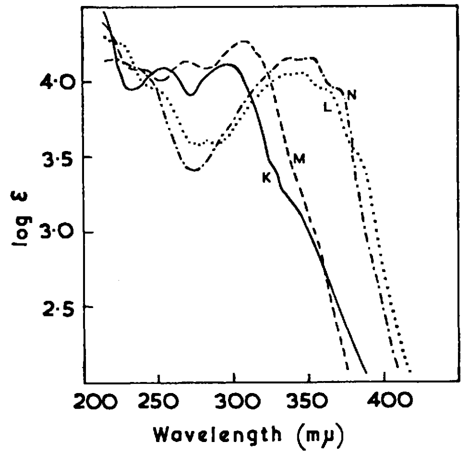


FIGURE 4 Ultraviolet spectra: 2-*m*- and *p*-nitrophenylbenzo-1,3,2-diazaboroline (K and L, respectively) and 2-*m*- and -*p*-nitrophenylbenzimidazole (M and N, respectively)

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[2] B. Bettman, G. E. K. Branch, and D. L. Yabroff, *J. Amer. Chem. Soc.*, 1934, **56**, 1865; T. Colclough, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 1956, 3006; J. C. Lockhart, *Chem. and Ind.*, 1961, 2006.

[3] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, 1962, p. 384.

TABLE 1

Ultraviolet spectra of the 2-nitrophenylnaphtho-boron compounds (II)

Compound X	Ar	$\lambda_{max.}$ (mμ) (log ε)
NH	C_6H_5	321(4·13), 327(4·07), 336(4·40)
NH	*o*-$C_6H_4 \cdot NO_2$	315(3·78), 322(3·79), 329(3·96)
NH	*m*-$C_6H_4 \cdot NO_2$	325(4·09), 336(4·16)
NH	*p*-$C_6H_4 \cdot NO_2$	Sp. sol. in cyclohexane
O	C_6H_5	304(3·76), 311(3·73), 318(4·04)
O	*o*-$C_6H_4 \cdot NO_2$	303(3·57), 309(3·53), 317(3·57), 323(3·42)
O	*m*-$C_6H_4 \cdot NO_2$	306(3·92), 312(3·86), 320(4·12)
O	*p*-$C_6H_4 \cdot NO_2$	310(3·94), 315(3·93), 322(4·04)

of the molecule most favourable to hydrogen bonding is one in which the phenyl and hetero-rings are coplanar. The absence of hypochromic effect in the spectrum of 2-*o*-nitrophenylbenzimidazole shows that no steric crowding occurs between the *o*-nitro-group and heterocyclic ring.

TABLE 2

Ultraviolet spectra of the 2-chlorophenylbenzo- and -naphtho-boron compounds

Compound X		Ar	$\lambda_{max.}$ (mμ) (log ε)
(I)	NH	C_6H_5	290(4·18), 297(4·22), 309(3·87)
(I)	NH	*o*-$C_6H_4 \cdot Cl$	297(4·16), 308(4·11), 322(3·71)
(I)	NH	*m*-$C_6H_4 \cdot Cl$	295(4·22), 303(4·19), 317(3·75)
(I)	NH	*p*-$C_6H_4 \cdot Cl$	295(4·27), 303(4·26), 316(3·82)
(I)	O	C_6H_5	272(4·10), 278(4·00)
(I)	O	*o*-$C_6H_4 \cdot Cl$	273(4·02), 281(3·95)
(I)	O	*m*-$C_6H_4 \cdot Cl$	272(4·06), 278(4·03)
(I)	O	*p*-$C_6H_4 \cdot Cl$	272(4·19), 278(4·18)
(II)	NH	C_6H_5	320(4·13), 328(4·07), 336(4·41)
(II)	NH	*o*-$C_6H_4 \cdot Cl$	325(4·10), 332(4·09), 340(4·26)
(II)	NH	*m*-$C_6H_4 \cdot Cl$	322(4·22), 329(4·17), 337(4·43)
(II)	NH	*p*-$C_6H_4 \cdot Cl$	322(4·28), 329(4·22), 337(4·52)
(II)	O	C_6H_5	304(3·76), 311(3·72), 318(4·03)
(II)	O	*o*-$C_6H_4 \cdot Cl$	306(3·73), 312(3·69), 320(3·96)
(II)	O	*m*-$C_6H_4 \cdot Cl$	305(3·74), 311(3·71), 319(4·00)
(II)	O	*p*-$C_6H_4 \cdot Cl$	305(3·86), 312(3·81), 319(4·12)

TABLE 3

Infrared spectra (cm.$^{-1}$) of the 2-aryl-benzo- and -naphtho-[2,3-*d*]-1,3,2-diazaborolines

(I; Ar = $C_6H_4 \cdot NO_2$)			(I; Ar = $C_6H_4 \cdot Cl$)		
o	*m*	*p*	*o*	*m*	*p*
1515s	1522s	1515s *	1496w	1502w	1511w
1475s	1505m	1508s	1473m	1475m	1487m
1431m *	1477s	1488m	1430s *	1435s *	1448s
1420sb	1435s	1441m *	1418vs	1422vs	1427vs
1389w *	1420s *	1420s	1383m	1397s	1394s
1355s *	1360m *	1400s	1351s	1362s *	1366s
1340s	1350s	1374w	1302w	1353s	1308w
1304w	1314m	1340sb	1282m	1330m *	1294w
1284w	1300m	1304m *	1271m	1297w *	1276s
1267s	1269s	1268s		1286w	1254w
				1270s	

(II; Ar = $C_6H_4 \cdot NO_2$			(II; Ar = $C_6H_4 \cdot Cl$)		
o	*m*	*p*	*o*	*m*	*p*
1522s	1531m *	1513s	1511w	1515w	1513w
1495w	1520m	1465w	1484w	1490w	1479w
1468m	1497m	1437s	1465m	1479m	1464w
1437s	1479m	1398s	1430s	1467m	1439s
1408w *	1443s	1390m *	1404w	1437s	1412w
1391s	1397m	1360m *	1385s	1403s	1395s
1346s	1350s	1348s	1320w	1388s	1366m *
1325w	1313m	1318w	1308m	1316w *	1347w *
1307m	1272m	1274m	1280w *	1309m	1322w *
1269m			1272m	1295w *	1312m
			1263w	1268m	1297w
			1240w		1274m

The large bathochromic shift of the main absorption bands caused by the introduction of a *p*-nitro-group into the 2-phenyl ring of the boron compounds clearly demonstrates that the heterocyclic ring allows conjugative interactions between the phenyl and benzo-systems.

TABLE 4

Infrared spectra (cm.$^{-1}$) of the 2-aryl-benzo- and -naphtho-[2,3-*d*]-1,3,2-dioxaboroles

(I; Ar = $C_6H_4 \cdot NO_2$)			(I; Ar = $C_6H_4 \cdot Cl$)		
o	*m*	*p*	*o*	*m*	*p*
1524s	1529s	1522s	1480m *	1473s	1472s
1480m *	1485m	1497w	1468s	1430w *	1429w
1471s	1470s	1468s	1424m	1410s	1390m
1433w	1427m	1440w *	1388m	1367m *	1370s
1389m	1387m	1398m	1370m *	1362s	1351m
1370m	1370m	1374m	1360m	1351m *	1330s
1348s	1348s	1347s	1340m *	1329s	1316m *
1329s	1326s	1327s	1326s	1318s *	1300w
1304m	1311m	1302m *	1319s *	1292m	1285w
1278m	1282m	1282m	1280w	1284m	1269w
1250m	1233s	1259m	1262m	1269m	1236s
1232s		1235s	1231sb	1235s	

(II; Ar = $C_6H_4 \cdot NO_2$)			(II; Ar = $C_6H_4 \cdot Cl$)		
o	*m*	*p*	*o*	*m*	*p*
1534s	1531m	1524s	1508w	1513w	1510w
1515m	1515m	1493w *	1473w	1481w	1493w
1481w	1490m	1458m	1452m	1456m	1452m
1456s	1458m	1429w	1443w	1428w *	1435w
1439m	1429m	1399w	1420m	1408m	1389w
1373s	1383m	1385m	1365s	1368m	1372m
1347s	1357s *	1355s *	1335vs	1341vs	1346vs
1338s	1340s	1337sb	1297m	1295m	1300m
1302m	1316m *	1304m	1290m	1280m	1287m
1284w	1287m	1274w	1267m	1256w *	1267m *
1250s	1238sb	1250m *	1258m	1238s	1238s
1238s		1238s	1241s		
1227s					

* Shoulder.

TABLE 5

Assignments in the infrared spectra of the benzo- and naphtho-diazaborolines

Compound Ar		B–N asym. stretch	B–N sym. stretch	C–N asym. stretch	NO_2 asym. stretch	NO_2 sym. stretch
(I)	*o*-$C_6H_4 \cdot NO_2$	1420	1355 or 1340 *	1267	1515	1355 or 1340 *
(I)	*m*-$C_6H_4 \cdot NO_2$	1420	1360 or 1350 *	1269	1522	1360 or 1350 *
(I)	*p*-$C_6H_4 \cdot NO_2$	1420	1340 *	1268	1515	1340 *
(I)	*o*-$C_6H_4 \cdot Cl$ ...	1418	1351	1271	—	—
(I)	*m*-$C_6H_4 \cdot Cl$ ...	1422	1353	1270	—	—
(I)	*p*-$C_6H_4 \cdot Cl$ ...	1427	1366	1276	—	—
(II)	C_6H_5	1440 †	1400 †	1275	—	—
(II)	*o*-$C_6H_4 \cdot NO_2$	1437	1391	1269	1522	1346
(II)	*m*-$C_6H_4 \cdot NO_2$	1443	1397	1272	1520	1350
(II)	*p*-$C_6H_4 \cdot NO_2$	1437	1398	1274	1513	1348
(II)	*o*-$C_6H_4 \cdot Cl$ ...	1430	1385	1272	—	—
(II)	*m*-$C_6H_4 \cdot Cl$ ...	1437	1388	1268	—	—
(II)	*p*-$C_6H_4 \cdot Cl$ ...	1439	1395	1274	—	—

* Broad composite band due to overlap of B–N and NO_2 sym. stretch. † Revised assignments from ref. 1.

The ultraviolet spectra of the 2-phenyl and 2-chlorophenyl compounds are similar (Table 2); no hypochromic effect is evident in the spectra of the *o*-chlorophenyl compounds, showing that steric crowding between the *o*-chlorine atom and heterocyclic ring is absent.

Infrared Spectra.—On introduction of nitro- or chloro-

TABLE 6

Assignments in the infrared spectra of the benzo- and naphtho-dioxaboroles

Compound Ar	B–O asym. stretch	C–O asym. stretch	NO_2 asym. stretch	NO_2 sym. stretch
(I) *o*-C_6H_4·NO_2 ...	1329	1232	1524	1348
(I) *m*-C_6H_4·NO_2	1326	1233	1529	1348
(I) *p*-C_6H_4·NO_2 ...	1327	1235	1522	1347
(I) *o*-C_6H_4·Cl	1326	1231	—	—
(I) *m*-C_6H_4·Cl ...	1329	1235	—	—
(I) *p*-C_6H_4·Cl ...	1330	1236	—	—
(II) *o*-C_6H_4·NO_2 ...	1338	1238	1534	1347
(II) *m*-C_6H_4·NO_2	1340	1238	1531	1357
(II) *p*-C_6H_4·NO_2 ...	1337	1238	1524	1355
(II) *o*-C_6H_4·Cl	1335	1241	—	—
(II) *m*-C_6H_4·Cl ...	1341	1238	—	—
(II) *p*-C_6H_4·Cl ...	1346	1238	—	—

substituents into the 2-phenyl ring some slight shifts of the B–N and B–O stretching frequencies are distinguishable, but not of sufficient magnitude to allow their interpretation in terms of changes in the B–N and B–O bond orders. The positions and intensities of bands occuring in the 1540—1225-cm.$^{-1}$ region of the spectra of the boron compounds are given in Tables 3 and 4. Some assignments, which agree with those made for similar compounds,[4] are listed in Tables 5 and 6.

EXPERIMENTAL

Ultraviolet spectra were determined for cyclohexane solutions with a Perkin-Elmer model **137** ultraviolet spectrophotometer. Infrared spectra were determined on samples dispersed in potassium bromide discs, using a Grubb–Parsons G.S.3 infrared spectrometer.

The boron heterocycles were prepared by distilling benzene or toluene solutions of the appropriate disubstituted benzene or naphthalene and substituted phenylboronic acid or anhydride. When all water had been removed, the solution was cooled and the solid deposited was purified by crystallisation from benzene or toluene, or by vacuum-sublimation (see Table 7). The *o*-nitrophenyl boron compounds were crystallised from light petroleum–benzene because of their high solubility in pure benzene.

Literature methods were used to prepare the nitrophenylboronic acids,[5] chlorophenylboronic anhydrides,[6] and 2-nitrophenylbenzimidazoles.[7]

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[5/1004 *Received, September* 17*th*, 1965]

TABLE 7

Preparation of the boron heterocycles

Compound			M. p.	Yield (%)	Found (%)				Formula	Required (%)			
	X	Ar			C	H	N	Cl		C	H	N	Cl
(I)	NH	*o*-Ph·NO_2	107—109°	69	60·4	4·2	17·8	—	$C_{12}H_{10}BN_3O_2$	60·3	4·2	17·6	—
(I)	NH	*m*-Ph·NO_2	224—225 *	71	60·8	4·2	17·4	—	,,	,,	,,	,,	—
(I)	NH	*p*-Ph·NO_2	272—274	52	59·9	4·3	17·8	—	,,	,,	,,	,,	—
(I)	NH	*o*-Ph·Cl	119—120	73	62·8	4·7	12·3	15·2	$C_{12}H_{10}BN_2Cl$	63·1	4·4	12·3	15·5
(I)	NH	*m*-Ph·Cl	159—160	77	63·6	4·2	12·3	15·3	,,	,,	,,	,,	,,
(I)	NH	*p*-Ph·Cl	223—224 †	70	63·3	4·5	12·2	15·6	,,	,,	,,	,,	,,
(I)	O	*o*-Ph·NO_2	109—110	87	60·1	3·5	5·7	—	$C_{12}H_8BNO_4$	59·8	3·3	5·8	—
(I)	O	*m*-Ph·NO_2	179	85	60·1	3·6	5·7	—	,,	,,	,,	,,	—
(I)	O	*p*-Ph·NO_2	233	95	60·0	3·4	5·8	—	,,	,,	,,	,,	—
(I)	O	*o*-Ph·Cl	118—120	75	62·2	3·6	—	15·4	$C_{12}H_8BO_2Cl$	62·5	3·5	—	15·4
(I)	O	*m*-Ph·Cl	110	70	62·9	3·5	—	15·7	,,	,,	,,	—	,,
(I)	O	*p*-Ph·Cl	150—151 ‡	67	62·4	3·6	—	15·8	,,	,,	,,	—	,,
(II)	NH	*o*-Ph·NO_2	194—196	89	65·9	4·5	14·4	—	$C_{16}H_{12}BN_3O_2$	66·4	4·2	14·5	—
(II)	NH	*m*-Ph·NO_2	284—286	96	66·4	4·3	14·6	—	,,	,,	,,	,,	—
(II)	NH	*p*-Ph·NO_2	>310 §	91	66·3	4·0	14·3	—	,,	,,	,,	,,	—
(II)	NH	*o*-Ph·Cl	249—250	63	68·8	4·6	10·1	12·8	$C_{16}H_{12}BN_2Cl$	69·0	4·3	10·1	12·7
(II)	NH	*m*-Ph·Cl	>300 §	61	69·0	4·5	10·3	12·7	,,	,,	,,	,,	,,
(II)	NH	*p*-Ph·Cl	>300 §	54	68·8	4·6	10·2	12·7	,,	,,	,,	,,	,,
(II)	O	*o*-Ph·NO_2	158—159	79	65·8	3·7	4·9	—	$C_{16}H_{10}BNO_4$	66·0	3·5	4·8	—
(II)	O	*m*-Ph·NO_2	241—243	91	65·6	3·8	5·0	—	,,	,,	,,	,,	—
(II)	O	*p*-Ph·NO_2	289 §	94	65·7	3·7	4·7	—	,,	,,	,,	,,	—
(II)	O	*o*-Ph·Cl	213—214	93	68·9	3·7	—	12·5	$C_{16}H_{10}BO_2Cl$	68·5	3·6	—	12·6
(II)	O	*m*-Ph·Cl	218—219	93	68·6	3·5	—	12·8	,,	,,	,,	—	,,
(II)	O	*p*-Ph·Cl	269—271 ¶	94	68·8	4·0	—	12·4	,,	,,	,,	—	,,

* Lit. (E. Nyilas and A. H. Soloway, *J. Amer. Chem. Soc.*, 1959, **81**, 2681), m. p. 218—219°. † Lit. (E. Nyilas and A. H. Soloway, *loc. cit.*), m. p. 219—221°. ‡ Lit. (W. Gerrard, M. Howarth, E. F. Mooney, and D. E. Pratt, *J. Chem. Soc.*, 1963, 1582), m. p. 148—149°. § Decomp. ‡ Lit. (W. Gerrard *et al.*, *loc. cit.*), m. p. 294—295°.

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[4] F. K. Butcher, W. Gerrard, M. Howarth, E. F. Mooney, and H. A. Willis, *Spectrochim. Acta*, 1964, **20**, 79.

[5] W. Seaman and J. R. Johnson, *J. Amer. Chem. Soc.*, 1931, **53**, 711.

[6] F. R. Bean and J. R. Johnson, *J. Amer. Chem. Soc.*, 1932, **54**, 4415; G. E. K. Branch, D. L. Yabroff, and B. Bettman, *ibid.*, 1934, **56**, 937; H. G. Kuivila and E. J. Soboczenski, *ibid.*, 1954, **76**, 2675.

[7] R. Weidenhagen, *Ber.*, 1936, **69***B*, 2263.