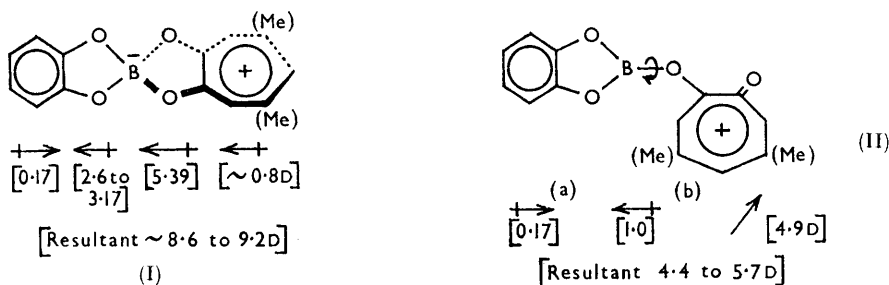


449. Novel Spiroborates and a Dipole Moment Study of 1,3,2-Dioxabora-azulene-2-spiro-2'-(1',3',2'-benzodioxaborole).

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The large dipole moment (8.24 D) of 5(7)-methyl-1,3,2-dioxabora-azulene-2-spiro-2'-(1',3',2'-benzodioxaborole) confirms the spiran co-ordinated structure previously suggested. Stable spiroborates are formed from *n*-butoxybenzodioxaborole with 8-hydroxyquinoline or its *N*-oxide, but not with 3-hydroxy- γ -pyrone.

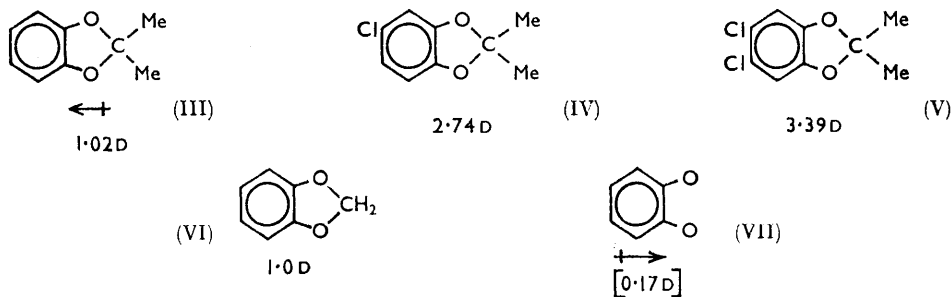
THE compound ¹ formed from 2-*n*-butoxy-1,3,2-benzodioxaborole with β -methyltropolone could have the spiran structure (I), or the non-co-ordinated structure (II). Ultraviolet (u.v.) and infrared (i.r.) spectroscopic measurements, together with the low solubility and non-hygroscopicity of the compound, indicate structure (I).¹ A dipole-moment measurement has been made to clarify the assignment of structure.



(Me) denotes alternative positions for the β -methyl group.

In the absence of dipole-moment data for known structures analogous to (I) or (II), we have attempted to estimate the moments of these from a consideration of molecules containing parts of these structures. Experimental moments are quoted and derived part-moments are enclosed in brackets.

We assume that the spiran structure (I) has its four oxygen-boron bonds arranged with D_{2d} or higher symmetry, so that their moments cancel.



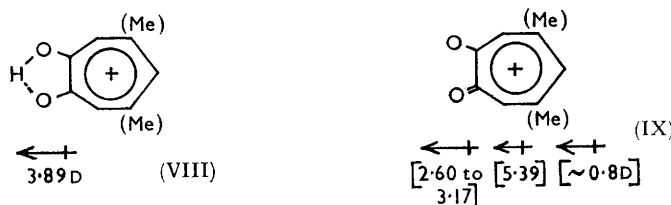
The dipole moments of compounds (III)—(VI) were measured by Boesecken² but their directions are not known. The moment of (III) may be combined in either direction along the axis of symmetry with the moments of chlorobenzene (1.58 D) or of *o*-dichlorobenzene (2.27 D) to estimate the moments of (IV) and (V).³ Comparison of these estimates with

¹ Balaban, Mihai, Antonescu, and Frangopol, *Tetrahedron*, 1961, **16**, 68.

² Boesecken, *Rec. Trav. Chim.*, 1936, **55**, 145.

³ Smyth, "Dielectric Behaviour and Structure," McGraw-Hill, New York, 1955.

the measured moments establishes the direction shown for (III), and this is assumed also to be the direction of (VI). We allow a moment⁴ of 1.0 D for each H₂C-O bond in (VI) and assume $\angle\text{O-CH}_2\text{-O} = 108^\circ$, to derive a moment of 0.17 D away from the benzene ring for the contribution of (VII).



The dipole moment β -methyltropolone (VIII)⁵ acts in the direction shown. We assume that the structure is symmetrical and contains a contribution⁴ of 1.5 D towards the heptagon due to $\text{O}\cdots\text{H-O}$ bonding, to derive the contribution of 5.39 D in (IX).

Next we consider the dipole-moment contribution of the donation of an electron pair from tropolone to boron. Phillips, Hunter, and Sutton⁶ assign a gross moment of 3—4 D. in the sense $\text{O}^{\delta+}-\text{B}^{\delta-}$ which is the difference between the electron-transfer moment (μ_A) and the moment (μ_B) due to asymmetrical sharing of electrons. μ_B is estimated as 1.5 D in the sense $\text{O}^{\delta-}-\text{B}^{\delta+}$ from the Pauling electronegativity difference,⁴ so that μ_A would be 4.5—5.5 D. We assume that this transfer becomes symmetrical, and with half our nett value acting down each of two tropolone oxygen-boron bonds inclined at $109\frac{1}{2}^\circ$ we derive a moment of 2.6—3.17 D (IX). An approximate indication of the dipole moment, from classical polarisation and mesomerism in the tropolone system, caused by the formation of the donor bond, may be found from a comparison of the measured moments of nitromethane (3.2 D) and nitrobenzene (4.0 D).⁷ We allow a contribution of approximately 0.8 D (IX) for these effects.

We assume that the trigonal structure (II) has its three O-B bonds arranged with D_{3h} symmetry, so that their moments cancel. The contribution of (VII) will be as before.



The dipole moments⁵ of the two isomeric β -methyltropolone ethers (X) are 4.78 and 4.99 D, lying approximately in the direction from the centre of the heptagon towards the carbonyl group. We assign a mean moment of 4.9 D to the mixture of isomers and subtract the H₃C-O bond moment⁴ of 1.0 D to derive the contribution of (XI).

The vector additions are shown under (I) and under (II) which indicates the freedom of rotation of part (IIa) relative to (IIb). The measured dipole moment is 8.24 ± 0.03 D which clearly points to the spiran structure (I), indicated by earlier work.¹ The separation of suitably substituted derivatives into optical antipodes would provide additional confirmation of this result.

The preparation and spectra of spiroborates (XII—XV) are given in the Experimental section.

Compounds (XIV) and (XV) both form stable, non-hygroscopic, yellow crystals with high melting points. In the i.r. spectrum of (XIV), the very strong N-O stretching band

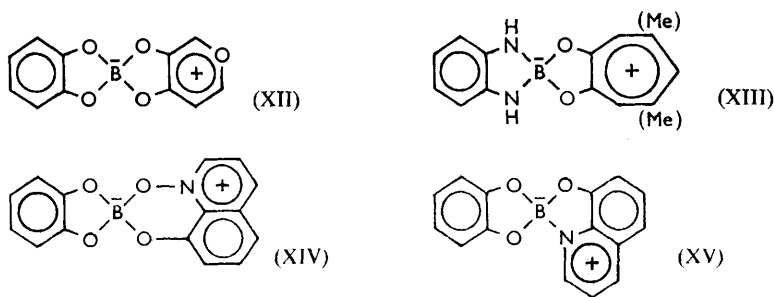
⁴ Smith, "Electric Dipole Moments," Butterworths, London, 1955.

⁵ Saxby, B.Sc. Thesis, Oxford, 1952.

⁶ Phillips, Hunter, and Sutton, *J.*, 1945, 146.

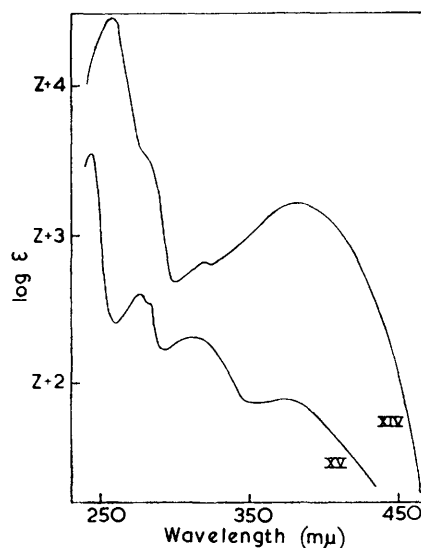
⁷ Wesson, "Tables of Electric Dipole Moments," Massachusetts Institute of Technology, 1947.

of quinoline *N*-oxide at 1281 cm^{-1} is replaced by a weak band, showing that the N-O group is involved in complex formation. The u.v. spectra (the Figure) of (XIV) and (XV) in



1,2-dichloroethane are very similar, and resemble the spectrum of (I).¹ They contain four main bands at (i) 382 and 372 $\text{m}\mu$ and (ii) 320sh and 306 $\text{m}\mu$, respectively, attributable to (i) 1,3-dioxa-2-bora-3a-azaniaphenaline and (ii) 1-oxa-2-bora-2a-azonia-acenaphthene moieties; and at (iii) 280sh and 275 $\text{m}\mu$ and (iv) 257 and 244 $\text{m}\mu$, respectively, both

FIG. 1. Absorption spectra of (XIV) ($Z = 1$) and (XV) ($Z = 0$) in 1,2-dichloroethane.



attributable to the benzodioxaborole moiety. Bands (i) and (ii) have low extinction coefficients; band (iii) shows evidence of vibrational structure similar to the corresponding band in benzodioxaborole; band (iv) is of very high intensity. The arguments for these assignments are the same as in the previous report.¹

Account being taken of the similarity between tropylium and pyrylium,⁸ it was surprising to find that (XII) is colourless, slightly hygroscopic, and rather unstable. Co-ordination is shown by the disappearance of bands due to pyrone C=C and C=O stretching⁹ at 1665 and 1630 cm^{-1} and by the presence of a band at 1644 cm^{-1} characteristic of the pyrylium ring¹⁰ (vibration mode 8a in Wilson's notation¹¹). However, the co-ordination is so readily affected by traces of moisture that in a potassium bromide pellet the pyrone bands replace the pyrylium band. The u.v. absorption spectrum has only one band with

⁸ Balaban and Nenitzescu, *Rev. Chim. (Acad. R.P.R.)*, 1961, **6**, 269.

⁹ Katritzky and Jones, *Spectrochim. Acta*, 1961, **17**, 64.

¹⁰ Balaban, Mateescu, and Elian, *Tetrahedron*, 1962, **18**, 1083.

¹¹ Wilson, jun., *Phys. Rev.*, 1934, **45**, 706.

two peaks at 269 and 273 μ attributable to the dioxaborole group, and a very weak absorption beyond 300 μ .

This unexpected difference between (I) and (XII) cannot be due to steric factors because the two molecules are very similar, and the difference in \angle O-B-O between the seven- and six-membered ring compounds is only $360^\circ/6 \times 7 = 8.5^\circ$, assuming constancy of \angle B-O-C and radial direction of the C-O bonds. It implies that the difference in resonance energy between the tropylium cation and tropone is larger than the same difference between the pyrylium cation and pyrone.

EXPERIMENTAL

Dipole-moment measurements were made on dilute solutions of spiran (I) in benzene at 25°, and details are given in the Table. Dielectric constants were measured on a capacity meter

TABLE.

$10^6 w$	ϵ	v	n	$10^6 w$	ϵ	v	n
0	2.2741	1.14149	1.49790	462	2.2882	1.14131	1.49805
113	2.2778	1.14134	1.49802	788	2.2976	1.14121	1.49809
217	2.2808	1.14143	1.49805	960	2.3027	—	1.49813

$\epsilon = 2.2741 + 29.5w$, $v = 1.1415 - 0.39w$, $n = 1.49801 + 0.115w$, $\tau P_{2\infty} = 1.461.8$ c.c., $\epsilon P_2 = 72.5$ c.c., $\epsilon P_{2\infty} = 1389.3$ c.c., $\mu = 8.24 \pm 0.03$ D.

w = weight fraction; ϵ = dielectric constant; v = specific volume; and n = refractive index.

operating at 400 kc./sec. Refractive indices were measured with a Pulfrich refractometer and densities with a Sprengel-Ostwald pycnometer of about 4 c.c. capacity. The results were calculated by Halverstadt and Kumler's method.¹²

Infrared measurements were made with a Jena UR-10 spectrophotometer either of mulls in Nujol or of potassium bromide pellets. Ultraviolet measurements were made with dichloromethane solutions on a Jena VSU-1 spectrophotometer.

The Pentaoxa-spiroborate (XII).—3-Hydroxy- γ -pyrone was prepared¹³ by distilling, at ca. 300° in an atmosphere of carbon dioxide, a mixture of equal quantities of copper powder and meconic acid, which had been previously dried at 120°. The solid distillate was extracted with hot chloroform, the extract filtered, and concentrated, and the residue crystallised (alcohol-cyclohexane); the product had m. p. 116—117° (lit.,¹⁴ m. p. 117°); ν_{\max} . (KBr pellet) 3100br, 1665vs, 1630vs, 1578m, 1468m, 1410m, 1331m, 1245vs, 1211s, 1190w, 1112s, 1038w, 1000m, 953w, 888s, 875w, 862w, 847s, 766m, 758m, 705m, 562m, and 520m cm^{-1} .

A solution of 3-hydroxy- γ -pyrone (1.2 g.) in the minimum amount (ca. 10 ml.) of dry dichloromethane or alcohol-free chloroform was treated with 2-n-butoxy-1,3,2-benzodioxaborole (2.5 g.)¹ (ν_{\max} . in liquid film: 3064m, 3055sh, 3038sh, 2960vs, 2936s, 2875ms, 1631m, 1557s, 1524s, 1510s, 1490vs, 1475vs, 1458vs, 1390vs, 1350vs, 1295ms, 1287ms, 1262s, 1240vs, 1138m, 1124m, 1096s, 1075s, 1035ms, 1010m, 975mw, 900mw, 872m, 860m, 810ms, 773m, 746s, 728sh, 698m, and 670ms cm^{-1}) in the same solvent (3 ml.) in a dry-box. The precipitate was filtered off and washed with dry solvent. A white compound, m. p. 202°, was obtained (Found: C, 56.7; H, 3.2; B, 4.9. $\text{C}_{11}\text{H}_7\text{BO}_5$ requires C, 57.45; H, 3.1; B, 4.7%; ν_{\max} . (Nujol mull) 3120w, 3045w, 1644m, 1580s, 1545s, 1495m, 1478m, 1370m, 1320w, 1285m, 1242s, 1220m, 1162m, 1140s, 1102vs, 1075vs, 1016w, 1008w, 989m, 950w, 801m, 790w, 830w, and 765w cm^{-1}). The m. p. of a stored sample decreased (Found, after 1 yr., 95°) and its i.r. spectrum showed bands (3100 br., 1665, and 1630 cm^{-1}) characteristic of 3-hydroxy- γ -pyrone.

5(7)-*Methyl-1,3,2-dioxabora-azulene-2-spiro-2'-(1,3,2-diazaboraindane)* (XIII).—Fractionation of a mixture of *o*-phenylenediamine (4.3 g.) and tri-*n*-butylborate (20 g.) afforded a distillate of butanol and butyl borate and left a residue containing 2-n-butoxy-1,3,2-diazaborole, which was dissolved in benzene and treated with β -methyltropolone. A yellow product, m. p. 85—86°, was obtained, markedly soluble in benzene (Found: N, 12.0. $\text{C}_{13}\text{H}_{11}\text{BN}_2\text{O}_2$ requires N, 11.8%).

¹² Halverstadt and Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

¹³ Borsche, *Ber.*, 1916, **49**, 2538.

¹⁴ Ost, *J. Prakt. Chem.*, [2], 1879, **19**, 177.

The Tetraoxa-azaspiroborate (XIV).—8-Hydroxyquinoline 1-oxide was prepared¹⁵ from 8-hydroxyquinoline and peracetic acid, and had m. p. 136° after recrystallisation from ethanol.

Solutions in dichloromethane of 2-n-butoxy-1,3,2-dioxaborole (0.4 g.) and of the 1-oxide (0.3 g.) were mixed and in a few seconds a precipitate of *compound* (XIV) was formed; it was washed thoroughly with dichloromethane and then had m. p. 281° and was insoluble in the usual solvents, except 1,2-dichloroethane (Found: C, 65.0; H, 3.65; B, 3.8; N, 4.9. $C_{15}H_{10}BNO_4$ requires C, 64.6; H, 3.6; B, 3.9; N, 5.0%); ν_{max} (KBr pellet) 3093s, 3073s, 3054m, 3038m, 1610s, 1596sh, 1562s, 1528m, 1492vs, 1478sh, 1469sh, 1430sh, 1403s, 1384s, 1373m, 1338s, 1312m, 1248vs, 1225vs, 1186ms, 1175ms, 1155sh, 1140vs, 1110vs, 1093vs, 1055s, 1044m, 1008m, 966s, 941s, 920sh, 910vs, 873ms, 828vs, 762s, 750vs, 726m, 655mw, and 618mw cm^{-1} .

Preparation of the Trioxa-azaspiroborate XV.—Benzene solutions of 8-hydroxyquinoline (1.0 g.) and 2-n-butoxy-1,3,2-dioxaborole (1.32 g.) afforded a yellow precipitate of (XV) which was filtered off and washed with benzene. The product had m. p. 220° and was insoluble in the usual solvents; its solubility in dichloroethane is less than that of (XIV) (Found: C, 68.9; H, 4.1; B, 3.4; N, 5.1. $C_{15}H_{10}BNO_3$ requires C, 68.5; H, 3.8; B, 4.1; N, 5.3%); ν_{max} (KBr pellet) 3090mw, 3062ms, 3050ms, 3030m, 1630m, 1602sh, 1592s, 1553s, 1490vs, 1460s, 1421ms, 1395ms, 1299vs, 1243vs, 1231vs, 1225ms, 1208s, 1188ms, 1153ms, 1112vs, 1108sh, 1075vs, 1031s, 1010s, 978vs, 935ms, 911s, 896s, 876m, 830sh, 810ms, 800mw, 787mw, 768mw, 741sh, 737vs, 703ms, 679m, and 627mw cm^{-1} .

Reaction of 2-n-Butoxy-1,3,2-diazaborole and 3-hydroxy- γ -pyrone.—Benzene solutions of 2-n-butoxy-1,3,2-diazaborole and 3-hydroxy- γ -pyrone yield on admixture a dark red product which was hygroscopic and could not be purified.

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¹⁵ Khaletskii, Pesin, and Tsin, *Zhur. obshchei Khim.*, 1958, **28**, 2348.