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TROPOPHENYLENE AND TROPOVINYLENE SPIROBORATES

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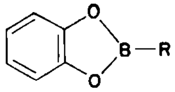
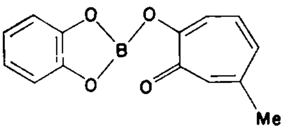
Abstract—The reaction of tropolones with 2-alkoxy-1,3,2-dioxaboroles yields crystalline compounds, e.g. III, whose spectra and structure are discussed.

THE ability of boron to take part in aromatic systems[1] such as borazole was recently demonstrated also for carbon-containing rings.[2–5] In benzodioxaboroles (I)[3,4,6] the large electronegativity difference between boron and oxygen tends to bring about charge localizations and thus to reduce the aromaticity. In order to obtain indications about the coördinative power of boron in such compounds, thence about their aromaticity, the reaction of dioxaboroles with tropolones was investigated.

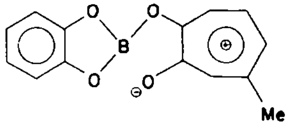
2-n-Butoxy-4,5-benzo-1,3,2-dioxaborole (I, R = OBu) and β-methyltropolone, either alone or in benzene solution, react exothermally to give a yellow crystalline compound which may be recrystallized from benzene, is unsensitive to atmospheric moisture but is decomposed by hydroxylic solvents, and which after its analysis and



I



II a



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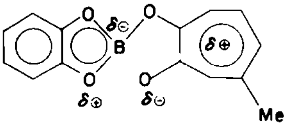
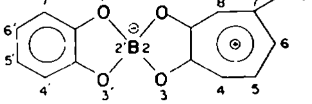


IIc



III

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[1] A. T. Balaban, *Studii si Cercetari Chim. Acad. R.P.R.*, 7, 257 (1959).

[2] M. J. S. Dewar, V. P. Kubba and R. Pettit, *J. Chem. Soc.* 3073 (1958) and subsequent papers in the series; J. M. Davidson and C. M. French, *Ibid.* 191 (1960).

[3] M. J. S. Dewar, V. P. Kubba and R. Pettit, *J. Chem. Soc.* 3076 (1958).

[4] R. L. Letsinger and S. B. Hamilton, *J. Amer. Chem. Soc.* **80**, 5411 (1958); W. Gerrard, M. F. Lappert and B. A. Mountfield, *J. Chem. Soc.* 1529 (1959).

[5] E. E. van Tamelen, G. Brieger and K. G. Untch, *Tetrahedron Letters* No. 8, 14 (1960).

[6] L. H. Thomas, *J. Chem. Soc.* 823 (1946); F. Joy and M. F. Lappert, *Proc. Chem. Soc.* 353 (1960); R. L. Letsinger and S. B. Hamilton, *J. Org. Chem.* **25**, 592 (1960).

mode of formation can have either structure II or III.* Evidence in favour of the latter structure is deduced on the basis of the following arguments.

Ultra-violet absorption spectra measured in various solvents (Fig. 1) present four bands, indicated in the decreasing wavelength order A, B, C and D. A comparison with the spectra of catechol[3] and benzodioxaboroles[3] on one hand and of tropolone[7,8] and copper tropolone[8] on the other hand makes it probable that the first two bands are due to the tropolone moiety and that the last two bands are due to the catechol moiety. An uncoördinated structure II would result in a spectrum not largely different from a superposition between the spectra of n-butoxy-dioxaborole (Fig. 2) and of tropolone ethers or esters. A coördinated structure III on the other hand would have

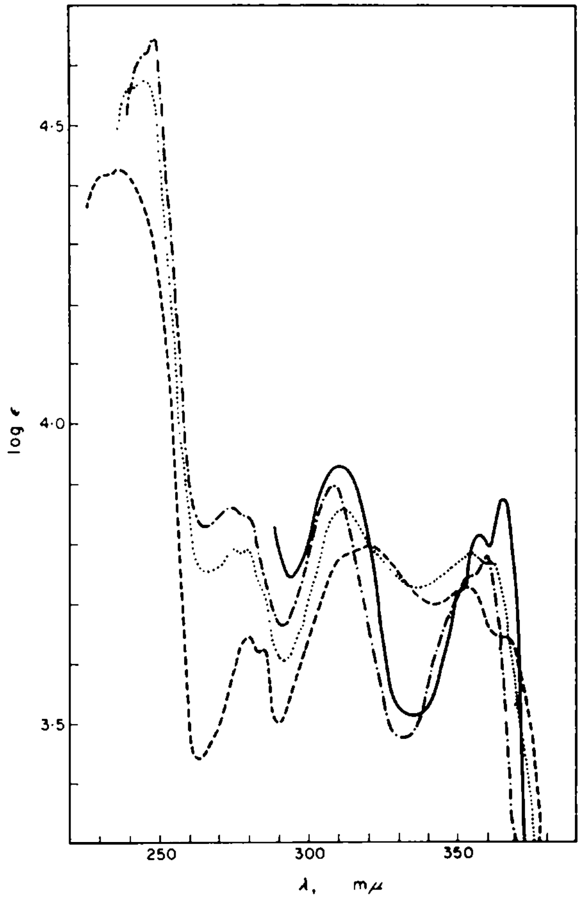

FIG. 1. Absorption spectra of tropophenylene spiroborate (III) in benzene (full line), di-n-butyl ether (dashed line), dioxan (dotted line) and 1,2-dichloroethane (dashed-dotted line).

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* The semi-systematic name tropo-phenylene-tetraoxo-spiroborate is proposed for the ring system III with the numbering system shown (for brevity, the specification "tetraoxo" will be omitted in the subsequent discussion, but as the four oxygen atoms in III might be partially or totally replaced by -S- or -NR- groups, this specification is generally considered necessary). Alternatively, III may be regarded as a benzoderivative of the tropovinylene spiroborate system (cf. VI). We wish to thank Dr. K. L. Loening, Chairman of the Boron Nomenclature Committee, Chemical Abstracts Service, for his kind advice concerning these names.

[7] W. E. Doering and L. H. Knox, *J. Amer. Chem. Soc.* **73**, 828 (1951).

[8] J. W. Cook, A. R. Gibb, R. A. Raphael and A. R. Sommerville, *J. Chem. Soc.* 503 (1951).

a spiranic configuration with the two moieties in perpendicular planes and fairly independent electronic systems, hence the UV spectrum would not be largely different from a superposition of the spectra of catechol (owing to sp^3 hybridization of the boron atom in III, aromaticity in the dioxaborole ring is no longer possible) and of chelated tropolone compounds such as copper tropolone. Clearly the feebly-structured band C in III (275–279 mμ, ε 5–7000) is much closer to the feebly-structured 280 mμ band in catechol (ε 6000) than to the strongly-structured 280 mμ band (ε 22,000) in n-butoxy-benzodioxaborole (Fig. 2). Also, bands A and B resemble the spectrum of copper or sodium tropolone salts[8] rather than the spectrum of tropolone or tropolone ethers.

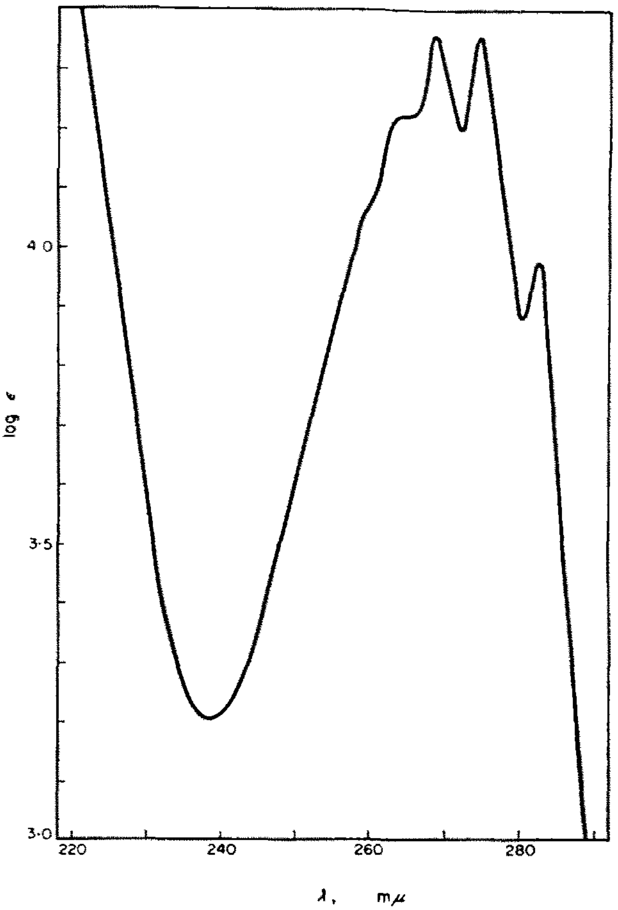


FIG. 2. Absorption spectrum of n-butoxy-benzodioxaborole in cyclohexane.

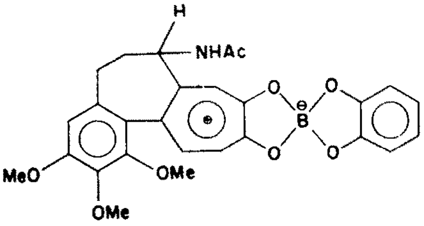
Another argument in favour of structure III is the marked solvent effect on band A (6 mμ in passing from benzene to ethylene dichloride), which is not unexpected with dipolar compounds.[9] Ethers as solvents for III (cf. Fig. 2) are seen to affect considerably the spectrum, probably because they are also able to coördinate with boron.

[9] E. M. Kosower, *J. Amer. Chem. Soc.* **80**, 3253 (1958) and subsequent papers in the series.

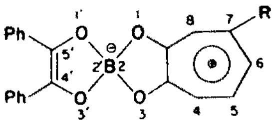
In dibutyl ether the tropolonic maximum at 321 mμ is clearly recognizable and it is probable that in this solvent a structure II is present. In 70 per cent aqueous perchloric acid compound III yields a spectrum identical with that of a mixture of catechol and β-methyltropolone.

The infra-red absorption spectrum shows evidence of boron-oxygen bonds in the 1100 cm^{-1} region and in the strong 1240 and 1455 cm^{-1} bands.[10] There is no evidence of tropolonic carbonyl stretching frequency at 1630 cm^{-1} as would be expected for structure II, but instead a strong band appears at 1596 cm^{-1} which probably represents a superposition of absorption frequencies associated to the phenyl ring and to the chelated tropolone system (copper tropolone absorbs[11] at 1595 cm^{-1}), again supporting formula III.

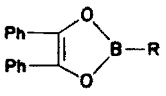
As a further means to discriminate between structures II and III, dipole moment measurements are now in progress.



IV



VI



V

The reaction of other tropolones with dioxaboroles was investigated.

n-Butoxy-dioxaborole (I, R = OBu) reacts with colchicein yielding a yellow compound which is assigned structure IV. n-Butoxy-dioxaborole yields on treatment with colchicein in benzene solution a yellow precipitate which differs from IV being amorphous and difficult to purify owing to extreme sensitivity to atmospheric moisture; this adduct probably retains the tropolone methyl ether structure of colchicein.

From the reaction of benzoin and tri-n-butyl borate the yet unreported 2-n-butoxy-4,5-diphenyl-1,3,2-dioxaborole (V, R = OBu) was formed, since on treatment with β-methyltropolone a compound corresponding to structure VI precipitated.

Thus the reaction between dioxaboroles I or V with tropolones seems to be general; the formation of tropophenylene (III and IV) or tropovinylene (VI) spiroborates may be useful for the identification and characterization of both tropolones and dioxaboroles. These spiroborates are easily purified and non-hygroscopic (the adducts of dioxaboroles with tropolone ethers seem to be hygroscopic, at least in the case of colchicein) and their analytical applications are now being investigated.

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[10] L. J. Bellamy, W. Gerrard, M. F. Lappert and R. L. Williams, *J. Chem. Soc.* 2412 (1958); J. A. Blau, W. Gerrard, M. F. Lappert, B. A. Mountfield and H. Pyszora, *Ibid.* 380 (1960).

[11] B. E. Bryant, J. C. Pariaud and W. C. Fernelius, *J. Org. Chem.* **19**, 1889 (1954); H. P. Koch, *J. Chem. Soc.* 512 (1951).

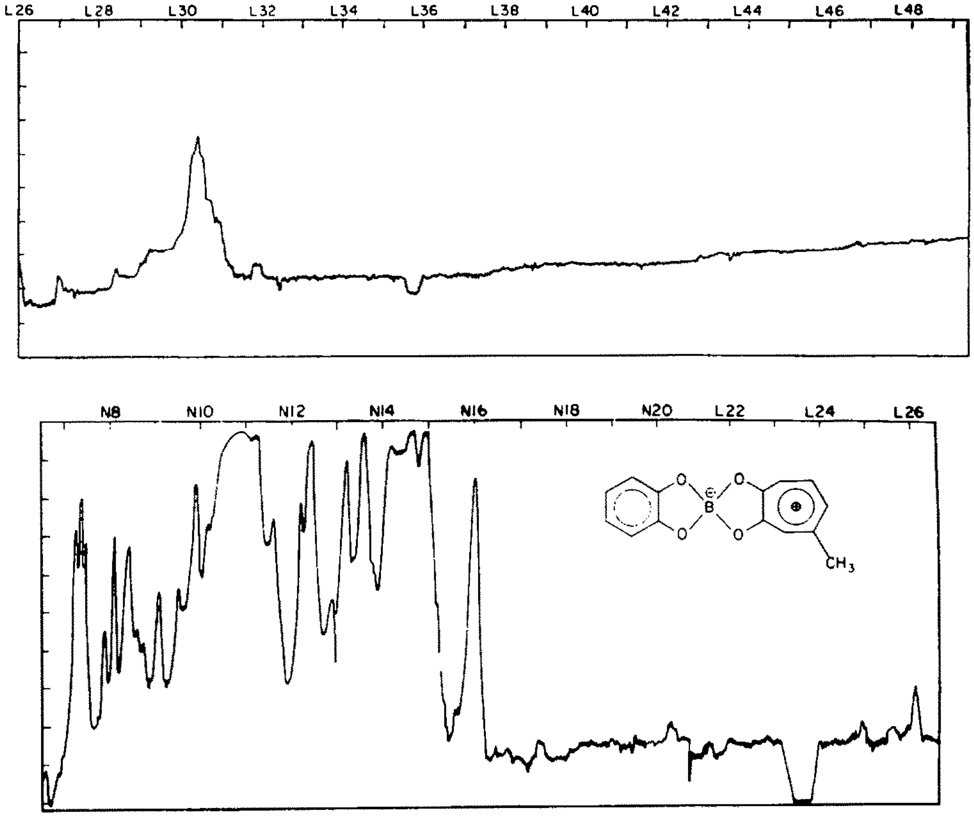

FIG. 3. The infra-red spectrum of 7-methyl-tropophenylene-tetraoxo-spiroborate.

EXPERIMENTAL

5-(7)-*Methyl-tropo-phenylene-tetraoxo-spiroborate* (III). n-Butoxy-benzodioxaborole (I, R = OBu) was prepared in 90% yield by distillation at reduced or atmospheric pressure of an equimolar mixture of catechol and tri-n-butyl borate: colourless liquid, b.p. 110°/2 mm, 245°/760 mm, very sensitive to atmospheric moisture; it attacks the skin and reacts explosively with conc nitric acid.

β-Methyltropolone, m.p. 76° was prepared by hydrogen peroxide oxidation of purpurogallin followed by decarboxylation;[12] using 20 g crude purpurogallin and subliming directly the oxidation product at 220°/760 mm, 1·5 g β-methyltropolone were obtained.

Equimolar amounts of n-butoxy-benzodioxaborole and β-methyltropolone react exothermally forming a yellow crystalline non-fluorescent product. In benzene solution the yield is 92–96%. The product may be recrystallized from benzene, m.p. 210°. In dioxan it is readily soluble yielding a yellow solution. Water does not dissolve it, but hot alcohol or acetic acid gradually dissolve it giving colourless solutions. (Found: C, 66·8; H, 4·85; B, 4·1. $C_{14}H_{11}BO_4$ requires: C, 66·2; H, 4·4; B, 4·3%). The carbon–hydrogen combustion was prolonged for 90 min, until the carbon value no longer increased, in order to decompose all boron carbide, therefore the results are somewhat higher; at normal combustion times, hydrogen values were correct but carbon values were very low. The boron analysis was made by combustion of sample in ash-free filter paper bag in oxygen atmosphere, followed by titration in the presence of mannitol with 0·05 N NaOH (the blank was negligible). U.V. spectrum is shown in Fig. 1. I.R. spectrum: (in Nujol): 733, 743, 785, 809, 840, 858, 870, 905, 949, 985, 1011, 1045, 1080–1100, 1121, 1157, 1218, 1240, 1285, 1599 cm^{-1}; (in hexachlorocyclopentadiene): 1320, 1358, 1415, 1460, 1495 cm^{-1}.

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[12] R. D. Haworth and J. D. Hobson, *J. Chem. Soc.* 561 (1951).

Formation of IV *from colchicein and n-butoxy-benzodioxaborole.* Colchicein (0·5 g) was demethylated in nearly quantitative yield by boiling in 30 ml water and 0·3 ml conc HCl for 1 hr.[13]

Equimolar amounts of anhydrous colchicein and n-butoxybenzodioxaborole in benzene solution yield yellow non-hygroscopic crystals, readily soluble in benzene, purified through repeated precipitation with ligroin, m.p. ca. 140°. (Found: C, 63·7; H, 5·6; N, 3·2. $C_{27}H_{28}BNO_8$ requires: C, 64·3; H, 5·4; N, 2·8%). U.V. spectrum (1,2-dichloroethane): 380 mμ (ε 14000), 250 mμ (ε 40000); (cyclohexane): 377 mμ (ε 11300), 248 mμ (ε 32,000); in both cases a shoulder corresponding to a concealed band at ca. 275 mμ (ε ca. 12,000) is also visible. I.R. spectrum 1661, 1605, 1519, 1492, 1412, 1328, 1282, 1270, 1243, 1220, 1200, 1188, 1145, 1100 broad, 1014, 990, 928, 870, 851, 790, 775, 750, 726 cm^{-1}.

5-(7)-*Methyl-tropovinylene-tetraoxo-spiroborate* (VI, R = CH_3). Equimolar amounts of benzoin and n-butyl borate were fractionated in inert gas atmosphere at 2 mm until all n-butanol was eliminated. The residue which was very sensitive to atmospheric oxygen was dissolved in benzene and treated with a benzene solution of β-methyltropolone. Brick crystals were deposited, m.p. 262° (from benzene, sparingly soluble in the cold). (Found: C, 73·9; H, 5·1; $C_{22}H_{17}BO_4$ requires: C, 73·8; H 5·35%). U.V. spectrum (in di-n-butyl ether): 245 mμ (ε 40,000), 313 mμ (ε 10,200), 354 mμ (ε 9000); (in benzene): 315 mμ (ε 17,400), 351 mμ (ε 13,700), shoulders at 359, 367 mμ. I.R. spectrum: 1601, 1318, 1300, 1280, 1244, 1162, 1150, 1129, 1091, 1074, 796, 762, 728, 698 cm^{-1}.

Ultra-violet absorption spectra were recorded at room temp with a Zeiss VSU1 spectrophotometer. Infra-red absorption spectra were recorded in Nujol and hexachlorocyclopentadiene mulls with a Zeiss UR10 automatic spectrophotometer.

Acknowledgements—Our thanks are due to Miss E. Sliam and Miss M. E. Ionescu for elementary analyses and to Mr. G. Mateescu for infra-red absorption measurements.

[13] S. Zeisel, *Monatsh.* 7, 585 (1886); E. Boyland and E. H. Mawson, *Biochem J.* 32, 1204 (1938).