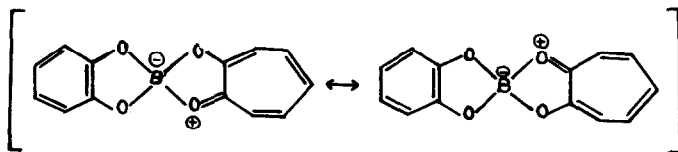
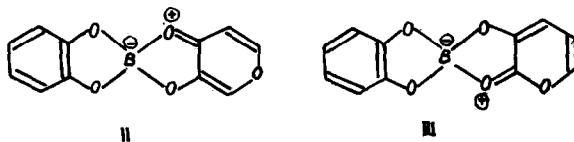


SPIROBORATES. SYMMETRY AND COORDINATION OF
SPIRANIC SUBSTITUTED 3-HYDROXY-2-PROPEN-1-ONE
o-PHENYLENE AND o-VINYLENE BORATES

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In previous papers of this series it was shown (1) that 2-alkoxy-1,3,2-dioxaboroles react with tropolones yielding stable yellow, non-hygroscopic, crystalline spiranic tropolone o-phenylene borates (tropophenylene spiroborates) (I), whose coordinated structure was confirmed by their high dipole moment (2). On the other hand, 3-hydroxy-4-pyrone afforded a colourless hygroscopic product (II) whose coordinative bond appears much weaker (2). The present note reports further compounds prepared by mixing at room temperature equimolar amounts of 1,3,2-dioxaboroles with bidentate ligands, in benzene solution or in the absence of a solvent.





3-Hydroxy-2-pyrone (3) behaves like 3-hydroxy-4-pyrone affording with 2-n-butoxy-4,5-benzo-1,3,2-dioxaborole a colourless hygroscopic product, 3-hydroxy-2H-pyran-2-one *o*-phenylene borate (III), m.p. 72° (from benzene-petroleum ether).

The difference in coordination between tropophenylene spiroborates (I) and pyrylophenylene spiroborates (II) or (III) can be attributed to a smaller difference between resonance energies of pyrone and pyrylium than between tropone and tropylium (2) as well as to a difference between delocalization energies due to the fact that in (I), but not in (II) or (III), the oxygen atoms can be pairwise equivalent.

In order to get more insight into this problem, spiranic substituted 3-hydroxy-2-propen-1-one *o*-phenylene and *o*-vinylene borates (IV), prepared from β -diketones (4,5) or β -ketoaldehydes and 1,3,2-dioxaboroles were studied. These stable, coloured, non-hygroscopic crystalline compounds (IV) are formed exothermally and may be recrystallized from benzene or benzene-petroleum ether, and a few representatives are listed in the table.

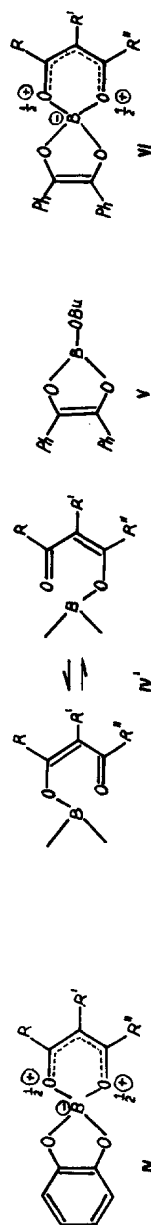
The NMR spectrum of IVb (obtained from benzodioxaborole and acetylacetone) in CDCl_3 with TMS as internal standard presents at room temperature three peaks with τ values

Table 1. Properties of Spiroborates

No.	Compound		M.p. °C	Colour	UV Spectrum in CH ₂ Cl ₂ m μ (lg ϵ)		IR in KBr ^a cm ⁻¹
	R	R' R''					
IVa	Me	H	109 ^b	pink	277, 283, 309,	383 s	1520
b	Me	H Me	192 ^c	yellow	287(4.13), 375s(2.18)		1575
c	Me	Me Me	133	"	283(3.81), 309(3.97), 381s(2.00)		1590, 1530, 1520
d	Me	H Ph	188 ^d	orange	274(3.83), 334(4.28), 435s(2.10)		1574, 1560
e	Me	H pC ₆ H ₄ OMe	153	colourless	257(4.46), 268s	274s	1581, 1520
f	Me	H pC ₆ H ₄ NO ₂	e	red	273, 337		1536, 1520
g	Ph	H Ph	229	red	288(4.11), 368(4.62)		1555, 1539
VIa	Me	H Me	151	orange	256(4.31), 291s		1570
b	Ph	H Ph	189	brown	262(4.26), 363(4.40)		1570

a. Most intense IR bands in the 1500-1600 cm⁻¹ range containing the C = C band at ca. 1570 cm⁻¹ and the C = O band at ca. 1540 cm⁻¹ (6). b. Hygroscopic. c. Lit. (5) mp. 192°.

d. Lit. (5) mp. 218°. e. Oil.



3.26 (four aromatic protons; catechol (7) has $\tau = 3.18$), 4.12 (one olefinic proton) and 7.78 (six methyl protons). The difference, 3.66 ppm, between the last two τ values, is in good agreement with the magnitude 3.58 ppm observed for enol-acetylacetonone (8). In extended spectra only the first peak shows splitting (A_2B_2); the methyl groups (therefore the two oxygen atoms also) appear as equivalent^x; the situation is similar to that of boron fluoride β -diketone complexes (9). We favour resonance (IV) over rapid equilibrium (IV') because the dipole moment of tropophenylene spiroborates also indicates resonance and not equilibrium.

Copper acetylacetonate is decomposed by benzodioxaborole in benzene affording IVb.

By distilling slowly butanol and excess tributyl borate from a mixture of benzoin and tributyl borate under reduced pressure in inert atmosphere, the residue consists in V which affords in benzene crystalline precipitates VI with β -diketones (VI assumes resonance as in IV). On exposure to the atmosphere these complexes VI are gradually decomposed to benzil.

A very pronounced fine structure of the 280 $m\mu$ band of compounds IV and VI is apparent in cyclohexane solution; the interval between vibrational peaks is ca. 820 cm^{-1} ; e.g. IVg has peaks at 238.6, 243.5, 249.1, 255.0, 260.1, 277.0 and 282.9 $m\mu$, and IVd at 250, 256, 261, and 285 $m\mu$.

^x Low temperature NMR spectral determinations are under way.

Similar complexes with other bidentate ligands (cf. also (2,10)) were prepared from benzodioxaborole and anthranilic acid (colourless, m.p. 202°), *o*-aminobenzaldehyde (red, m.p. 105°), salicylaldehyde pale yellow, m.p. 220° , α -aminopyridine (colourless, m.p. 198°), 5,7-dibromo-8-hydroxyquinoline (golden yellow, m.p. 277°), ethyl

β -aminocrotonate (colourless, melts at 112° and resolidifies to a yellow product m.p. 305° ; recrystallization of the colourless product affords the yellow compound); *o*-phenanthroline (yellow, m.p. crude 229° , recrystallized from chloroform-petroleum ether m.p. 180°); 2,4,6-triphenyl-1,5-pentenedione (pseudobase of 2,4,6-triphenylpyrylium gave glistening brown leaflets m.p. 215°); 4-methyl-3-hepten-2,6-dione (pseudobase of 2,4,6-trimethylpyrylium gave a yellow product, m.p. 120°). No such crystalline complexes could be prepared from saturated β -hydroxyketones such as diacetonol, or from non-enolizable β -diketones such as 3,3-dimethyl-2,4-pentanedione.

All products mentioned gave satisfactory analyses for C, H, B, and N. Full details are given in a paper under press in Revue Roumaine de Chimie.

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