

THE ACCEPTOR ABILITY OF THE $-B(OR)_2$ GROUPO.EXNER^a and R.BOSE^b^a *Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague 6*^b *Fisheries Research Board of Canada,
Vancouver Laboratory, Vancouver 8, Canada*

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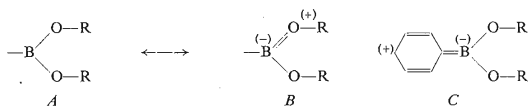
Dipole moments of the cyclic boronic esters I–VI yielded the group moment of 1.9 D for the $C-B(O-C)_2$ grouping in the axially symmetrical, not deformed shape. Its direction from B to C arises from the contribution of the mesomeric formulation B. When the group is bonded to the aromatic nucleus, its moment is reduced by the mesomeric dipole moment of 0.4 D, which originates in the mesomeric formula C. In the five-membered cycle structure the $O-B-O$ angle is deformed, the weight of the formula B lessened and of C increased; the mesomeric dipole moment reaches 0.7 D. This interpretation is confirmed by the proton chemical shifts. The $B(OR)_2$ group is thus one of the rare acceptor groups capable of mutual conjugation even with such weak donor groups as the unsubstituted benzene nucleus.

The comparative study of dissociation constants and reactivities of benzene derivatives¹ revealed that many acceptor groups are less conjugated with the benzene nucleus than the usual donor groups, and much less than it had been assumed in the traditional interpretation. In particular the mesomeric effect of the groups NO_2 , CN, CF_3 , SO_2X is almost zero, providing there is, at the same time, no donor group present in a suitably conjugated position. The effects of these groups differ little when they act from the *meta* or *para* position, respectively, and the small systematic differences were attributed to the π -inductive effect¹. Similarly the so-called mesomeric dipole moments, represented by the dipole moment difference between an aromatic and an aliphatic derivative², may be explained by the induction within the π -electron system and do not necessarily prove any conjugation^{3,4}.

An actual conjugation may occur only in certain monosubstituted benzenes with acceptor substituents; e.g. the M-effect of the COX groups, although small is, nevertheless, real¹. The only strongly conjugated acceptor seems to be the $B(OR)_2$ group which is unique with respect to the occurrence of the electron sextet in the non-polar formula (A). The electron gap can be filled either by the n-electrons of the oxygen atoms (B), or by the π -electrons of the aromatic nucleus (C). The M-effect

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of the B(OR)₂ group as a whole then arises from the relative contribution each mesomeric form makes to the electron density on boron.



From the dissociation constants of 3- and 4-carboxybenzeneboronic acids⁵ the σ_R constant of 0.21 was assessed for the substituent B(OH)₂, revealing the strongest acceptor ability of the groups investigated¹.

TABLE I
Polarization Data of Cyclic Boronates in Benzene Solution (25°C)

No	Compound	Reference	P_2 cm ³	R_D^a cm ³	$\mu(5\%)^b$ D	$\mu(15\%)^b$ D
I		13	93.7	35.0	1.67	1.62
II		14	76.6	41.6	1.27	1.18
III		15	224.6	49.4	2.90	2.86
IV		16	150.0	39.7	2.30	2.25
V		17	146.8	46.3	2.19	2.14
VI		^c	351.6	54.1	3.79	3.76

^a Calculated using Vogel's increments⁸ valid for 20°C, the atomic refraction⁶ of boron 3.1 cm³, and the increment⁶ of 0.84 cm³ for the conjugation C₆H₅-B; ^b correction for atomic polarization 5% or 15% of the R_D value, respectively; ^c this paper.

* This agreement can serve also as test of the experimental accuracy which may be somewhat better than previously⁶ since the compounds are less sensitive to the air humidity.

In this paper we attempt to estimate the mesomeric dipole moment of the $B(OR)_2$ group using essentially the classical approach². In order to compare dipole moments of aromatic and aliphatic derivatives, compounds *I–VI* (Table I) have been selected. The ring closure in these molecules fixes the conformation^{6,7} which otherwise need not be exactly the same in all the derivatives; in addition the relative weight of the formulas *B* and *C* can be controlled to a certain degree by changing the ring size. The bromine atom in the *para* position assists in determining the moment direction.

The experimental dipole moments are collected in Table I. By comparing the moments of *II* and *III*, or *V* and *VI*, one can deduce that they are oriented approximately along the molecule axis, in the direction from the atom *B* to the atom *C*. This statement applies more exactly for molecules *II* and *III* which may be assumed to be practically planar, but even in *V* and *VI* at least the five ring atoms might be expected to lie in a plane in accord with the conformation of 2,4-pentenediol borate⁹. Assuming exact planarity, the *para* bromine atom should enhance the dipole moment by 1.60 D, while experimentally the differences found are 1.68 and 1.62 in *III* and *VI*, respectively. Since the mesomeric moment arising from structure *C* is oriented from the atom *C* to the atom *B*, it follows that the moments of *I* and *IV* have the same direction as the others, *i.e.* from the atom *B* to the atom *C*. Hence the deciding contribution to all the dipole moments in Table I originates in the structures of the type *B*.

With this in mind let us compare the moments of the two aliphatic derivatives *I* and *IV*. It is easily seen by analogy with carbocyclic compounds¹⁰ that the endocyclic double bond is less stable in the 5-ring due to unfavourable bond angles than in the 6-ring. Hence the moment of *I* is expected to be reduced and *IV* should more closely represent a true, undistorted $B(OR)_2$ group in its *Z,Z*-conformation;* its group moment may be given approximately as 1.9 D including the bonds $C-B(O-C)_2$. The mesomeric dipole moment of the whole group is then represented by the difference between *V* and *IV*, or, in the more sophisticated approach, allowance is to be made for different values of $H-C_{a1}$ and $H-C_{ar}$ formal bond moments in the system used by us⁶. Hence the proper value of the mesomeric moment should be c. 0.4 D (from C_6H_5 to *B*) corresponding to the contribution of formula *C* (including the two formulas with the charges in *ortho* positions) of c. 3%. In 5-ring compounds the mesomeric moment is enhanced to c. 0.7 D, corresponding to 5% contribution of *C*. The result is easily rationalized, since from the two competing mesomeric structures, *C* involves an exocyclic double bond and is favoured in the 5-ring¹⁰. The mesomeric dipole moment in open-chain derivatives cannot be simply determined due to the unsymmetrical conformation^{6,7} of the $B(OR)_2$ group but it is probably

* More accurately the difference between *I* and *IV* may be also based upon the presence of an additional methylene group and somewhat different geometry. With appropriate corrections the actual effect of the five-membered ring may be given by some 0.4 D. When we assess roughly the dipole moments of *A* and of two equivalent *B* formulas to be 0.9 and 5.1 D, respectively, we may say that the contribution of some 30% of *B* in *IV* is reduced to some 20% in *I*.

TABLE II
Chemical Shifts of Protons in Cyclic Boronates

Compound	CH ₂ O	CH ₂ (CH ₂ O)	CH ₂ B	(CH ₂) ₂	CH ₃	C ₆ H ₅ (<i>o</i>)	C ₆ H ₅ (<i>m,p</i>)
<i>I</i> ^a	4.11	—	0.80	1.34	0.88	—	—
<i>II</i> ^a	3.90	—	—	—	—	7.80	7.21
<i>IV</i> ^a	3.87	1.84	0.60	1.27	0.84	—	—
<i>V</i> ^b	4.04	1.91	—	—	—	7.74	7.27

^a Shifts in p.p.m. against tetramethylsilane as internal standard, measured as neat liquids; ^b in CDCl₃ solution.

not far from 0.4 D. Our first estimate⁶ of 0.2 D seems to be too low. The conjugation cannot be called in question with respect to the possible induction in the π -electron system, as has been done in the case of the nitro group³. This is because the suppositious mesomeric moment is in the same direction as the group moment in the case of the NO₂ group, but opposite in the case of B(OR)₂; in the latter case it could only increase by some hundredths of D when corrected for the induced moment.

The foregoing interpretation is further supported by the NMR chemical shifts (Table II). While the hydrogen atoms of the butyl groups in *I* and *IV* are strongly shifted to higher fields, the effect is most pronounced in *IV* (see particularly the methylene group next to boron). This difference is in accord with the greater electron attracting power of boron in *I*, due to the reduced contribution of structure *B*. The same effect is observed with aromatic *ortho* protons, when comparing *II* and *V*. The shifts for the CH₂ groups adjacent to oxygen are less variable and reflect less clearly the contribution of mesomeric formulas.

Summarizing, we can state that the B(OR)₂ is a relatively strong acceptor, capable of conjugating with even such weak donors as the unsubstituted phenyl group. This conclusion follows from the dipole moments in Table I as well as from the σ_R values¹; compare also the σ_R constant of the B(OH)₂ group based on IR spectra¹¹. Finally the acceptor ability of the 5-membered cyclic group B(OCH₂)₂ is the most pronounced.

The dipole moments now measured can serve to check once more the values of bond moments (+)B—C(−) 0.7 D and (+)O—B(−) 0.25 D, used previously in determining the conformation^{6,7}. The latter value is purely formal, of course, and as it includes the contribution of the mesomeric form *B* it cannot be applied to 5-membered cyclic compounds given in Table I. Only compound *IV* can be used for the test but the computed value of 2.74 D is in only fair agreement with the experimental value. Although the possibility⁷ does exist that the bond moments have been slightly underestimated, nevertheless, they comply with the open-chain derivatives. Hence it is probable that the electronic distribution is somewhat distorted even in the 6-ring and no completely universal bond moments can be derived at present. Nevertheless, the previous qualitative conclusions⁶ concerning conformation are not materially affected by this uncertainty.

EXPERIMENTAL

Materials

All cyclic boronates I—VI were prepared from the dihydric alcohols and the appropriate boronic acid by the usual procedure¹² and following the removal of solvent *in vacuo* were recovered in a pure state by distillation at 0.1 Torr. The purity of the products was established by examination of the NMR spectra and by gas chromatography on 10% SE30 on Gas Chrom P.

2-(4'-Bromophenyl)-1,3,2-dioxaboran (VI), yield 80%, m.p. 63°C. For $C_9H_{10}BBrO_2$ (240.9) calculated: 44.87% C, 4.18% H, 33.17 Br, 4.49% B; found: 44.88% C, 4.04% H, 33.30% Br, 4.33% B.

Measurements

Dipole moments were measured by the same technique as in the previous work⁶. All operations were carried out in a dry box. The NMR spectra were recorded on a 100 MHz Varian spectrometer at 28.5°C.

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