

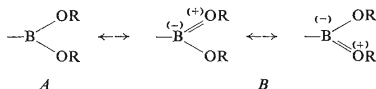
DIPOLE MOMENTS AND CONFORMATION OF BORONIC ESTERS

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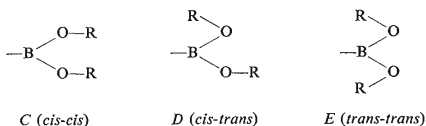
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Dipole moments of boronic esters 1–10 have been measured in benzene solution and the mean moment of 1.6 D at the angle 150° to the C—B bond computed for the C—B(OR)₂ group. Hence, the conformation of this group is certainly not axially symmetric and the planar *cis-trans* form D with the C_s symmetry is compatible with experiments although several non-planar forms cannot be excluded with certainty. The group moment cannot be quite reliably divided into separate bond moments, but it seems that the values of Lumbroso and Grau for the B—C and O—B bonds are not far from reality.

The conformation of the functional group in boronic esters is of interest as a part of a broader problem, the conformation of two equivalent bonds going from one central atom¹. Symmetrical conformations of such groups with a C₂ or C_s symmetry seem *a priori* to be most probable and were in fact found for example with acetals², acylals³, carboxylic acid anhydrides⁴ and gem-disulfones¹. However, the unsymmetrical conformation of dithioacetals has been proven with certainty¹ although the exact shape of the molecule is not known. With boronic esters the situation is different from that with dithioacetals, resembling rather that of carboxylic anhydrides⁴, as a result of mesomerism A ↔ B, which gives the B—O bond a partial double bond character and is reflected in its length⁵, although not in its force constant⁶.



Hence the planar conformations C—E have to be considered first. Of these, the *cis-cis* form (C) is less probable for steric reasons. The actual form of boronic esters has been little studied; much more attention has been devoted to easily accessible alkyl borates, the conformation of



which imposes other problems⁵⁻¹¹. Lumbroso and Grau¹¹ preferred the *cis-trans* form (D) on the basis of dipole moment measurement of a single substance (butyl butaneboronate), while the conformation of dimethoxyborane remained uncertain¹² and the *trans-trans* form (E) was claimed for bromodimethylthioborane¹³.

We followed the same experimental approach as formerly¹⁻⁴ which is based on dipole moment measurement in solution and makes use of the comparison with a *para* halogen derivative³. To calculate theoretical dipole moments the values of bond moments C—B and B—O and the mesomeric moment B—C₆H₅ are needed, which are not reliably known¹¹. Therefore we centered our interest on benzyl derivatives 5 and 6 in which at least the last moment is eliminated. The polyderivatives of methane 7-9 were useful to estimate the overall symmetry of the B(OR)₂ group; particularly from the compound 9 one can decide at once whether this group is axially symmetric or not.

EXPERIMENTAL AND RESULTS

Materials. The compounds 1-10 were described previously¹⁴⁻¹⁷.

Measurement of dipole moments. The same technique was used as in previous work¹⁻⁴ except that all operations were carried out in a dry box to avoid hydrolysis. Molar refraction of compounds 1-4 and 10 was determined experimentally^{14,15}, for the remaining ones it was calculated using Vogel's increments¹⁸ and the value 3.1 cm³ for the boron atom. The literature values for the latter differ^{14,19,20}. From comparison of several classes of compounds¹⁴ the above value seems most probable whereas the value 3.94 cm³ from areneboronic esters includes conjugation increment¹⁴ and the value 2.24 cm³ from alkyl borates¹⁹ is exceptionally low when compared with the others^{14,20}. The discrepancy does not affect markedly the final values of dipole moments. Experimental values of polarization, molar refraction and dipole moments are listed in Table I. The correction to atomic polarization may be of importance with the compounds investigated due to their low moments (compare boric acid esters^{7,11}). Recently Smyth has questioned the correction and called it an excuse for inaccuracies of both the method and the experiment²¹, but the experimental data²², even those by Smyth himself²³, do not confirm this postulate for all compounds. We have given the usual values with 5% or 15% correction as possible limits.

Calculation of theoretical dipole moments. Most calculations were carried out graphically with an accuracy of about ±0.03 D. The bond moments H—C_{al} 0.3, H—C_{ar} 0 D, C—O 0.74 D, C_{ar}—Cl 1.60 D were used throughout as previously¹⁻⁴. The bond angles ∠C—B—O = ∠O—B—O = 120°, ∠B—O—C = 113° were taken according to ref.⁵.

DISCUSSION

The values of Table I can be considered internally consistent, especially the small difference between compounds 3 and 4 is in the expected direction. They are further of the same order of magnitude as values for similar compounds from the literature^{7,8,11}. Let us consider first the two derivatives of toluene- α -boronic acid (5 and 6) and apply our graphical method of comparison³. It requires to compute moments expected for individual conformations and plot them as μ^2 in a graph,

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

No	Compound	∞P_2^3 cm ³	R_D cm ³	μ (5%) ^a D	μ (15%) ^a D	μ calc.
1	2-CH ₃ C ₆ H ₄ B(OC ₂ H ₅) ₂	109.9	57.70 ^b	1.55	1.46	1.58
2	3-CH ₃ C ₆ H ₄ B(OCH ₃) ₂	94.6	48.37 ^b	1.46	1.38	1.33
3	4-CH ₃ C ₆ H ₄ B(OCH ₃) ₂	89.2	48.49 ^b	1.37	1.28	1.19
4	4-CH ₃ C ₆ H ₄ B(OC ₂ H ₅) ₂	103.3	58.05 ^b	1.44	1.34	1.19
5	C ₆ H ₅ CH ₂ B(OC ₄ H ₉) ₂	127.9	75.6 ^c	1.54	1.41	1.46
6	4-ClC ₆ H ₄ CH ₂ B(OC ₄ H ₉) ₂	248.8	80.5 ^c	2.83	2.76	2.60
7	CH ₂ [B(OCH ₃) ₂] ₂	90.2	40.0 ^c	1.53	1.47	1.69
8	CH[B(OCH ₃) ₂] ₃	139.5	56.6 ^c	1.98	1.90	1.76
9	C[B(OCH ₃) ₂] ₄	142.0	73.2 ^c	1.78	1.68	1.60
10	C ₆ H ₅ B(C ₂ H ₅)OC ₄ H ₉	98.1	61.09 ^b	1.29	1.17	1.47

^aCorrection for atomic polarization 5% or 15% of R_D , respectively; ^bExperimental values^{14,15} at 25°C; ^cComputed with atomic refraction of boron 3.1 cm³ and Vogel's increments¹⁸ valid for 20°C.

the values for the unsubstituted compound on the *x*-axis and for its *para* chloro derivative on the *y*-axis. Due to the mesomerism within the group B(OR)₂ we started from planar forms C—E and used the bond angles and bond moments given in the experimental section. The main problem it to choose reliable moments for the bonds B—C and O—B since the only available values of Lumbroso and Grau¹¹ and Becher²⁴ were derived in a complicated way and with many assumptions. We used the moments ⁺B—C⁻ 0.7 D, corresponding to B—R 0.4 D in ref.¹¹ and ⁺O—B⁻ 0.25 D; in the latter value¹¹ the mesomerism A ↔ B rather than the mere polarity of atoms B and O is expressed. The graphical representation (Fig. 1) shows that only the unsymmetrical conformation D is compatible with experiment when a free rotation around the bond C—B is assumed. The result is, however, strongly dependent on the choice of bond moments B—C and O—B; on the other hand, different combinations of these values can afford the same final result.

Non-planar forms, arising eventually only by oscillations around the equilibrium position, have also been claimed for alkyl borates^{5,7,11}, besides the planar one^{9,10}. Hence we considered some simple non-planar conformations for alkyl boronates, too. In Fig. 1 the transformation of the *cis-cis* form (C) into *trans-trans* (E) by two paths is shown, *i.e.* by the rotation of both alkoxy groups in the same direction, transitory conformations having the C₂ symmetry (full line), and in the opposite direction with the C_s symmetry (broken line). Further unsymmetrical conformations arise from D by the rotation in the same direction (dotted line), free rotation around

the C—B bond being supposed in each case. Considering the uncertainty in the bond moments, several conformations can be viewed as compatible with experiment.

In order to obtain further independent evidence we studied the polyderivatives of methane 7–9. The compound 9 gives direct and unambiguous proof that the group —B(OR)₂ is not axially symmetrical since its moment would be zero. Assuming a free rotation around the C—B bonds the effective moments of compounds 7–9 are given by

$$\bar{\mu}^2(7) = 2m^2 - 0.667m^2 \cos^2 \alpha + 0.8m \cos \alpha + 0.12,$$

$$\bar{\mu}^2(8) = 3m^2 - 2m^2 \cos^2 \alpha + 0.6m \cos \alpha + 0.09,$$

$$\bar{\mu}^2(9) = 4m^2 \sin^2 \alpha,$$

where m is the moment of the C—B(OR)₂ group, including the C—B bond, and α is its angle with this bond. The concept of free rotation is an artificial one, of course; it can only mean that several forms are populated with approximately equal probabilities. In the case under consideration an actually free rotation is far from reality;

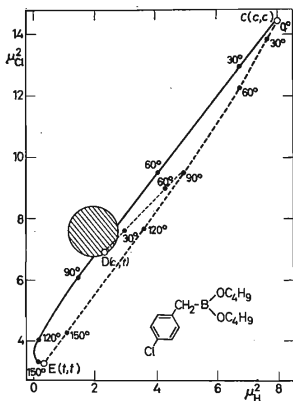


FIG. 1

Comparison of Dipole Moments Experimentally Determined (hatched circle) and Computed for Conformations C—E and Various Non-Planar Ones

x-Axis butyl toluene- α -boronate 5, y-axis its *para*-chloro derivative 6.

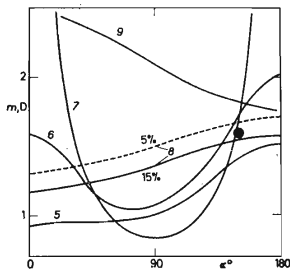


FIG. 2

Graphical Determination of the Moment of the C—B(OR)₂ Group

The curves connect pairs of values m and α compatible with experiment for a given compound (5–9); ● values chosen.

particularly in compound 9 no rotation is possible, according to Stuart–Briegleb models, and in compound 8 it is strongly restricted. Nevertheless we attempted to estimate best values of m and α with respect to all compounds 5–9, assuming the free rotation. Each curve in Fig. 2 corresponds to one compound and connects all pairs of values in the m vs α plane, complying with the experimental moment. The effect of the correction for P_A is shown at compound 8 – where it is most marked – by a dashed line for the 5% correction; the remaining lines correspond to the 15% correction. The values $m = 1.6$ D and $\alpha = 150^\circ$ can be reasonably chosen, they compare favourably with the figures 1.67 D and 144° computed as a vector sum of bond moments given by Lumbroso and Grau¹¹. The moments listed in Table I were computed with the former values. It is true that the conformation and bond moment of the C—B(OR)₂ group need not be the same in overcrowded compounds 9 and 8 but Fig. 2 gives no support for such a suspicion, and shows the importance of *para*-substituted derivatives³ since without the compound 6 no conclusion could be reached.

With the compounds 1–4 and 10 the mesomeric moment, expressing in a formal manner the conjugation with the benzene nucleus, is to be accounted for. However, its small value, combined with the uncertainty in the remaining bond moments, gives no real chance to estimate it directly from experimental moments. A quantitative study revealed that the B(OH)₂ group on the benzene nucleus exerts almost as strong a mesomeric effect as the COX groups²⁵. Hence we calculated the expected moments with a mesomeric moment ⁺Ph—B⁻ 0.2 D (Table I). With compounds 1, 2 and 10 the averages (in μ^2) of the two extreme conformations were taken. The disagreement in the case of the *ortho* derivative 1 is easily understood for steric reasons but no more detailed conclusion is possible without knowing the actual conformation of the B(OR)₂ group. Could we disregard the unknown mesomeric moment, the compound 10 would yield an independent test of the bond moments¹¹ B—C and O—B. However, the mesomeric moment can hardly be large enough to account for the discrepancy with the experimental value, even ⁺Ph—B⁻ 0.7 D would not be sufficient. Hence it seems that one of these bond moments or both have been somewhat overestimated.¹¹

We conclude that the group moment of 1.6 D at an angle of 150° is a reasonable estimate for the C—B(OR)₂ group. We prefer not to attempt its resolution into individual bond moments since the conformation of the group is not sufficiently proven. The dipole moment data exclude any axially symmetric conformation; it follows that if only planar forms are considered as admissible, the only possibility is the *cis-trans* form (D). However, non-planar conformations with the C_s symmetry or even the unsymmetrical ones, resembling D, cannot be excluded with certainty; particularly in overcrowded molecules 9 and 8 the pure *cis-trans* conformations is almost impossible. In general, conformation of boron compounds imposes serious problems^{5–13} and further progress is probably not possible without special model compounds.

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