small yield in this work. Its fluorine content was found to be only 13.6% compared to a theoretical of 30.2% for phenyldifluoroborane. A possible explanation of the source of this 75–80° boiling product is afforded by our observation that ether–boron fluoride can undergo extensive decomposition on fractional distillation to give ethylene and other incompletely characterized products,[17] one of which boils sharply at 78°. Benzene is also a possible product in this reaction since it also has been observed that partially decomposed ether–boron fluoride is strongly acidic. It is probable that the product obtained by Krause from the reaction of boron fluoride with phenylmagnesium bromide contains benzene and one of the decomposition products of ether–boron fluoride. It is also possible that appreciable amounts of toluene may be present in the material reported by Krause[6] as *p*-tolyldifluoroborane (b.p. 95–97) along with decomposition products of ether–boron fluoride.

The reaction of zinc diphenyl with distilled ether–boron fluoride recently has been reported[8] to yield phenyldifluoroborane in 46% yield. In this case the product is again uncharacterized and is reported as having a boiling point of 82 to 85° at 730 mm. The product is reported as obtained by repeated distillations of the reaction product through a column. Under such conditions ether–boron fluoride could produce material boiling at that temperature and again benzene may be present due to the action of partially decomposed ether–boron fluoride on the zinc diphenyl. The action of zinc alkyls on boron chloride has been shown to result in complete alkylation.[18]

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[17] P. A. McCusker and L. J. Glunz, unpublished work.

[18] H. J. Becher, *Z. physik. Chem., Frankfurt*, **2**, 276 (1954).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Organoboron Compounds. V. Electric Moments of Some Alkyl- and Aryldihalogenoboranes in Benzene and Dioxane[1-3]

BY COLUMBA CURRAN, PATRICK A. MCCUSKER AND HENRY S. MAKOWSKI

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The electric moments of organodihalogenoboranes in benzene reveal a strong resonance involving structures of the type $^{+}C_6H_5{=}^{-}BX_2$ which make a greater contribution to the chloro- than to the fluoro- compounds. The moments in dioxane indicate that the chloro- compounds are practically completely solvated and the fluoro- compounds only partially solvated. Carbon is negative with respect to boron in the dioxanates.

Electric moments of alkyldihalogenoboranes are of interest in determining the relative importance of resonance involving halogen-to-boron double bond character in the fluoro, chloro, bromo and iodo compounds. The present study is limited to fluorides and chlorides. The moments of the aryldihalogenoboranes offer a direct measurement of the effect of π-electron delocalization on the overall polarity of the molecules. Of all elements, trivalent boron appears most likely to have large contributions of resonance structures of the type $^{+}C_6H_5{=}^{-}MX_2$ because of its unsaturated character and its position in the top row in the periodic table. Evidence for C=B double bond character in the phenyldichloroborane has been obtained from the electron diffraction studies of Coffin and Bauer.[4] The C–B bond distance in this compound is 1.52 Å. compared to a value of 1.56 Å. for trimethylborane.[5]

Previous work in this Laboratory[6] has revealed a moment of 4.90 for normally non-polar boron trichloride when it is solvated in dioxane. Moments of the organodihalogenoboranes have been obtained in dioxane to study the extent of coördination between oxygen and boron in these solutions and to determine the effect of this coördination on the polarity of the C–B and B–X bonds.

Experimental

Preparation of Solutions.—The preparation and purification of the compounds measured have been reported in preceding papers.[3,7,8] Solutions for measurement were prepared, in the weight fraction range 0.01 to 0.05, by pipetting portions of freshly distilled compounds in a nitrogen-filled dry-box into weighed glass-stoppered 60-ml. weighing bottles. The weighed samples were diluted with solvent in a similar manner.

Measurements and Calculations.—Dielectric constants were measured by the heterodyne beat method, using a one megacycle crystal controlled oscillator. The glass dielectric cell, constructed by J. C. Balsbaugh, Marshfield Hills, Mass., has five concentric nickel plates supported by wires imbedded in glass. The center, inner and outer plates are connected to the ground lead. The cell has an air capacity of 100 μμf, and was modified by the addition of inlet and outlet glass tubes. Solutions were introduced into the cell through glass tubing under a pressure of dry nitrogen. The cell was calibrated with benzene, ϵ 2.2730. Densities were determined with a Lipkin pycnometer having a volume of 5 ml. The average density of the benzene used was 0.8732 and that of the dioxane 1.0284.

Polarizations at infinite dilution were calculated by the Hedestrand method, using extrapolated values of $\Delta\epsilon/wf_2$ for the solutions listed in Table I and average values for the other solutions, which did not show a regular variation of the $\Delta\epsilon/wf_2$ ratio with concentration. The moments in De-

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[1] Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September, 1955; see Abstracts, p. 2R.

[2] From the dissertation submitted by Henry S. Makowski in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Notre Dame, 1957.

[3] Paper IV, P. A. McCusker and H. S. Makowski, THIS JOURNAL, **79**, 5185 (1957).

[4] K. P. Coffin and H. S. Bauer, *J. Phys. Chem.*, **59**, 193 (1955).

[5] H. A. Levy and L. O. Brockway, THIS JOURNAL, **59**, 2085 (1937).

[6] T. J. Lane, P. A. McCusker and C. Curran, *ibid.*, **64**, 2076 (1942).

[7] P. A. McCusker and L. J. Glunz, *ibid.*, **77**, 4253 (1955).

[8] P. A. McCusker, E. C. Ashby and H. S. Makowski, *ibid.*, **79**, 5182 (1957).

bye units were calculated from the relation $\mu = 0.221 \sqrt{P_{2\infty} - 1.05MR_D}$ at 25°.

In Table I are listed the dielectric constants and weight fractions of those solutions for which an extrapolated value of $\Delta\epsilon/wf_2$ was used in calculating the electric moments.

TABLE I

WEIGHT FRACTIONS AND DIELECTRIC CONSTANTS OF SOLUTIONS

In benzene		In dioxane	
wf_2	ϵ	wf_2	ϵ
Phenyldifluoroborane		*n*-Hexyldichloroborane	
0.01495	2.3150	0.00000	2.2082
.03150	2.3752	.01203	2.3966
.04603	2.4280	.02961	2.7106
.05767	2.4708	.04325	2.9688
p-Tolyldifluoroborane		Phenyldifluoroborane	
0.01373	2.3372	0.00000	2.1984
.03354	2.4321	.01128	2.3502
.05069	2.5183	.02618	2.5586
.06475	2.5880	.03983	2.7546
		.04871	2.8889
Phenyldichloroborane		*p*-Tolyldifluoroborane	
0.03331	2.3854	0.00000	2.2088
.05320	2.4525	.01435	2.3787
.07035	2.5105	.02760	2.5433
		.04314	2.7426
p-Tolyldichloroborane		.05725	2.9278
0.01494	2.3420	Phenyldichloroborane	
.03230	2.4251	0.00000	2.2081
.04829	2.5016	.03127	2.8089
.06730	2.5950	.04482	3.0952
In dioxane		.05464	3.3090
n-Amyldichloroborane		*p*-Tolyldichloroborane	
0.00000	2.2077	0.00000	2.2081
.01513	2.4723	.01370	2.4330
.03192	2.8030	.02563	2.6506
.04453	3.0689	.04279	2.9791
		.05540	3.2326

TABLE II

DIELECTRIC AND DENSITY RATIOS, POLARIZATIONS AND ELECTRIC MOMENTS AT 25°

Halogenoborane	Solvent[a]	$\Delta\epsilon/wf_2$	$\Delta d/wf_2$	$P_{2\infty}$	MR_D	μ
n-Amyldifluoro-	B	1.95	−0.01	86	29.38	1.64
	D	11.64	− .01	264		3.37
n-Amyldichloro-	B	1.51	.09	90	39.49	1.55
	D	16.54	.13	454		4.49
n-Hexyldifluoro-	B	1.69	− .01	89	34.02	1.61
	D	10.03	− .004	259		3.30
n-Hexyldichloro-	B	1.39	.08	96	44.07	1.55
	D	14.97	.10	454		4.46
Phenyldifluoro-	B	2.99	.15	107	30.78	1.90
	D	13.22	.23	302		3.63
Phenyldichloro-	B	3.37	.23	141	41.71	2.19
	D	17.91	.32	499		4.72
p-Tolyldifluoro-	B	4.78	.09	164	35.89	2.48
	D	11.63	.17	300		3.58
p-Tolyldichloro-	B	4.71	.17	196	47.13	2.68
	D	15.87	.27	487		4.63

[a] B, benzene; D, dioxane.

Discussion of Results

The electric dipole moment of difluoromethane has been determined by Lide[9] from microwave measurements to be 1.96, compared to the value 1.62 for dichloromethane. From Table II it is seen that the moment of RBF_2 is 1.63 compared to 1.55 for $RBCl_2$. The smaller difference in moment for the latter pair suggests a greater $^-B{=}^+X$ double bond character in the fluoroboranes, in accord with expectations. The increase in moment 0.64 from amyl- to phenyldichloroborane indicates strong resonance involving the $^+C_6H_5{=}^-BCl_2$ structures. The moment of $C_6H_5BF_2$, 1.90, compared to that of $C_6H_5BCl_2$, 2.19, indicates a resonance competition between structures involving $^-B{=}^+F$ and $C{=}^-B$ bonds and reveals that the B–Cl bond is much more polarizable than the B–F bond. The increases in moment from the phenyl to the tolyl compounds, 0.58 and 0.49 for the fluoro and chloro compounds, respectively, suggest an appreciable hyperconjugation effect $H\,^+H_2C{=}C_6H_4{=}^-BX_2$ in the *p*-tolyldihalogenoboranes.

The organodihalogenoboranes show expected increases in moment from benzene to dioxane solution. The fact that the increases are significantly greater for the chloro than for the fluoro compounds suggest that the latter are less completely solvated than the former. This indicates less unsaturation of the boron outer shell in the fluoro compounds, due to greater $^-B{=}^+X$ double bond character, and is in line with the observation that boron trifluoride has smaller heats of reaction with pyridine and with nitrobenzene than does boron trichloride.[10]

In the event of incomplete solvation of the organodichloroboranes with dioxane, it would be expected that the aryl compounds would be appreciably less solvated than the alkyl derivatives because the former undergo a significant loss in resonance stabilization by the formation of the O → B bond which saturates the boron and excludes any C=B double bond character in the dioxanate. The fact that in dioxane phenyldichloroborane has a larger moment, 4.72, than that of the hexyl analog, 4.49, strongly suggests that these compounds are practically completely solvated in dioxane.

Considering the difference in moment of the phenyl and *p*-tolyl groups to be 0.4 in the dioxanates, a vector treatment of the observed moments of phenyl- and *p*-tolyldichloroborane in dioxane, 4.72 and 4.63, reveals that the phenyl group is negative with respect to boron and that the B → C dipole is at an angle of 75° to the over-all moment of the dioxanate. In the absence of any C=B double bond character, the phenyl group is negative with respect to the alkyl group, and this angle of 75° accounts for the larger moment observed for $C_6H_5BCl_2{\cdot}C_4H_8O_2$ than for the alkyl analogs.

From the vector treatment indicated above it is seen that the O → B bond in the dioxanate makes an angle of about 5° with the over-all moment, and the resultant of the B → Cl dipoles makes an angle of about 50° with the over-all moment. It is not possible to assign definite values to the O → B dipole and the BCl_2 resultant from these data, but a number of considerations suggests the values 3.3 and 1.8, respectively, for these vectors.

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(9) D. R. Lide, THIS JOURNAL, **74**, 3548 (1952).

(10) H. C. Brown and R. B. Holmes, *ibid.*, **78**, 2173 (1956).