Adsorber	Support	Obsd. rotation
$NaClO_3$	D	+0.067 ± 0.003°
$NaClO_3$	L	0
$NaClO_3$	Merck	+0.071 ± 0.003°
$NaClO_3$	50%D-50%L	+0.017 ± 0.002°

by Merck $NaClO_3$ must be due primarily to the *dextro* form in this mixture of the antipodes. It must be emphasized that this is due to the fact that the preferential adsorption is not equal for both antipodes, a phenomenon which has been noticed by other authors for adsorbers which differ both in chemical constitution and (if minerals) locality of occurrence. This indicates that the adsorption mechanism, even if extensible to ionic compounds, must be quite complex.

These results indicate that preferential adsorption on optically active solids is a general phenomenon, since several other authors have also carried out similar separations of substances which are different in chemical constitution and bond type.

Apart from these general theoretical considerations, this work indicates that it may be possible to use sodium chlorate for other investigations in preferential adsorption, because the substance may be usable without separation of the antipodes as a result of unequal preferential adsorption by them.

[CONTRIBUTION FROM CHEMICAL DEPARTMENT, NAGOYA UNIVERSITY, NAGOYA, JAPAN]

The Dipole Moments and the Structure of Borazole and its Derivatives

BY HARUYUKI WATANABE[1] AND MASAJI KUBO

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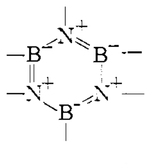
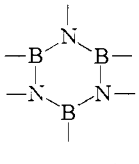
The dielectric constants and densities of dilute solutions of borazole, B-trichloroborazole, B-trichloro-N-trimethylborazole, hexamethylborazole, B-triethyl-N-trimethylborazole, hexaethylborazole, B-trimethyl-N-triphenylborazole and B-triethyl-N-triphenylborazole in benzene have been measured and used to calculate the dipole moments of the molecules. The values of the moments are considerably great for this kind of molecules apparently having a symmetric structure. A possible explanation is afforded first by the deviation from the coplanar structure and secondly by the excitation of molecular vibrations leading to temporary polar structures of the molecules. The possibilities of these alternatives are discussed for various substituted borazoles.

Introduction

A perfectly coplanar structure for certain substituted benzenes has for some time been disputed by some authors. Bastiansen and Hassel[2] in their study of a number of chloro- and bromobenzenes found that with the exception of *p*-dibromobenzene with its bromine atoms far apart, all models representing plane molecules gave sets of interatomic distances in poor agreement with the values obtained from electron diffraction experiments. These investigators tried models in which carbon–halogen bonds were bent out of the plane of the C_6-hexagon and showed that under these circumstances a better agreement between calculated and observed distances could be reached.

Borazole is isoelectronic with benzene. However, since nitrogen is more electronegative than boron, electrons are presumed to be denser around nitrogen atoms than around boron atoms, thus are not distributed uniformly over the six atoms of the ring as in the benzene molecule. The structure may be represented by an intermediate state between the two electronic states





For this reason, the deviation from the coplanar structure, if it exists at all, is presumed to be more pronounced in borazole derivatives than in substituted benzenes.

The dipole moment of borazole has been determined by Ramaswamy[3] as 0.67 D. in the gaseous state. Owing to the lack of sufficient stability of this compound, the author himself does not place much reliance on his data and suggests that further confirmation is required. Some of the derivatives of borazole are more stable than their mother compound and yet no data are found in the literature on the dipole moments of any of these derivatives. The present investigation has been undertaken in an effort to bring to light possible deviations from the coplanar structure by measuring the dipole moments of borazole and some of its drivatives.

Materials

Borazole was prepared by the reduction of B-trichloroborazole described below. The method was essentially the same as that proposed by Schaeffer, *et al.*,[4] differing in that $NaBH_4$ was used in place of $LiBH_4$ and that triethylene glycol dimethyl ether rather than dibutyl ether was employed as a solvent. Triethylene glycol dimethyl ether having a boiling point quite different from that of borazole was more suitable than diethylene glycol dimethyl ether.[5] Sodium borohydride (23.5 g.) was dissolved in 120 cc. of triethylene glycol dimethyl ether in an atmosphere of dry nitrogen. B-Trichloroborazole (30 g.) suspended in 75 cc. of the same solvent was gradually added to it at room temperature. Stirring was continued for about 2 hr. After the reaction was over, the product was distilled under reduced pressure and was collected in a trap cooled with Dry Ice. The yield of crude borazole was about 10 g. Vacuum distillation was repeated five times immediately before physical measurements.

B-Trichloroborazole and B-trichloro-N-trimethylborazole were prepared by essentially the same method as de-

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[1] Shionogi Pharmaceutical Co. Ltd., Amagasaki, Japan.

[2] O. Bastiansen and O. Hassel, *Acta Chem. Scand.*, **1**, 489 (1947).

[3] K. L. Ramaswamy, *Proc. Indian Acad. Sci.*, **A2**, 364, 630 (1935).

[4] R. Schaeffer, M. Steindler, L. Hohnstedt, H. S. Smith, Jr., L. B. Eddy and H. I. Schlesinger, THIS JOURNAL, **76**, 3303 (1954).

[5] The use of this solvent was suggested by G. W. Schaeffer, private communication.

scribed by Brown and Laubengayer.[6] After being sublimed several times under reduced pressure, they were identified by their melting points, 83.5–84.5° and 154–156°, the values reported in the literature being 83.9–84.5° and 153–156°, respectively.[6,7]

Hexamethylborazole and B-triethyl-N-trimethylborazole were prepared from B-trichloro-N-trimethylborazole and a suitable Grignard reagent by the method of Ryschkewitsch, Harris and Sisler.[8] The crude products were sublimed or distilled several times in vacuum, the melting points being 98–99° and 0°, respectively. B-Triethyl-N-trimethylborazole underwent gradual decomposition. The slightly higher apparent moment described below may be due partly to the contamination of decomposition products in the sample.

Hexaethylborazole was prepared from B-trichloro-N-triethylborazole and ethylmagnesium bromide by slightly modifying the method mentioned above.[7,8] Anhydrous ether, B-trichloro-N-triethylborazole, which was prepared from boron trichloride, ethylamine hydrochloride and triethylamine, and magnesium turnings 30% in excess of the equivalent amount were introduced into a 500 ml. three-neck round-bottom flask in a manner similar to that of Turner and Warne.[7] The flask was fitted on one neck with a reflux condenser, a cold-finger condenser cooled with Dry Ice and a Drierite tube connected in series, while a dropping funnel was fixed to another neck. Ethyl bromide slowly was added 30% in excess through the dropping funnel to the rapidly stirred reaction mixture over a period of 1 hr. After the addition of ethyl bromide, the reaction mixture was refluxed for another 5 hr. A saturated aqueous solution of ammonium chloride was added drop by drop to the well stirred reaction mixture while the system was cooled intermittently. The aqueous layer was removed and the ether solution was evaporated. Sublimations in vacuum yielded a pure sample, m.p. 88.5–89.5°. The freezing point depression in benzene gave a mol. wt. of 254 as compared to the calculated value of 248.5. The infrared and ultraviolet spectra of this compound revealed the presence of a borazole ring in the molecule.[8–11]

B-Trimethyl-N-triphenylborazole and B-triethyl-N-triphenylborazole were synthesized according to the procedure reported by Groszos and Stafiej.[12] The melting points were 264–266° and 169–170°, respectively. Repeated recrystallization from ether solutions by adding methanol raised the melting point of the former compound to the constant temperature mentioned above but not to the reported value of 267–269°. A mol. wt. of 355 was obtained by freezing point depression in benzene, the calculated value being equal to 351.

Experimental Method and Results

The measurements were carried out at 25° on dilute solutions in benzene. The dielectric constants were measured by means of a heterodyne beat apparatus provided with a platinum cell.[13] For each solute, determinations were made on solutions of four or five different concentrations appropriately chosen below about 5% by weight. The graphical plots of the dielectric constant as well as the density of solutions against the concentration in weight % gave linear dependence within experimental errors. The slopes of these straight lines were evaluated by the least squares method and the molar polarizations of the solutes were calculated by a method similar to that introduced by Halverstadt and Kumler,[14] differing in that densities were used rather than the specific volumes. The sum of electronic and atomic polarizations of each of these compounds was approximated with 1.05 times the molar refraction for the D line. The refractive index and density data were available for borazole,[15] permitting the evaluation of its molar refraction. For substituted borazoles, necessary corrections were made on this value.

The results are shown in Table I, in which ϵ_1 and d_1 denote the dielectric constant and density of the solvent; α and β are the changes of the dielectric constant and density of the solution with the weight fraction of the solute; other notations have their usual significances.

TABLE I

DIPOLE MOMENTS OF B-TRI-X-N-TRI-Y-BORAZOLES IN BENZENE SOLUTIONS AT 25°: $\epsilon_1 = 2.272$, $d_1 = 0.8724$

Compound X	Y	α	β, g./cc.	$P_{2\infty}$, cc.	MR_D, cc.	μ, D.
H	H	0.000	−0.038	28.7	22.31	0.50
Cl	H	.175	.326	45.3	36.9	.56
Cl	CH_3	.117	.273	57.9	50.8	.47
CH_3	CH_3	.240	.003	63.3	50.0	.72
C_2H_5	CH_3	.299	.013	81.3	63.9	.83
C_2H_5	C_2H_5	.000	.006	84.3	77.7	.37
CH_3	C_6H_5	.236	.152	114.5	108.5	.18
C_2H_5	C_6H_5	.279	.141	133.0	122.3	.47

The only data found in the literature to be compared with the present results are those of Ramaswamy[3] on borazole. His value for the moment of this compound is based on molar polarizations at two different temperatures, 25 and 95°, one of which at higher temperature was presumed by the author to be unreliable. The value 23.76 cc., at 25°, is in poor agreement with the molar polarization at infinite dilution, 28.7 cc., observed by the present writers, even if the fact is taken into account that the former was evaluated from the dielectric constant of the vapor while the latter was determined in solutions.

Discussion

Some of the values of moments calculated in this way are considerably large for this kind of molecules, apparently having a symmetric structure, all the more so because the sum of electronic and atomic polarizations was assumed to be equal to 1.05 times the molar refraction for the D line rather than that extrapolated to the infinite wave length. A possible explanation for this is afforded first by the deviation from the coplanar structure as suggested in the introduction and secondly by the excitation of molecular vibrations having a low frequency and large effective charge which lead to the existence of a temporary moment. In the latter case, although the molecule is nonpolar, the atomic polarization assumes a fairly large value. A conceivable type of such vibrations is, for instance, the normal mode of vibration in which atoms or groups attached to boron oscillate in phase along a direction perpendicular to the ring plane and those bonded to nitrogen move in the

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(14) I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

(15) L. B. Eddy, S. H. Smith, Jr., and R. R. Miller, *ibid.*, **77**, 2105 (1955).

opposite direction. The difference between the two explanations is simply whether the potential as a function of the normal coördinate in question has a double minimum or not. Although the dipole moment data alone do not permit a choice between these alternatives, the high apparent moment of B-trichloroborazole, for which steric hindrance is presumed to be inappreciable, seems to favor a potential curve having a single minimum. In fact, Coursen and Hoard[16] have carried out X-ray crystal analysis on this compound and found that the molecules as they exist in the crystal are planar within experimental errors, no boron or nitrogen atom departing from the plane of the chlorine atoms by more than 0.01 Å. On the other hand, the high moment of hexamethylborazole suggests the importance of the steric effect which favors a non-planar polar structure. This effect is certainly great in a B-trimethyl-N-triphenylborazole. However, since from steric reasons phenyl groups presumably are oriented at right angles to the central ring and hold methyl groups between them, the bending of methyl groups out of the plane of the central ring does not lead to an appreciable gain in stability as in hexamethylborazole. Accordingly, the out-of-plane vibrations of B-trimethyl-N-triphenylborazole will be excited to a lesser extent than in a hexamethylborazole molecule and the moment of the former compound will be smaller than that of the latter compound, as was actually found in the present investigation. The discussion on the moments of ethyl-substituted borazoles is open to speculation owing to the axes of internal rotation involved but the values of the moments are of right order of magnitude.

It is of interest to compare the present results with those from a different physical method of attack. Bauer[17] studied borazole by means of an electron diffraction experiment using the visual method. He confirmed the benzene-like structure of this molecule but suggested that deviations from a planar model could amount to about 0.1 Å. to either side of the molecular plane before discrepancy between the theoretically calculated curve and the visual appearance of photographs became evident. B-Trichloroborazole and N-trimethylborazole were also studied,[18] but the analysis of diffraction data was made assuming D_{3h} symmetry. From the stand-point of the present investigation, it is very desirable to carry out similar experiments on hexasubstituted borazoles having substituted atoms or groups exerting greater steric effects than hydrogen atoms.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING (RESEARCH DIVISION) OF NEW YORK UNIVERSITY]

The Thermal Decomposition of Trialkylboranes[1]

BY PAUL F. WINTERNITZ AND ARRIGO A. CAROTTI

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The disproportionation of trialkylboranes containing C_2 and C_4 alkyl substituents by heating to give unsaturated hydrocarbons and diborane-6 derivatives has been substantiated. However, tri-*n*-amylborane-3 gave *trans*-2-pentene, hydrogen and a heterocyclic boron compound of formula $(-CH_2)_3CH(CH_3)-B-C_5H_{11}$, (1-*n*-amyl-2-methylboracyclopentane) in a 1:1:1 molar ratio. Heating tri-*n*-hexylborane-3 under reflux resulted in the formation of trans-3-hexene, hydrogen, a relatively small quantity of a heterocyclic boron compound of formula $(-CH_2)_4CH(CH_3)-B-C_6H_{13}$, (1-*n*-hexyl-2-methylboracyclohexane), a polymer of empirical formula $[B(C_6H_{13})]_x$ and tri-*n*-hexylborane-3. Trialkylboranes containing unsaturated alkyl substituents are tentatively assumed to give diborane-4 type compounds.

According to Rosenblum,[2] Stock[3] and Meerwein[4] the thermal decompositions of tri-*n*-butyl-, tri-*n*-propyl-, triethyl- and trimethylborane-3 give mainly unsaturated hydrocarbons and alkylated boron hydrides. Rosenblum[5] described the disproportionation of tri-*n*-butylborane-3 as $2(C_4H_9)_3 \rightarrow (C_4H_9)_2B_2H_4 + 4\ C_4H_8$ and suggested a hydride bridge exchange mechanism for this reaction.

We have investigated the thermal decomposition of triethyl-, tri-*n*-propyl- and tri-*n*-butylborane-3[6] in a nitrogen atmosphere concurrently with Rosenblum and obtained the same general results reported by previous workers. The following general conclusions can be drawn: (1) Most trialkylboranes give, on pyrolysis in an inert atmosphere, substituted diboranes with the release of unsaturated hydrocarbons with the same number of carbon atoms as the original alkyl substituents. (2) The ease of decomposition increases with increasing molecular weight of the alkyl substituents. (3) The extent of decomposition increases with temperature; depending on the nature of the alkyl substituent, more than one may be lost at relatively higher temperatures. (4) Some of the resulting liquid and/or solid products contain boron to hydrogen bonding.

Anticipating that diborane-6 and diborane-6

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(1) (a) This investigation was carried out under subcontract to Olin-Mathieson Chemical Corporation, 4350-3, under United States Air Force prime contract AF 33(600)33920. (b) Presented at the Spring 1959 meeting of the Am. Chem. Soc. in Boston, Mass.

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(5) L. Rosenblum, NACA Research Memorandum, E56L18; February, 1957.

(6) Yearly Report covering work conducted from July 1, 1955 to June 30, 1956, under Olin-Matheson Chemical Corp. Subcontract N-3181 under Contract NOa(s)-52-1023.