THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 29, NUMBER 1 JULY, 1958

Dipole Moment of Ammonia-Borane

J. R. WEAVER, S. G. SHORE, AND R. W. PARRY
Department of Chemistry, University of Michigan, Ann Arbor, Michigan
(Received January 16, 1958)

The dipole moment of ammonia-borane, H_3NBH_3, has been measured as 4.9 debye units in dioxane solution; the results are discussed briefly.

CRYSTALLINE ammonia-borane, H_3NBH_3, has a highly ordered boron-nitrogen arrangement and almost negligible vapor pressure at room temperature.[1] Such properties suggest a high dipole moment for the molecule, since the isoelectronic C_2H_6 is a gas at room temperature and boils at $-88°C$. Quantitative information regarding the size of the dipole is of considerable interest.

Because of low volatility and thermal instability of the compound at elevated temperatures, dipole moment measurements have been made in dilute dioxane solution using a heterodyne beat method. A value of 4.9 debye units has been obtained. This value is of the proper magnitude for the dipoles to make a significant contribution to the observed physical properties. The rather similar solid Me_3NBF_3 has a moment of 5.8 debyes,[2] melts at 138°C and boils at 233°C. The related compound Me_2OBF_3 has a moment of 4.35 debyes, melts at $-14°C$ and boils at 128°C.

The value for H_3NBH_3 is of some interest in connection with earlier arguments relative to the structure of the "diammoniate of diborane." It has been suggested[3] that the dimeric character of the "diammoniate of diborane," $B_2H_6 \cdot 2NH_3$, in liquid ammonia is an experimental illusion which results from strong dipole-dipole interaction between monomeric H_3NBH_3 units. Although the dipole moment of H_3NBH_3 is indeed high, it has been demonstrated recently[4] that H_3NBH_3 is monomeric in liquid ammonia. Such behavior is consistent with an earlier observation to the effect that salts such as NH_4Br and $NaBH_4$ have molecular weights corresponding to ion pairs in liquid ammonia even though the strongly polar M^+X^- units have a high over-all moment. [e.g., the moment for the gaseous KCl molecule is 6.30 (5b).][5] The ion pair observation is indeed consistent with behavior expected from theoretical considerations of salts in a solvent such as liquid ammonia.[6]

EXPERIMENTAL

1. Apparatus

The precision heterodyne beat apparatus was built in the Central Physical Chemistry Research Laboratory of the Chrysler Corporation of Detroit, Michigan, and was generously donated to the University of Michigan by the Chrysler Corporation. The unit consists of a fixed frequency oscillator which is controlled at one megacycle by a quartz crystal.[7] The output of a variable frequency oscillator, having the dielectric cell as part of its tank circuit, is combined in

[1] (a) E. L. Lippert and W. N. Lipscomb, J. Am. Chem. Soc. **78**, 503 (1956); (b) E. Hughes, *ibid.* **78**, 502 (1956); (c) S. G. Shore and R. W. Parry, *ibid.* **77**, (1955).

[2] H. S. Booth and D. R. Martin, *Boron Trifluoride and Its Derivatives* (John Wiley and Sons, Inc., New York, 1949), pp. 44, 48, 69.

[3] L. E. Agromonov, J. Gen. Chem. (U. S. S. R.) **9**, 1389 (1939); *ibid.* **10**, 1120 (1940); Chem. Abstracts **34**, 1267 (1940); *ibid.* **35**, 1333 (1941); E. Wiberg, A. Bolz, and P. Buchheit, Z. anorg. Chem. **256**, 287, 301 (1948).

[4] S. G. Shore and R. W. Parry, J. Am. Chem. Soc. **80**, 8 (1958).

[5] (a) Parry, Kodama, and Schultz, J. Am. Chem. Soc. **80**, 24 (1958). (b) C. J. F. Bottcher, *Theory of Electric Polarization* (Elsevier Press, Amsterdam, Netherlands, 1952), p. 330.

[6] D. A. MacInnes, *The Principles of Electrochemistry* (Reinhold Publishing Corporation, New York, 1939), p. 372.

[7] S. C. Hight and G. W. Willard, Proc. Inst. Radio Engrs. **25**, 549 (1937).

a vacuum tube mixer with the output of the fixed frequency unit. The output of the mixer is equal to the difference between the frequencies of the two inputs. The variable oscillator is then tuned until this frequency, as indicated on the frequency meter, becomes zero. Frequencies can be compared with an error of less than one cycle per second. More detailed design details are available upon request.

The cell used was of a standard type[8] with a capacitance of about 30 $\mu\mu$farads. The dielectric constant of pure dioxane at 25°C was taken from Bureau of Standards tables as 2.209[9]; the value was used for calibration.

The index of refraction of solutions was determined using a Bausch and Lomb precision Abbe refractometer. The data obtained showed rather bad scatter, but the effect of the deviations on the final value of the dipole moment was trivial.

2. Reagents

Reagent grade dioxane was purified by refluxing with dilute hydrochloric acid for 6 hours, washing with potassium hydroxide solution and drying with potassium hydroxide pellets. Final drying was effected by storing the liquid in contact with $LiAlH_4$ for several days; the dry reagent was distilled in the vacuum line directly onto H_3NBH_3 as described below.

Ammonia-borane, prepared as previously described,[1(c),4] was placed on the frit of a special vacuum line filtration assembly and leached with pure dry dioxane into a special narrow neck, high precision density cell. The solution was transferred from the density cell into the dielectric cell under dry nitrogen. Special precautions to avoid exposure to water vapor were taken. The ammonia-borane concentration was obtained after completion of the physical measurements by hydrolyzing the solution with 3*M* HCl in a sealed tube at 100°C for about 5 days. The liberated hydrogen was measured; nitrogen was determined by a micro-Kjeldahl procedure, and boron by titration of boric acid with NaOH in the presence of mannitol. The consistency of the analytical data served as a cross check on the identity and purity of the solute. Typical hydridic H/B/N ratios were: 2.97/0.98/1.00; 3.01/1.03/1.00; ···/0.95/1.00; 2.92/0.93/1.00.

[8] R. J. W. LeFevre, *Dipole Moments* (John Wiley and Sons, Inc., New York, 1953), third edition, p. 51.

[9] A. A. Maryott and E. R. Smith, Natl. Bur. Standards Circ. **514**, 12 (1951).

3. Data and Interpretations

All measurements were taken at or corrected to 25°C. Density and dielectric constant measurements on 8 dioxane solutions, ranging in concentration from 0.0201 mole fraction H_3NBH_3 to pure dioxane gave values of $(\partial d/\partial x)_0 = -0.2$ and $\partial\epsilon/\partial x = 34.0$. Detailed data are shown in Table I. These values, when used in the Hedestrand equation,[10] gave a value of 506 cm³ for the apparent total polarization of the solute. Values of the refractive index of the pure solvent (1.4194) and for the solution of mole fraction 0.0156 and 0.0159 (1.4206 and 1.4209) indicated values of dn/dx (i.e., the change in refractive index with mole fraction) of 0.09 from which the sum of the electronic and atomic polarizations was estimated as about 15 cm³. The orientation polarization was thus 491 cm³ giving a value of $4.88 \pm 0.1D$ for the dipole moment.

TABLE I. Data for calculation of dipole moment of ammonia-borane.

Mole fraction H_3NBH_3	Density of solution	Dielectric constant
0.0000	1.028_8	2.209 (reference 9)
0.0030		2.312
0.0040		2.348
0.0079	1.027_0	2.478
0.0091		2.523
0.0156	1.026_3	2.719
0.0159	1.026_5	2.743
0.0201	1.025_9	2.893

It is perhaps somewhat fortuitous that a value of 4.8*D* was obtained from the temperature coefficients of the dielectric constants of the solution and pure dioxane over the temperature range of 21°C to 41°C. The temperature coefficient of the molar polarization of ammonia-borane was 1.60 cm³/mole×deg.

[10] See reference 5(b), p. 301. Other methods of treating the data, such as that of Onsager, gave values ranging from 4.7 to 4.9*D*.

ACKNOWLEDGMENT

The authors wish to express their sincere appreciation to the Chrysler Corporation for the heterodyne beat apparatus used in this investigation, and to the Wright Air Development Center for financial support. This work was conducted under Contract AF-33(616)-3343 with the United States Air Force. The sponsoring agency was the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.