stirred overnight in an inert atmosphere. The white solid was filtered off, washed with pentane to remove any unchanged starting material, and dried by pumping at room temperature. The product is soluble in acetone and acetonitrile, moderately soluble in carbon tetrachloride.

Anal. Calcd. for $B_{20}H_{16}\cdot[O(C_2H_5)_2]_2$: C, 24.9; H, 9.45; B, 56.2. Found: C, 24.8; H, 9.89; B, 55.7.

Infrared absorptions as a Nujol mull included: 3550 (w), 2600 (s, sh), 2525 (s), 1330 (m), 1280 (m), 1140 (m), 1090 (s), 1050 (m), 1010 (s), 970 (s), 960 (s), 930 (s), and 790 (m) cm.$^{-1}$. When heated at 125° under vacuum, the solid decomposed, as confirmed by the infrared spectrum of the residue.

Molecular weight determinations by osmometry in acetonitrile yielded 356 on the basis of a curve plotted with three points (calcd. for $B_{20}H_{16}\cdot[O(C_2H_5)_2]_2$, 380.6).

The B^{11} resonance pattern in acetonitrile showed a broad weak absorption centered at +10.1 p.p.m. and a group of four peaks at +20.8, +27.8, +34.8, and +41.4 p.p.m. In deuterated dimethyl sulfoxide, the H^1 resonance spectrum consisted of a methyl multiplet at −1.3 p.p.m. and a methylene multiplet at −3.8 p.p.m. No protons bonded to boron were observable. Double irradiation at 19.2 Mc. gave rise to a new broad peak at −2.0 p.p.m.

$B_{20}H_{16}\cdot[N(CH_3)_3]_2$.—Anhydrous trimethylamine was bubbled through a solution of 0.63 g. of icosaborane-16 in 200 ml. of pentane kept under nitrogen. A yellow precipitate formed at once. After the amine had been admitted for 2 hr. at room temperature, the precipitate was filtered off and recrystallized from acetonitrile.

Anal. Calcd. for $B_{20}H_{16}\cdot[N(CH_3)_3]_2$: C, 20.5; H, 9.76; B, 61.6; N, 8.05. Found: C, 20.8; H, 9.66; B, 59.6; N, 8.30, 8.42.

Infrared absorptions occur at 3600 (m), 3200 (m), 2550 (s), 1310 (m), 1260 (m), 1100 (s), 980 (s), 850 (m), 800 (m), and 720 (m) cm.$^{-1}$. H^1 resonance measurements in acetonitrile showed a singlet at −2.7 p.p.m.

$B_{20}H_{16}\cdot[P(C_6H_5)_3]_2$.—A solution of 0.1 g. of icosaborane-16 in 30 ml. of pentane was mixed at room temperature with a solution of 0.5 g. of triphenylphosphine in 50 ml. of pentane in an inert atmosphere. A white precipitate formed at once. After the solution had been stirred for 0.5 hr., the precipitate was collected.

Anal. Calcd. for $B_{20}H_{16}\cdot[P(C_6H_5)_3]_2$: C, 57.2; H, 6.13; B, 28.6; P, 8.19. Found: H, 6.66; B, 30.8; P, 7.30.

Infrared absorptions included 2550 (s), 1190 (w), 1160 (m), 1100 (s), 995 (m), 930 (w), 740 (s), 720 (s), and 690 (s) cm.$^{-1}$. The H^1 resonance spectrum in acetonitrile showed a broad singlet at −7.3 p.p.m.

$B_{20}H_{16}[S(CH_3)_2]_2$.—Dimethyl sulfide (25 ml.) was added with stirring to a solution of 0.84 g. (3.6 mmoles) of icosaborane-16 in 175 ml. of pentane. A white solid formed. The mixture was stirred for 2 hr. in an inert atmosphere. The solid was filtered off, washed three times with pentane, and recrystallized from acetonitrile.

Anal. Calcd. for $B_{20}H_{16}\cdot[S(CH_3)_2]_2$: C, 13.4; H, 7.91; B, 60.6; S, 18.0. Found: C, 13.4; H, 7.91; B, 59.8; S, 17.4.

Infrared absorptions included 2640 (s, sh), 2550 (s), 1090 (m), 1040 (m), 970 (s), 925 (m), and 840 (w) cm.$^{-1}$.

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Polarization and Complexation Effects in Solutions of Borazine Derivatives

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Polarization measurements were made on solutions of hexamethylborazine in *n*-heptane, *p*-xylene, and hexafluorobenzene at 25°, in benzene at 15, 20, and 25°, and on the pure substance from 29.8 to 104.9°. The data suggest that the hexamethylborazine molecule is nonpolar and that the apparent dipole moment for the molecule arises from large values of the atom polarization. The absence of significant solute–solvent interaction in these systems is also suggested by spectral studies.

Although X-ray, electron diffraction, and infrared spectral studies indicate that the borazine ring is planar and has D_{3h} symmetry,[1] the results of two polarization investigations suggest that this ring system possesses a dipole moment significantly greater than zero. On the basis of the earliest measurement (gas phase),[2] borazine was assigned a dipole moment of 0.67 D.; however, there is evidence that the sample had undergone partial decomposition, rendering this measurement suspect. More recently, dipole moments in the range 0.2–0.7 D. were obtained for borazine and six of its derivatives in benzene.[3] The moments were attributed to either the nonplanarity of the borazine ring or very low-frequency molecular vibrations which cause high atomic polarizations. The possibility that the moments are due to π-complexation between the solute and solvent molecules, as occurs in benzene solutions of iodine,[4] was not considered.

Experimental

Materials.—Hexamethylborazine was prepared in 85% yield by the reaction of B-trichloro-N-trimethylborazine (prepared from boron trichloride and methylammonium chloride[5–7]) with methylmagnesium bromide; m.p. 98.9–99.3° (cor.). The ultraviolet spectrum of hexamethylborazine in *n*-heptane is featureless above 230 mμ and the infrared spectra of benzene, carbon tetra-

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chloride, or carbon disulfide solutions of the product are identical with those recorded in the literature[8,9] except that additional bands at 1180 (w) and 1197 (m) cm.$^{-1}$ were observed.

Anal. Calcd. for $B_3C_6H_{18}N_3$: C, 43.77; H, 11.02. Found: C, 44.07; H, 11.02.

Tetracyanoethylene (Eastman Organic Chemicals) was recrystallized twice from chlorobenzene and sublimed *in vacuo* at 55°; m.p. 196.5–197.5° (lit.[10] 198–200°). *p*-Benzoquinone (Eastman Organic Chemicals) was sublimed *in vacuo* at 55°; m.p. 112.3–113.0° (lit.[11] 113.5°).

Benzene (Phillips Petroleum Co., min. 99 mole %) was shown to be pure by its mass spectrum and by vapor phase chromatography and was used as a calibration standard after drying over calcium hydride and distillation; $n^{25}\text{D}$ 1.4979 (lit.[12] 1.4979), d^{25}_4 0.8738 (lit.[12] 0.8737). *n*-Heptane, $n^{25}\text{D}$ 1.3855 (lit.[13] 1.3851), d^{25}_4 0.6803 (lit.[13] 0.6795), and *p*-xylene, $n^{25}\text{D}$ 1.4933 (lit.[12] 1.4932), d^{25}_4 0.8571 (lit.[12] 0.8567) were Phillips Petroleum Co. research grade hydrocarbons. Freshly distilled chlorobenzene (b.p. 131–132°) was extracted with concentrated sulfuric acid until the acid layer remained colorless, refluxed over calcium hydride, and redistilled; $n^{25}\text{D}$ 1.5220 (lit.[14] 1.5214), d^{25}_4 1.1016 (lit. 1.1010,[15] 1.1004[14]). Hexafluorobenzene (Consolidated Zinc Corp., Ltd.) was cooled to −2° with stirring until approximately half of the sample had crystallized; the liquid phase was decanted and the solid was melted and distilled from calcium hydride; $n^{25}\text{D}$ 1.3750, d^{25}_4 1.6051. All purified solvents were refluxed over calcium hydride and distilled immediately before use.

Spectra.—Ultraviolet spectra of solutions in *n*-heptane were measured in matched silica cells (1.000 cm.) using a Cary Model 14 recording spectrometer. Infrared spectra were determined in the 300–700 cm.$^{-1}$ region as polycrystalline mulls in dry paraffin oil (Nujol) with a Beckman IR-7 spectrophotometer equipped with cesium iodide optics.

Polarization Measurements.—Densities of solutions were measured with a bicapillary pycnometer,[16] and refractive indices were measured with a Bausch and Lomb Abbé 3-L refractometer. Values for the refractive index at infinite wave length were estimated from the achromatization compensator setting on the instrument and the dispersion tables supplied for the prism (Series 522) used with the instrument.

The dielectric constants of solutions were measured at a frequency of 5×10^5 sec.$^{-1}$ with a General Radio 1422-MD standard variable capacitor, a conventional heterodyne beat oscillator,[17] and a cell incorporated in a liquid handling system which permitted measurements to be conducted in a dry helium atmosphere. A cell constant was obtained at the beginning of each determination using pure solvent, except in the case of hexafluorobenzene where the cell constant for benzene was used to evaluate the dielectric constant. Kerosine, circulated with an air stirrer, was used in the constant temperature bath (±0.05°) to minimize electrical effects. Because of the sensitivity of the lead capacitance to environment the kerosine was kept at a constant level.

Electronic polarization values were calculated from the Clausius–Mosotti equation using the square of the refractive index at infinite wave length as the dielectric constant at optical frequencies; this is equivalent to assuming that the electronic polarization is equal to the molar refraction at infinite wave length. The molar refraction at infinite dilution was obtained by extrapolation of a graph of the molar refraction *vs.* concentration. Because the bond order of the B–N bonds in borazine is not known, the procedure used to obtain the molar refraction in this investigation is considered less ambiguous than calculation from group or bond refractions. The total polarization was calculated using the Debye procedure[18] in which values for the solute polarization are calculated at several concentrations and extrapolated to infinite dilution. In cases where the graphs of the dielectric constant *vs.* mole fraction and the density *vs.* mole fraction were linear, the total polarization was calculated by the Hedestrand–Halverstadt–Kumler method[18]; in these cases dipole moments were determined by the Higasi[19] method also.

Dielectric Constant of Solid Hexamethylborazine.—The cell used for dielectric constant measurements of solids contained two 2.2-cm.^{2} silver plates held parallel at a distance of 1 mm. by Teflon spacers. Chlorobenzene was used to calibrate the cell because the temperature dependence of the dielectric constant of this substance is known.[20] The temperature dependence of the dielectric constant of hexamethylborazine as determined with this apparatus is shown in Table I.

TABLE I

TEMPERATURE DEPENDENCE OF THE APPARENT DIELECTRIC CONSTANT OF HEXAMETHYLBORAZINE[a]

t, °C.	ϵ	t, °C.	ϵ
29.8	2.328	90.1	2.332
34.6	2.329	94.5	2.330
39.6	2.329	95.6	2.330
44.7	2.332	96.5	2.330
49.9	2.334	97.7	2.332
54.7	2.338	98.6	2.332
59.6	2.339	99.6	2.314
64.5	2.337	100.6	2.280
69.5	2.337	101.5	2.265
74.5	2.336	102.7	2.264
79.7	2.335	104.9	2.258
85.1	2.332		

[a] M.p. 98.9–99.3°.

The Temperature Dependence of Dipole Moments.—Higasi's method[19] for the determination of dipole moments is easily adaptable for atmosphere-sensitive compounds. According to Higasi's method the electric dipole moment, μ, is given by

$$\mu = \beta(\partial \epsilon_{12}/\partial f_2)^{1/2} \qquad (1)$$

where ϵ_{12} is the dielectric constant of a solution in which the mole fraction of the solute is f_2 (the subscripts 1 and 2 refer to solvent and solute, respectively) and β is a constant defined by eq. 2,

$$\beta = [27kTM_1/4\pi N d_1(\epsilon_1 + 2)]^{1/2} \text{ (Debyes)} \qquad (2)$$

where k is the Boltzmann constant, T the absolute temperature, N the Avogadro number, and d the density. This method is useful only when the plot of ϵ_{12} *vs.* f_2 is a straight line. Equation 1, derived by differentiation of the Debye equation for binary solutions, has been applied with success to atmosphere-sensitive organometallic compounds[21] since it requires only dielectric constant measurements. Implicit in the derivation are the assumptions that the molar refraction calculated from the sodium D-line is equal to the sum of the molar atomic and molar electronic polarizations and that eq. 3, where M is the molecular weight

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$$\frac{\partial d_{12}}{\partial f_2}\left[\frac{(\epsilon_1 - 1)}{d_1{}^2(\epsilon_1 + 2)}\right] = \frac{M_2}{M_1}\left[\frac{(n\text{D}^2)_2 - 1}{d_2(n\text{D}^2)_2 + 2} - \frac{(\epsilon_1 - 1)}{d_1(\epsilon_1 + 2)}\right] \quad (3)$$

and $n\text{D}$ is the sodium D-line refractive index, is approximately valid. The approximations hold best for very polar molecules, *i.e.*, where $\partial\epsilon_{12}/\partial f_2$ is quite large (*e.g.*, <3).

Experimental results of dielectric constant measurements on solutions of C_6H_5Cl in C_6H_6 are tabulated in Table II and indicate that the Higasi method can be readily adapted for use in the 15–35° temperature range. Slopes of the linear ϵ_{12} *vs.* f_2 plots were calculated by the least-squares method. Within experimental error, the dipole moment of C_6H_5Cl calculated by this method is temperature independent, and the mean dipole moment (1.595 D.) is in good agreement with the values reported in the literature for benzene solutions (1.56 D.[22] and 1.6 D.[23]).

TABLE II

DIPOLE MOMENTS OF CHLOROBENZENE IN BENZENE AT VARIOUS TEMPERATURES AS DETERMINED BY HIGASI'S METHOD

t, °C.	β, D.	ϵ_{12}	$f_2 \times 10^1$	$\frac{\partial\epsilon_{12}}{\partial f_2}$	μ, D.
15.00	0.8244	2.2940	0	3.66	1.58
		2.43622	0.33794		
		2.51793	0.60297		
		2.56133	0.72416		
25.00	0.8476	2.2740	0	3.46	1.58
		2.4112	0.39595		
		2.4676	0.56257		
		2.5192	0.70621		
		2.5676	0.84870		
35.00	0.8657	2.2540	0	3.57	1.63
		2.35358	0.25284		
		2.53335	0.76164		
		2.66705	1.1537		

Discussion

Complexation.—No spectrophotometric evidence was found for complexation between hexamethylborazine (10^{-2} *M*) and benzene (10^{-2} *M*), *p*-xylene (10^{-2} *M*), or hexafluorobenzene (10^{-3} *M*), respectively, in *n*-heptane, although a solution of hexamethylborazine in hexafluorobenzene turned yellow on standing for 2 days at room temperature. Hexamethylborazine (m.p. 98.2–99.0° cor.) was recovered from the yellow solution by evaporation, indicating that no extensive chemical reaction had occurred.

A yellow-green color formed immediately after mixing hexamethylborazine and picric acid (10^{-4} *M*) solutions. Broad maxima were found at 344 and 422 mμ, indicating formation of the picrate ion. (Briegleb and Angerer[24] found maxima at 322 and 400 mμ for sodium picrate in a 2% solution of butanol in *n*-heptane.) After 4 hr. a yellow precipitate had formed. The probable formation of a picrate salt is evidence for the amine-like character of the ring nitrogen atoms in hexamethylborazine.

Interactions between methyl-substituted borazines and various electron-pair acceptors in solutions have been suggested on the basis of spectral evidence.[25] However, the existence of molecular complexes of borazines is not necessarily indicative of their electronic nature since complexes would be expected to form if the electrons on nitrogen were either localized or delocalized. It is well established that both π-systems and amines form molecular complexes with Lewis acids.

Polarization.—Although the Higasi method is not recommended for nonpolar or slightly polar substances, as indicated by the variation in the calculated moments of hexamethylborazine in various solvents, neglecting the atomic polarization for molecules with appreciable moments should not introduce large errors.

The temperature dependence of the dielectric constants of solutions of hexamethylborazine in benzene (Tables III and IV) indicates that appreciable solvent–solute interactions are not present, because the slopes of the dielectric constant *vs.* mole fraction graphs would be expected to increase with decreasing temperature in systems where such interactions are appreciable. In addition, the fact that the dielectric constants of these solutions are independent of the concentration leads to the suggestion that the dielectric constants of benzene and hexamethylborazine are of similar magnitude; the data in Table I support this suggestion, although the absolute accuracy of the dielectric constants on solid samples is no better than ±1% because of voids in the solid between the capacitor plates caused by either contraction during cooling or by inclusion of bubbles in the liquid before solidification. This is complicated further by the observation that the apparent dielectric constant of a solid is dependent upon the spacing of the capacitor plates.[26]

The temperature dependence of the dielectric constant of hexamethylborazine at its melting point indicates that this compound is nonpolar (Table I). The small decrease in the dielectric constant at the melting point can be attributed to a difference between the densities of the solid and liquid phases. The dielectric constant was not observed to increase over the whole temperature range studied, which indicates that the orientation of polar molecules does not contribute to the total polarization.[27]

The solution dipole moment of tetracyanoethylene in benzene was studied as a model system since other data[28] suggest that it forms a π-complex with benzene. A summary[29] of the data for these polarization measurements is presented in Table V. The polarization extrapolation for the Debye method is rather uncertain, and the total polarization value from the Hedestrand–Halverstadt–Kumler method is probably the more accurate. The magnitude of the observed dipole moment (0.8 D.) is larger than that of iodine dissolved in benzene (0.6 D.[4]), which is in accord with the greater stability of the tetracyanoethylene–benzene complex as

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TABLE III

POLARIZATION OF HEXAMETHYLBORAZINE IN BENZENE AT 25.00°[a]

f_1	$f_2 \times 10^2$	ϵ_{12}	$n^{25}{}_D$[b]	$d^{25}{}_4$, g. cm.$^{-3}$	P_{12}, cm.^{3}	P_2, cm.^{3}	$(R_\infty)_{12}$, cm.^{3}	$(R_\infty)_2$, cm.^{3}
1	0	2.2740	1.4980	0.87378	26.648	...[c]	25.233	...[d]
0.006107	0.38936	2.2735	1.4977	0.87384	26.754	53.8	25.328	49.5
0.992629	0.73709	2.2733	1.4974	0.87390	26.852	54.4	25.410	49.1
0.989531	1.0469	2.2735	1.4972	0.87395	26.945	55.0	25.484	49.1
0.985470	1.4531	2.2740	1.4968	0.87401	27.070	55.7	25.579	49.0
0.983201	1.6798	2.2744	1.4967	0.87406	27.141	56.0	25.633	49.4
0.988924	1.1075	2.2735	1.4971	0.87396	26.962	55.0	25.497	49.0
0.984160	1.5841	2.2735	1.4967	0.87404	27.101	55.3	25.610	49.0
0.979841	2.0158	2.2738	1.4964	0.87411	27.230	55.5	25.713	49.0
0.973054	2.6946	2.2742	1.4958	0.87422	27.433	55.8	25.871	48.9

[a] These data yield $\partial\epsilon_{12}/\partial f_2 = 0$; $\beta = 0.8476$; μ (Debye) = 0.44 D. (assuming $P_a = 0$); μ (Higasi) = 0 D. [b] $n^{25}{}_D - n^{25}{}_\infty = 0.0216$. [c] Extrapolated value; $P_2 = 53.1$ cm.^{3}. [d] Extrapolated value; $(R_\infty)_2 = 49.2$ cm.^{3}.

TABLE IV

TEMPERATURE DEPENDENCE OF THE DIELECTRIC CONSTANT OF HEXAMETHYLBORAZINE IN BENZENE

15°		35°	
$f_2 \times 10^2$	ϵ_{12}	$f_2 \times 10^2$	ϵ_{12}
0	2.2940	0	2.2540
0.45972	2.2931	0.30985	2.2537
1.2949	2.2928	0.52207	2.2537
1.8008	2.2925	0.81505	2.2536
2.6052	2.2926	1.1483	2.2538

compared with the iodine–benzene complex and a greater atomic polarization for tetracyanoethylene as indicated by the low-frequency bands present in its infrared spectrum (Table VI). The atomic polarization of iodine in benzene can be assumed to be zero if the possibility of contributions to the atomic polarization arising from complexation is disregarded.

TABLE V

POLARIZATION OF HEXAMETHYLBORAZINE AND TETRACYANOETHYLENE AT 25.00°

Solute	Solvent	Method[a]	$\frac{\partial\epsilon_{12}}{\partial f_2}$	$\frac{\partial d_{12}}{\partial f_2}$	β, D.	P_T, cm.^{3}	P_O, cm.^{3}	P_E, cm.^{3}	P_A, cm.^{3}	μ, D.
$(CH_3)_3B_3N_3(CH_3)_3$	C_6H_6	D	...	...	...	53.1	3.9[b]	49.2	0[c]	0.44
		H	0	...	0.8476	53.1	0[c]	49.2	3.9[b]	0.0
$(CH_3)_3B_3N_3(CH_3)_3$	n-C_7H_{16}	D	...	...	...	55.3	12.9	42.4	0[c]	0.79
		H	0.4711	...	1.1869	53.1	0[c]	42.4	12.9	0.81
$(CH_3)_3B_3N_3(CH_3)_3$	p-$(CH_3)_2C_6H_4$	D	...	...	...	53.3	3.9[b]	49.4	0[c]	0.44
$(CH_3)_3B_3N_3(CH_3)_3$	C_6F_6	D	...	...	...	48.0	0[b]	48.0	0[c]	0.0
$(CN)_4C_2$	C_6H_6	D	...	...	...	54.0	14.2[b]	34.8	5.0[c]	0.83
		HHK	0.825	0.363	...	57.2	17.4[b]	34.8	5.0[c]	0.92
		H	0.825	...	0.8476	...	...	...	...	0.77

[a] D, HHK, and H refer to the Debye, Hedstrand–Halverstadt–Kumler, and Higasi methods, respectively. [b] Derived quantity. [c] Assumed quantity.

TABLE VI

INFRARED SPECTRA OF TETRACYANOETHYLENE, HEXAMETHYLBORAZINE, AND B-TRIMETHYLBORAZINE IN THE CESIUM IODIDE REGION

$C_2(CN)_4$	$B_3(CH_3)_3N_3(CH_3)_3$	$B_3H_3N_3(CH_3)_3$	Assignment[a]
428 w	396 m	400 w	ν_{17}
443 w	574 s	567 m	ν_{10}
553 s	...	...	..
577 s	...	...	..
587 w	...	...	..

[a] The assignments are for $B_3(CH_3)_3N_3(CH_3)_3$ and $B_3H_3N_3(CH_3)_3$ and correspond to the vibrational modes of $B_3H_3N_3H_3$.[9]

Data necessary for the Debye calculation of the polarization and for the Higasi calculation of the dipole moment for hexamethylborazine in solutions of benzene are given in Table III; a summary[29] of the results for this system and for solutions of hexamethylborazine in n-heptane, p-xylene, and hexafluorobenzene is given in Table V. The values of the atomic polarization obtained from both the Debye and the Hedestrand–Halverstadt–Kumler methods are given in Table VII. It would be tempting to suggest that the dipole moment for hexamethylborazine in benzene and p-xylene is due to an interaction with these solvents since this solute does not exhibit a dipole moment in hexafluorobenzene. Spectral data indicate the iodine does not interact with hexafluorobenzene, suggesting that the latter is not as good a Lewis acid as benzene, which would imply that the borazine is acting as a Lewis acid in its interaction with benzene. However, the surprisingly large dipole moment for hexamethylborazine in n-heptane, which we are unable to explain, appears to negate this argument.

The variation in the atomic polarization values (Table VII) could arise from experimental error since these values are obtained from small differences between large extrapolated quantities. However, the possibility that there is some variation with solvent cannot be excluded. Giving double weight to the polarization values in benzene solution (which seem to be the most reliable), the atomic polarization of hexamethylborazine can be estimated as 7 cm.^{3}. In any case, the magnitude of the difference between the total

TABLE VII

ATOMIC POLARIZATION OF HEXAMETHYLBORAZINE IN VARIOUS SOLVENTS

Solvent	Method[a]	$\frac{\partial \epsilon_{12}}{\partial f_2}$	$\frac{\partial d_{12}}{\partial f_2}$	P_T, cm.^{3}	P_E, cm.^{3}	P_A, cm.^{3}
n-C_7H_{16}	D	...	...	55.3	42.4	12.9
	HHK	0.471_1	0.177_6	61.3	42.4	18.9
C_6H_6	D	...	...	53.1	49.2	3.9
	HHK	0.016_0	0.012_4	56.0	49.2	6.8
p-$(CH_3)_2C_6H_4$[b]	D	...	...	53.3	49.4	3.9
C_6F_6	D	...	...	48.0	48.0	0
	HHK	0.44_4	-1.00_6	55.7	48.0	7.7

[a] D, Debye; HHK, Hedestrand–Halverstadt–Kumler. [b] The graph of dielectric constant *vs.* mole fraction was not a straight line and the Hedestrand–Halverstadt–Kumler calculation was not applicable.

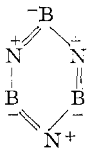
polarization and the electronic polarization for hexamethylborazine can be adequately accounted for by a variation in the atomic polarization, making the assumption of the existence of a polar species in this system unnecessary.

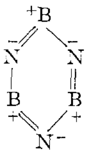
The relationship between the atomic polarization and infrared absorption intensities and frequencies is given in eq. 4.[30,31] A_i is the integrated absorption

$$P_A = C\Sigma\frac{A_i}{\nu_i} \qquad (4)$$

intensity of the fundamental vibration of frequency ν_i, and C is a collection of molecular constants. Because the square of the frequency of vibration occurs in the denominator of eq. 4, intense absorptions at very low frequencies contribute most to the atomic polarization. On the basis of the calculated atomic polarization of hexamethylborazine, intense absorptions in the low-frequency region of the infrared spectrum would be expected. The bands observed in the infrared spectra of tetracyanoethylene and hexamethylborazine are summarized in Table VI; the spectrum of B-trimethylborazine is also given for comparison. No attempt is made to assign the tetracyanoethylene bands since supporting Raman data are not available. Tentatively, the bands at approximately 570 cm.$^{-1}$ observed for the two borazines can be assigned to a ring distortion corresponding to the ν_{17} (symmetry species E′) vibration in $H_3B_3N_3H_3$ which occurs at approximately 520 cm.$^{-1}$.[9,32] The corresponding frequency in the Raman spectrum of $H_3B_3N_3H_3$ is 459 cm.$^{-1}$ (m, depolarized).[33] The bands at approximately 400 cm.$^{-1}$ can be assigned to a B–N torsional mode corresponding to the ν_{10} (symmetry species A_2'') vibration which occurs at 415 cm.$^{-1}$ in $H_3B_3N_3H_3$.

The high value of the atomic polarization in hexamethylborazine compared with that of benzene can be attributed to the absorption intensities (eq. 4) for ring distortion and B–N torsion which qualitatively are related to the bond moment of the B–N bond in the borazine ring. Bending modes contribute most to the atomic polarization of molecules containing light atoms because of the relatively small force constants compared with those of stretching modes.[34] For example, calculations show that 91% of the total atomic polarization of benzene (0.66 cm.^{3}) in the vapor phase is due to the ν_4 fundamental mode (symmetry species A_{2u}, 671 cm.$^{-1}$) which is largely an unsymmetrical, out-of-plane C–H bending mode,[31] and that 86% of the total atomic polarization of p-benzoquinone (7.0 cm.^{3}) is due to the out-of-plane C=O bending mode.[35] The magnitude of the atomic polarization of hexamethylborazine indicates that the intensities of the low-frequency borazine ring distortional modes stem from the existence of polar bonds between the ring boron and nitrogen atoms. The formalism of electron-pair bonds suggests that delocalization of the nitrogen p_z electrons into the vacant boron orbitals will lead to a charge distribution indicated by I. However, a survey of the reactions of borazine rings[1] suggests that the nitrogen atoms are negative sites compared with the adjacent boron atoms (II). Thus, energy could be gained in the formation of the borazines by partial delocalization of the electrons originally in the nitrogen p_z orbitals, whereas the electronegativity of the nitrogen in the borazine ring (approximately 3.5), being much higher than that of the boron (1.7), as shown by nuclear magnetic resonance measurements,[36] could give a bond polarization equivalent to II.


I


II

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