over, the homogeneity of the product may be established by carrying out separate determinations on individual fractions.

Two possible objections to the method of approximations exist. The individual approximations require tedious calculations. These might be reduced by the development of mathematical, rather than graphical, procedures for handling the data. Such a method was developed but in practice offered no advantage over the graphical procedure here described.[5] Again, a marked curvature in the log *K versus* $1/T$ plot might occur and lead to serious errors in the calculated results. However, up to the present time, such curvatures in the dissociation of addition compounds have been rarely encountered, and can then be avoided by working at lower pressures.

In view of the many advantages of, and the minor objections to, the method of approximations, this method appears highly promising for the determination of dissociation data for addition compounds.

Acknowledgment.—This investigation was aided by Grants No. 710 and 776 from the Penrose Fund of the American Philosophical Society. This assistance is gratefully acknowledged.

Summary

1. An improved dissociation tensimeter is described.

2. A simplified method has been developed for determining the dissociation constants of addition compounds from tensiometric data by means of a graphical method of approximations.

3. The procedure has been applied to trimethylamine–trimethylboron. The results are in good agreement with earlier data obtained by the method of matched samples.

LAFAYETTE, IND. RECEIVED SEPTEMBER 15, 1949

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[5] This mathematical procedure is described in the Ph.D. Dissertation by Melvin Gerstein, "Acid-Base Studies in Gaseous Systems: The Dissociation of the Addition Compounds of Trimethylboron with Cyclic Imines," The University of Chicago Libraries, Chicago, Ill., September, 1945.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

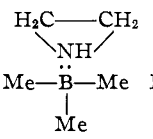
Acid-Base Studies in Gaseous Systems. VII. Dissociation of the Addition Compounds of Trimethylboron and Cyclic Imines; I-Strain

BY HERBERT C. BROWN[1] AND MELVIN GERSTEIN[2]

Years ago Baeyer[3] pointed out that five- or six-membered rings were relatively easily formed and stable, whereas three- and four-membered rings appeared to be less readily formed and to be less stable. He attributed these differences between the three- and four-membered rings on the one hand and the five- and six-membered rings on the other to the strain involved in deforming the bond angle from its usual tetrahedral value (109°28′) to the 60 and 90° values required by the geometry of the small rings. With the years Baeyer's views on the effect of strain on the stability of three- and four-membered ring systems have received much experimental verification.[4]

Although there is now considerable evidence as to the effect of ring strain on the stability of small-membered rings, there is as yet relatively little information available on the effect of such ring strain on chemical properties which do not involve ring opening. For example, it would be of interest to know how ring strain affects the base strengths of ethylenimine and trimethylenimine. Unfortunately, these strained rings undergo rather rapid ring opening in aqueous solution[5] and measurement of the ionization constants of the bases offers experimental difficulties. Moreover, such data in aqueous solution would involve the usual difficulties in interpretation.

Experiment revealed that the addition compounds of trimethylboron with these cyclic imines were stable substances and did not undergo chemical change under the conditions required for measurement of the dissociation constants. Accordingly, it was decided to prepare and study the addition compounds of trimethylboron with ethylenimine (I), trimethylenimine (II), pyrrolidine (III) and piperidine (IV), in order to examine the effect of ring strain on the ability of the nitrogen atom to donate its electron pair.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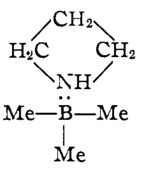
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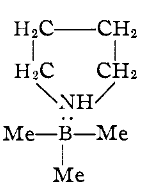
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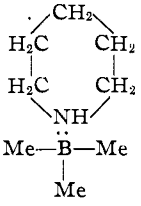
IV

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[1] Department of Chemistry, Purdue University, Lafayette, Ind.

[2] National Advisory Committee for Aeronautics, Cleveland, Ohio.

[3] Baeyer, *Ber.*, **18**, 2269 (1885).

[4] W. Hückel, "Der Gegenwärtige Stand der Spannungstheorie," Fortschritte der Chemie, Physik und Physikalischen Chem.," Serie A, Band 19, Heft 4, edited by A. Eucken, Gebrüder Bornträger, Berlin, 1927.

[5] Freundlich and Neumann, *Z. physik. Chem.*, **87**, 69 (1914).

This paper is the first of a number of papers dealing with the chemical effects of ring strain.

Materials

Trimethylboron was prepared and purified as described in an earlier paper in this series.[6]

Ethylenimine, prepared from monoethanolamine,[7] was distilled through a small fractionating column (efficiency: 15 theoretical plates) and collected over sodium in a tube which could be attached directly to the vacuum apparatus. The fraction used distilled at 54.8° at 746 mm. It exhibited a vapor pressure of 59 mm. at 0°. The imine underwent a slow polymerization in the storage tube. However, this polymerization offered no difficulty, since the monomer could be readily separated from the difficultly volatile polymer.

Trimethylenimine was prepared by the reduction of N,N-trimethylene-*p*-toluenesulfonamide,[8] using sodium in *n*-amyl alcohol. Unfortunately, the yields in this synthesis are low and insufficient product was obtained to permit fractionation in an efficient column. The crude product was collected over fused sodium hydroxide. It was then distilled into a tube containing sodium and allowed to stand in contact with the metal overnight. The liquid was then introduced into the high vacuum apparatus and subjected to a distillation from a U-tube at −46° to a U-tube at −64°. The distillate was sealed off in a tube containing sodium and heated to 60° for eight hours to remove the last traces of water. The trimethylenimine was then introduced into the vacuum apparatus and again distilled through a −46° U-tube into a −64° U-tube until the fractions collected in the −64° tube appeared to be tensiometrically homogeneous. The imine, purified in this manner, exhibited a vapor pressure of 49 mm. at 0°. Extrapolation of the vapor pressure curve gave a normal boiling point of 61°.[9]

Pyrrolidine was prepared by the catalytic hydrogenation of pyrrole.[10] The product was distilled through the 15-plate fractionating column The fraction distilling at 85.5° at 730 mm. was collected over sodium, introduced into the vacuum apparatus and used directly.

Piperidine (Eastman Kodak Company) was distilled through the same column. It boiled at 104.4° at 740 mm. The product, collected over sodium and introduced into the vacuum apparatus, exhibited a vapor pressure of 7.0 mm. at 0°.

Results

Ethylenimine-trimethylboron, $(CH_2)_2NH{:}B(CH_3)_3$.—Ethylenimine and trimethylboron readily react at room temperatures to form the addition compound. The product is a liquid at ordinary temperatures, m. p. 10–12°.

The saturation pressures of the compound were studied over the temperature range from 24.5 to 98.9°. The data are listed in Table I and are represented graphically in Fig. 1-A. A straight line drawn through the points in the log P *vs.* $1/T$ graph is represented by the equation

$$\operatorname{Log} P = -3022/T + 9.8598$$

The extrapolated boiling point is 159.5°.

TABLE I

SATURATION PRESSURES OF ETHYLENIMINE-TRIMETHYLBORON

Temp., °C.	24.5	28.0	34.8	45.1	55.4
Pres., mm.	0.49	0.74	1.16	2.31	4.57
Temp., °C.	64.5	75.0	85.3	90.3	98.9
Pres., mm.	8.17	15.37	27.35	36.01	50.08

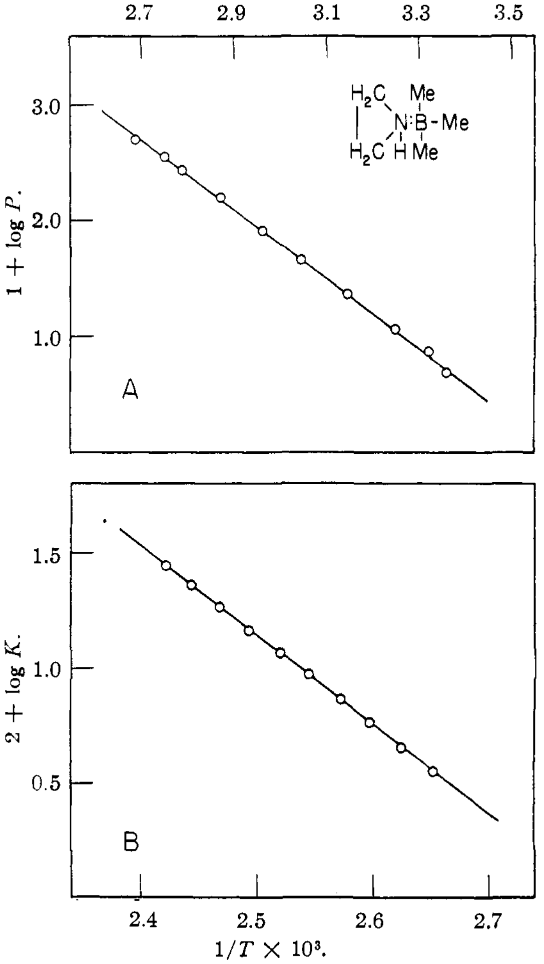

Fig. 1.—Ethylenimine-trimethylboron: A, saturation pressure data; B, dissociation data.

In view of the marked instability of ethylenimine in aqueous solutions, the addition compound

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[6] Brown, Bartholomay and Taylor, THIS JOURNAL, **66**, 435 (1944).

[7] Wenker, *ibid.*, **57**, 2328 (1935).

[8] Howard and Marckwald, *Ber.*, **32**, 2031 (1899).

[9] Howard and Marckwald, ref. 8, report b. p. 63° at 748 mm.; Ruzicka, Salomon and Meyer, *Helv. Chim. Acta*, **20**, 109 (1937), report b. p. 62° at 730 mm.; Jones, *J. Org. Chem.*, **9**, 484 (1944), reports b. p. 59.5–60.5°.

[10] Signaigo and Adkins, THIS JOURNAL, **58**, 709 (1936).

was carefully examined for chemical changes at elevated temperatures. Samples were maintained for several hours at temperatures between 100 and 140°. After such treatment the saturation pressures agreed perfectly with values obtained for the freshly prepared addition compound. No evidences of thermal instability under these conditions were observed.

Dissociation of the addition compound was studied over temperature ranges from 100° to 140° by the method of matched samples[11] and the method of approximations.[12] Results of four typical determinations, two by each method, are summarized in Table II.

TABLE II

THERMODYNAMIC CONSTANTS FOR ETHYLENIMINE-TRIMETHYLBORON

Method	Detn.	K_{100}	$\Delta F°_{100}$	ΔH	ΔS
Matched samples	1	0.0282	2645	17,590	40.1
	2	.0280	2650	17,630	40.2
Approximations	3	.0291	2622	17,570	40.1
	4[a]	.0284	2638	17,590	40.1

[a] Complete dissociation data are reported in Table III.

Complete dissociation data for a typical determination by the method of approximations are reported in Table III and represented graphically in Fig. 1-B. The variation of the dissociation constant with temperature is represented by the equation

$$\log K_p = -3846/T + 8.7612$$

The heat of dissociation, 17.59 ± 0.1 kcal., is surprisingly low, considerably below the 19.26 kcal. value obtained for the corresponding dimethylamine derivative.[6]

TABLE III

DISSOCIATION DATA FOR ETHYLENIMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obs.	Pressure, mm. Calcd.[a]	Degree of dissociation α	Dissociation constant K (atm.)
104.0	53.00	33.51	0.5816	0.0356
107.8	54.90	33.85	.6219	.0456
111.8	56.85	34.20	.6623	.0584
115.6	58.68	34.54	.6989	.0737
119.8	60.60	34.92	.7354	.0939
123.7	62.31	35.26	.7672	.117
127.9	64.02	35.64	.7963	.146
132.0	65.69	36.00	.8247	.184
136.1	67.23	36.36	.8490	.228
139.8	68.57	36.69	.8689	.278

[a] Pressure of ethylenimine and of trimethylboron (calculated to 0°) was 24.27 mm. as determined by the graphical method of approximations.

Trimethylenimine-trimethylboron, $(CH_2)_3NH:B(CH_3)_3$.—Trimethylenimine and trimethylboron form a liquid addition compound (m. p. −9 to −6°) which is considerably less volatile than the ethylenimine derivative, and in fact is less volatile than any of the addition compounds studied in these investigations. The saturation pressures are listed in Table IV and illustrated in Fig. 2-A. The data define a straight line which is given by the equation

$$\log P = -2881/T + 8.9521$$

The extrapolated "boiling point" is 201.4°.

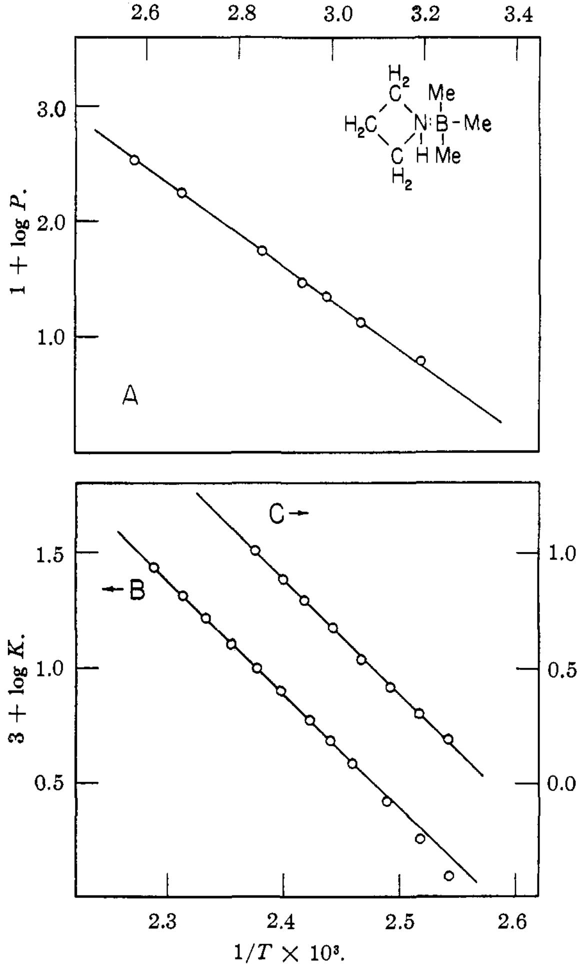

Fig. 2.—Trimethylenimine-trimethylboron: A, saturation pressure data; B, dissociation data (method of matched samples); C, dissociation data, small sample (method of approximations).

TABLE IV

SATURATION PRESSURES OF TRIMETHYLENIMINE-TRIMETHYLBORON

Temp., °C.	39.9	53.4	61.4	67.2
Pres., mm.	0.62	1.34	2.26	2.96
Temp., °C.	77.7	100.3	115.3	
Pres., mm.	5.57	17.65	34.12	

The compound is dissociated to a considerably lower degree than any of the other addition compounds previously studied. The low degree of dissociation and the low volatility both combined to render the usually negligible van der Waals

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(11) Brown, Taylor and Gerstein, *ibid.*, **66**, 431 (1944).

(12) Brown and Gerstein, THIS JOURNAL, **72**, 2923 (1950).

effects quite important, resulting in a definite curvature in the usual log K *vs.* $1/T$ graph (Table V, No. 2, Fig. 2-B). For this reason, attempts to apply the method of approximations[12] led to erratic results. These were resolved when the method of matched samples was used.

TABLE V

DISSOCIATION DATA FOR TRIMETHYLENIMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obs.	Pressure, mm. Calcd.	Degree of dissociation, α	Dissociation constant, K (atm.)
Determination No. 1[a]				
120.3	15.25	12.03	0.2677	0.00155
124.2	15.75	12.15	.2963	.00199
128.1	16.31	12.27	.3293	.00261
132.3	16.93	12.39	.3664	.00345
136.3	17.67	12.52	.4113	.00473
140.4	18.36	12.64	.4525	.00622
143.7	18.91	12.74	.4843	.00762
147.9	19.70	12.87	.5307	.0102
Determination No. 2[b]				
120.2	36.83	31.83	0.1571	0.00123
124.0	38.10	32.13	.1858	.00179
128.7	39.63	32.51	.2190	.00263
133.6	41.37	32.91	.2571	.00385
136.8	42.55	33.17	.2828	.00487
139.8	43.64	33.41	.3062	.00594
144.0	45.33	33.75	.3431	.00796
147.8	46.77	34.06	.3732	.00996
151.7	48.35	34.38	.4063	.0126
155.6	50.18	34.69	.4465	.0164
159.3	51.80	34.99	.4804	.0204
164.0	53.96	35.37	.5256	.0271

[a] Pressure of trimethylenimine and of trimethylboron (calculated to 0°) was 8.35 mm. as determined by the graphical method of approximations. [b] Pressure of trimethylenimine and of trimethylboron (calculated to 0°) was 22.10 mm.

To test the conclusion that the erratic results were due to the deviations resulting from strong van der Waals attractive forces, a determination was made using a relatively small sample to permit operating at much lower pressures. The data were handled by the method of approximations. This procedure leads to satisfactory linearity in the dissociation data (Table V, No. 1, Fig. 2-C) and to fair agreement in the thermodynamic constants calculated from the two sets of data (Table VI).

TABLE VI

THERMODYNAMIC CONSTANTS FOR TRIMETHYLENIMINE-TRIMETHYLBORON

Method	Detn. No.	K_{100}	$\Delta F°_{100}$	ΔH	ΔS
Approximations	1	0.000312	5982	22,690	44.8
Matched samples	2	.000322	5960	22,480	44.3

The variation of the dissociation constant with temperature is represented by the equation

$$\log K_p = -4915/T + 9.6797$$

It is apparent that the agreement between different runs was not as good as that obtained with the other compounds reported in the present paper and in previous papers in this series. Presumably this poor agreement is due to difficulties already mentioned, low volatility and low degree of dissociation, leading to high van der Waals deviations. Some six different determinations were made in an effort to improve the agreement. However, in these runs the values for the dissociation constant at 100° varied by as much as 6%; and the values for the heat of dissociation varied by some 0.3 to 0.5 kcal. The average of these constants for the six runs are in good agreement with Detn. 2 reported in Tables V and VI and these values are adopted for trimethylenimine-trimethylboron. However, in view of the experimental difficulties, a relatively large probable error of ±0.5 kcal. is assigned to the adopted value for the heat of dissociation.

Pyrrolidine-trimethylboron, $(CH_2)_4NH:B(CH_3)_3$.—The addition compound formed by the union of pyrrolidine and trimethylboron is a white crystalline solid which melts sharply at 43–44°. The saturation pressures were measured from 40 to 99.5°. The values are given in Table VII and represented graphically in Fig. 3-A. The saturation pressure data of the liquid are represented by the equation

$$\log P = -3403/T + 10.3797$$

The extrapolated "boiling point" is 191.3°.

TABLE VII

SATURATION PRESSURES OF PYRROLIDINE-TRIMETHYLBORON

Temp., °C.	40.0	51.8	60.9	70.7
Pres., mm.	0.32	0.83	1.56	3.06
Temp., °C.	80.4	90.2	99.5	
Pres., mm.	5.73	10.33	17.41	

The dissociation of the compound was studied over the temperature range from 120.7 to 156.2°. The compound is considerably more dissociated than the trimethylenimine complex under com-

TABLE VIII

DISSOCIATION DATA FOR PYRROLIDINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obs.	Pressure, mm. Calcd.[a]	Degree of dissociation, α	Dissociation constant, K (atm.)
120.7	36.01	24.24	0.4856	0.0146
124.3	37.35	24.46	.5270	.0189
128.2	38.68	24.70	.5660	.0240
132.3	40.12	24.95	.6080	.0310
136.2	41.52	25.19	.6483	.0396
139.0	42.64	25.37	.6807	.0484
144.6	44.46	25.71	.7293	.0665
148.3	45.60	25.94	.7579	.0810
152.7	46.94	26.21	.7909	.103
156.2	48.11	26.42	.8210	.131

[a] Pressure of pyrrolidine and of trimethylboron (calculated to 0°) was 16.81 mm. as determined by the graphical method of approximations.

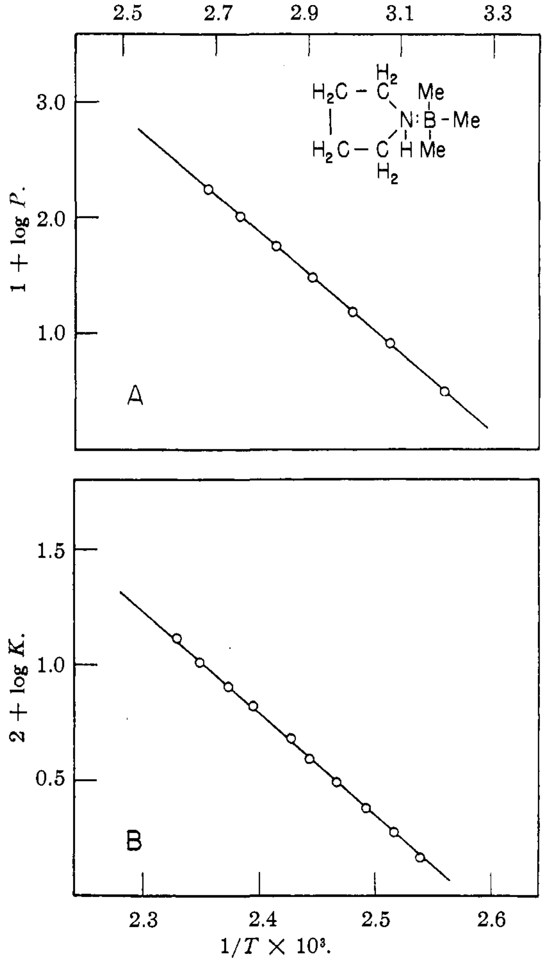

Fig. 3.—Pyrrolidine-trimethylboron: A, saturation pressure data; B, dissociation data.

parable conditions. The dissociation data are given in Table VIII and Fig. 3-B. The variation of the dissociation constants with temperature can be represented by the equation

$$\log K_p = -4466/T + 9.5136$$

The value of the dissociation constant at 100° is 0.00351. The heat of dissociation of the complex is 20.43 ± 0.2 kcal.

Piperidine-trimethylboron, $(CH_2)_5NH:B(CH_3)_3$.—Piperidine and trimethylboron react to form a 1:1 compound, which is solid at room temperature. It melts at 81.5–82.5°. The liquid shows a remarkable tendency to supercool and it was possible to observe the supercooled liquid at temperatures some 80° below the melting point. Saturation pressure data, over the temperature range from 50.0 to 99.0°, for the solid, liquid, and supercooled liquid are listed in Table IX and represented graphically in Fig. 4-A. The vapor tension values for the solid and liquid define straight lines which can be represented by the equations

$$\log P_{solid} = -4000/T + 12.2400$$
$$\log P_{liquid} = -3218/T + 10.0367$$

The lines defined by these equations intersect at 81.8° in good agreement with the experimentally observed melting point.

TABLE IX

SATURATION PRESSURES OF PIPERIDINE-TRIMETHYLBORON

		Solid		
Temp., °C.	50.0	55.3	60.2	66.0
Pres., mm.	0.74	1.13	1.72	2.77
Temp., °C.	70.4	75.7	80.0	
Pres., mm.	3.90	5.94	8.47	
		Liquid		
Temp., °C.	70.5	74.1	80.2	82.5
Pres., mm.	4.68	5.85	8.51	9.76
Temp., °C.	85.2	90.1	94.6	99.0
Pres., mm.	11.47	15.27	19.67	25.63

The vapor tension reaches 760 mm. at 176.5°. Thus, the extrapolated boiling points of the four addition compounds vary in the order: $(CH_2)_3NH$(201.4°) > $(CH_2)_4NH$(191.3°) > $(CH_2)_5NH$(176.5°) > $(CH_2)_2NH$(159.5°). This order is identical with the order of relative stabilities of

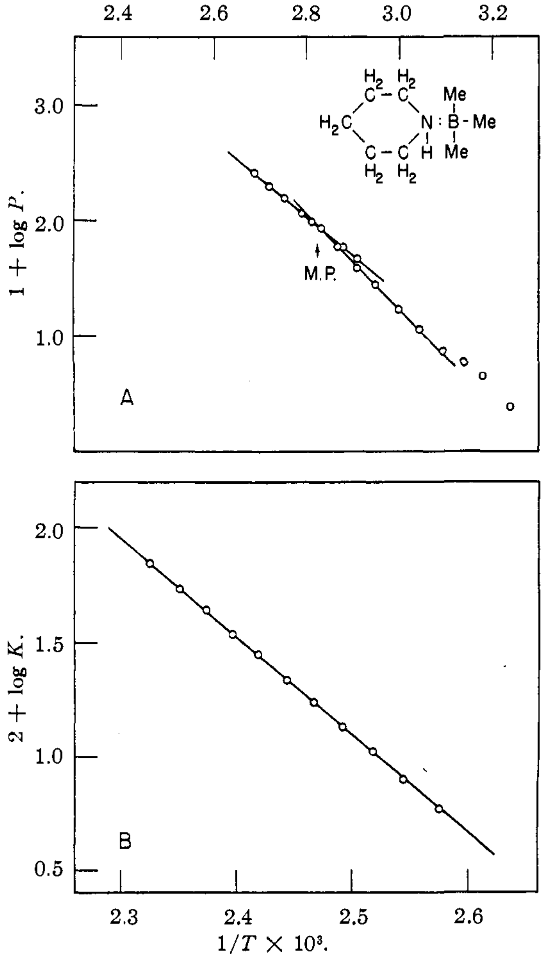

Fig. 4.—Piperidine-trimethylboron: A, saturation pressure data; B, dissociation data.

the addition compounds obtained in the dissociation studies and supports the generalization previously proposed.[13]

Dissociation of the addition compound was studied over the temperature range from 115.2 to 157.0°. The compound is somewhat more dissociated than the corresponding pyrrolidine derivative under similar conditions. In stability it resembles dimethylamine-trimethylboron quite closely.

The dissociation data are given in Table X and represented graphically in Fig. 4-B. The dissociation constants can be represented by the equation

$$\log K_p = -4296/T + 9.8336$$

The value of the dissociation constant at 100° is 0.0210 and the heat of dissociation is 19.65 ± 0.1 kcal.

TABLE X

DISSOCIATION DATA FOR PIPERIDINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obs.	Calcd.[a]	Degree of dissociation, α	Dissociation constant, K (atm.)
115.2	53.33	31.83	0.6755	0.0589
120.0	55.50	32.23	.7220	.0795
124.0	57.40	32.56	.7629	.105
128.2	59.11	32.90	.7967	.135
132.2	60.73	33.23	.8276	.174
136.1	62.13	33.55	.8519	.216
140.3	63.64	33.89	.8778	.281
144.1	64.81	34.20	.8950	.343
148.1	66.07	34.53	.9134	.438
152.2	67.21	34.87	.9274	.544
157.0	68.45	35.26	.9413	.700

[a] Pressure of piperidine and of trimethylboron (calculated to 0°) was 22.39 mm. as determined by the graphical method of approximations.

Discussion

To facilitate the discussion, the experimental results are summarized in Table XI together with earlier data for dimethylamine[6] and diethylamine.[14]

TABLE XI

SUMMARY OF RESULTS ON DISSOCIATION OF ADDITION COMPOUNDS

Addition compound of trimethylboron with	K_{100}	$\Delta F°_{100}$	ΔH	ΔS
Ethylenimine	0.0284	2640	17,590	40.1
Trimethylenimine	.000322	5960	22,480	44.3
Pyrrolidine	.00350	4190	20,430	43.5
Piperidine	.0210	2864	19,650	45.0
Dimethylamine	.0214	2850	19,260	43.6
Diethylamine	1.22	−147	16,310	44.1

The marked decrease in stability of diethylamine-trimethylboron (ΔH = 16.31 kcal.) over dimethylamine-trimethylboron (ΔH = 19.26 kcal.) was attributed to the larger steric requirements of the ethyl groups.[14] It was predicted that the tying back of the two ethyl groups in a ring, so that they could not rotate into position to interfere with the trimethylboron molecule, would lead to a considerable increase in stability. It will be observed that both piperidine-trimethylboron and pyrrolidine-trimethylboron show this predicted increase in stability over the diethylamine derivative.

In aqueous solution piperidine and pyrrolidine are bases of equal strengths.[15] Therefore, the increase in stability of pyrrolidine-trimethylboron over piperidine-trimethylboron is probably a result of decreased F-strain[6] in the five-membered derivative over that present in the piperidine compound. The results strongly indicate that the α-methylene groups in the piperidine ring are situated sterically with respect to the trimethylboron group in a manner similar to the two methyl groups in dimethylamine. The higher stability of the addition compounds formed by pyrrolidine indicates that the two α-methylene groups in the five-membered ring are pulled away from the trimethylboron group and involve less F-strain.

Arnold[16] has recently described a number of examples which support the conclusion that the steric effects of methylene groups in five-membered rings are considerably smaller than those in the corresponding six-membered rings.

It is possible in the same way to account for the marked increase in stability observed in the case of trimethylenimine. The geometry of the ring pulls the α-methylene groups far back and markedly reduces the F-strain in the addition compound.

F-Strain must be even less in ethylenimine-trimethylboron, but the stability of the addition compound shows a sharp drop. This marked reversal in stability of the imine addition compounds

$$\text{6-ring} < \text{5-ring} < \text{4-ring} >> \text{3-ring}$$

points to the operation of a new effect in the three-membered ring derivative which is sufficiently important to overcome the stabilizing effect of lower F-strain.

One possible explanation would involve the close similarity between cyclopropyl derivatives and the corresponding vinyl compounds.[17] Thus, acrylic acid, $CH_2{=}CHCO_2H$, is a somewhat stronger acid than acetic acid, $K_A = 5.5 \times 10^{-5}$ and 1.75×10^{-5}, respectively.[18] Similarly, the unknown vinylamine, CH_2CHNH_2, would be expected to be somewhat weaker than a typical

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[13] ". . . of two addition compounds of closely similar structure and molecular weight, the less stable exhibits the higher saturation pressure," Brown and Pearsall, THIS JOURNAL, **67**, 1765 (1945).

[14] Brown and Taylor, THIS JOURNAL, **69**, 1332 (1947).

[15] Craig and Hixon, THIS JOURNAL, **53**, 4367 (1931), report for pyrrolidine $K_B = 1.3 \times 10^{-3}$; Kolthoff, *Biochem. Z.*, **162**, 289 (1925), reports for piperidine $K_B = 1.6 \times 10^{-3}$.

[16] Arnold, *et al.*, THIS JOURNAL, **68**, 2176 (1946); **70**, 2791, 3505 (1948).

[17] Pertinent literature references are contained in a paper by Rogers and Roberts, THIS JOURNAL, **68**, 843 (1946). In this paper the authors report the interesting observation that the dipole moment of cyclopropyl chloride, 1.76 Debye, lies between the values for isopropyl chloride and vinyl chloride.

[18] "Lange's Handbook of Chemistry," Handbook Publishers, Sandusky, Ohio, 1946, pp. 1377-1383.

saturated aliphatic amine. If the analogy is accepted, ethylenimine should then be a slightly weaker base than dimethylamine.

Unfortunately, there are certain difficulties with this interpretation. The heats of dissociation of the addition compounds of ethylenimine-trimethylboron and trimethylenimine-trimethylboron differ by some 5 kcal. F-strain should be less in the ethylenimine derivative. Therefore, a lower limit of 5 kcal. may be assigned to the destabilization observed. Pyridine[18] with $K_B = 1.4 \times 10^{-9}$ is tremendously weaker than piperidine[15] with $K_B = 1.6 \times 10^{-3}$. Yet the heat of dissociation of pyridine-trimethylboron is 17.0 kcal.[19] as compared to the 19.6 kcal. value obtained in the present investigation for the piperidine addition compound. It therefore appears that the destabilization of ethylenimine-trimethylboron is far larger than can be accounted for merely in terms of the similarity of the ethylenimine ring to vinyl systems and the probable polar effects of such systems.[20]

It is here proposed that this decrease in stability is the result of the *internal strain in the ring*. The following interpretation is suggested.

According to the quantum mechanical picture of the nitrogen atom in an amine, the lone-pair of electrons may be considered to be located in the 2-s orbital, and the three bonded pairs may be considered to be occupying the three 2-p orbitals directed in space at angles of 90°. In a simple amine steric and electrostatic repulsions will generally lead to widening of the bond angles to magnitudes in the neighborhood of the tetrahedral value. The energy required to bring about such widening of the bond angles will presumably be small because of the stabilization introduced by hybridization of the orbitals.[21]

Addition of a proton or trimethylboron molecule to the lone pair of the nitrogen atom converts the atom to one with four bonds. The stablest form of such an atom involves four tetrahedral bonds.

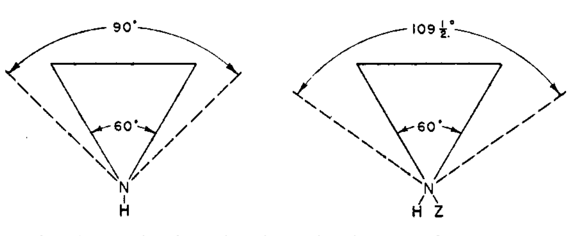

Fig. 5.—I-Strain, showing the increased angular deformation required of a tetrahedral as compared to a trivalent nitrogen atom (*Z* represents any generalized acid).

From this point of view, the free ethylenimine molecule may be considered to contain the strain involved in bending the two nitrogen-to-carbon bonds from their natural value of 90 to the 60° value required by the geometry of the ring. On the other hand, the ethylenimine-trimethylboron molecule may be considered to contain the larger strain involved in bending this angle from the 109°28′ value of a tetrahedrally coördinated nitrogen atom back to the approximately 60° value fixed by the ring (Fig. 5).[22]

According to this interpretation, formation of the addition compound involves an increase in the internal strain of the ring. The experimentally determined heat of dissociation of the addition compound will be decreased by the energy involved in this increase of internal strain.

In conformity with the symbolism introduced in earlier papers of this series, it is proposed that this effect be termed I-strain. Specifically, I-strain is that change in internal strain of a ring compound which results from a change in the coördination number (and the preferred bond angle) of a ring atom involved in the reaction.

The conversion of trimethylenimine into the trimethylboron derivative should also involve I-strain, and it is necessary to account for the high stability of this addition compound. In this case, I-strain should be considerably smaller than that involved in the case of ethylenimine. It is proposed that in the case of trimethylenimine this relatively small I-strain is overshadowed by a large decrease in F-strain, whereas in ethylenimine-trimethylboron I-strain is much larger and is sufficient to play a dominant role in determining the stability of the addition compound.

From this point of view, the use of a reference acid with a high F-strain factor, such as tri-*t*-butylboron, should cause the maximum to shift toward the three-membered ring, whereas a reference acid with low steric requirements should cause the maximum to shift toward the five-membered ring. In other words, if F-strain is larger than I-strain, the observed sequence should be

$$\text{6-ring} < \text{5-ring} < \text{4-ring} < \text{3-ring}$$

On the other hand, if F-strain is small compared

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(19) Brown and Barbaras, THIS JOURNAL, **69**, 1137 (1947).

(20) It would be desirable to have quantitative evidence on this point. It is hoped that a study of vinyldimethylamine-trimethylboron will yield a definite answer to the question as to how large a fraction of the destabilization should be assigned to the polar effects of the vinyl group and the three-membered ring.

(21) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, pp. 76–88.

(22) The bending constants for nitrogen in ammonia and in ammonium ion are quite similar. Thus, Herzberg, ("Infrared and Raman Spectra," D. Van Nostrand Co., New York, N. Y., 1945; pp. 177, 182) gives the bending constant, k_δ, for ammonia as $0.54\, l^2 \times 10^4$ dynes/cm., and for ammonium ion as $0.56\, l^2 \times 10^5$ dynes/cm., where l is the nitrogen to hydrogen bond distance in ammonia and in ammonium ion, respectively. The nitrogen to hydrogen bond distance is 1.01 Å. in ammonia and is estimated to be 0.03 Å. shorter in ammonium ion (Pauling, *idem.*, pp. 158–159). Thus, the energy required to produce a given deformation of the nitrogen bond angle is essentially the same in the two types of nitrogen compounds. It should be emphasized that these bending constants apply only to relatively small distortions of the bond angles from their equilibrium positions. However, there is little reason to doubt that a distortion of $49\frac{1}{2}^\circ$ in tetracoördinate nitrogen (from $109\frac{1}{2}^\circ$ to 60°) must involve a greater increase in energy than a distortion of 30° in trivalent nitrogen (from 90° to 60°).

to I-strain, the observed order should become either

6-ring $<$ 5-ring $>$ 4-ring $>$ 3-ring

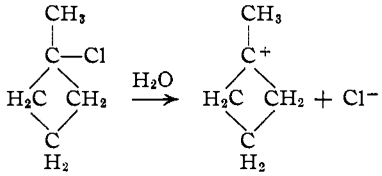
or

6-ring $>$ 5-ring $>$ 4-ring $>$ 3-ring

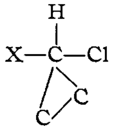
An investigation of this prediction will be undertaken.

Over the past several years, I-strain has been very helpful in accounting for the very unusual changes in chemical behavior which we have observed in the cycloalkane ring compounds as the size of the ring is varied.[23]

For example, the unimolecular hydrolysis of 1-chloro-1-methylcyclobutane is exceedingly slow—the energy of activation for the reaction is markedly greater than that of simple open chain tertiary aliphatic chlorides.[24] Since formation of the carbonium ion with a 120° angle at the unsaturated center would involve an increase in I-strain, the slowness of the reaction is reasonable and was, in fact, predicted.



The bimolecular displacement reactions of cyclopropyl chloride are exceedingly slow.[25] The activated complex involved in such displacement reactions ordinarily require that the three groups attached to carbon and not undergoing displacement shall be coplanar and situated at angles of 120° from each other. Here again the presence of the small ring will involve a large increase in I-strain in the activated complex and would be expected to hinder displacement reactions.



The utility of I-strain in understanding the chemistry of ring compounds will be developed in further papers now in preparation.

Acknowledgment.—This investigation was aided by Grants No. 710 and 776 from the Penrose Fund of the American Philosophical Society. This assistance is gratefully acknowledged.

Summary

1. The trimethylboron addition compounds with ethylenimine, trimethylenimine, pyrrolidine and piperidine have been prepared and characterized.

2. The dissociation of these compounds in the vapor phase has been studied. ΔH, ΔF and ΔS for the dissociations are reported. The stability of the addition compounds increase in the order: piperidine $<$ pyrrolidine $<$ trimethylenimine $\gg$ ethylenimine.

3. The increased stability of pyrrolidine-trimethylboron over diethylamine-trimethylboron is attributed to the reduced steric effect of the ring.

4. The increased stability of pyrrolidine-trimethylboron over piperidine-trimethylboron is attributed to the reduced steric effect of the α-methylene groups of a five- as compared to a six-membered ring.

5. The low stability of the ethylenimine derivative is attributed to an increase in ring strain resulting from the conversion of the ring nitrogen atom from its trivalent to the tetravalent state.

6. I-Strain is defined. The concept is useful in understanding not only the behavior of ethylenimine, but also the effect of ring size on the chemical properties of the halocycloalkanes and other ring compounds.

LAFAYETTE, IND. RECEIVED SEPTEMBER 15, 1949

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(23) Unpublished work with Roslyn Silber Fletcher, Rolf B. Johannesen and Mitchell Borkowski.

(24) For example, in 80% ethanol the first order rate constants are 0.00223 and 0.0321 hr.$^{-1}$ for 1-chloro-1-methylcyclobutane and *t*-butyl chloride, respectively. The corresponding energies of activation are 22.8 and 24.2 kcal., respectively. A complete report of our work on the 1-chloro-1-methylcycloalkanes will be prepared shortly.

(25) Gustavson, *J. prakt. Chem.*, [2] **43**, 396 (1891).