ADDITION COMPOUNDS
OF N-METHYL CYCLIC IMINES
WITH TRIMETHYLBORON* †

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Abstract — A manometric investigation was made of the addition compounds of trimethylboron with the N-methyl derivatives of ethylenimine (aziridine), trimethylenimine (azetidine), pyrrolidine and piperidine. The stability order obtained was 3->4->5->6-membered ring. This order is different from that reported by BROWN and GERSTEIN[1] for the trimethylboron addition compounds with the unsubstituted cyclic imines, the order being 4->5->6->3-membered ring. The complete reversal in position of the 3-membered ring upon substituting a methyl group for the hydrogen on the nitrogen in this series is due to large steric interaction. This effect becomes more pronounced as the ring size increases, thereby leading to the systematic decrease in stability. Only in the case of the 3-membered ring does methyl substitution result in a more stable addition compound. For the other ring compounds methyl substitution results in decreased stability, the decrease becoming progressively larger as the ring size increases.

In a manometric study of the trimethylboron addition compounds of the unsubstituted cyclic imines, BROWN and GERSTEIN[1] observed a stability order of 4- > 5- > 6- > 3-membered ring which they attributed to the opposing effects of two steric factors, namely "F-strain" and "I-strain". "F-strain" was presumed to arise from the interaction of the methyl groups of the trimethylboron with the α-methylene hydrogen atoms of the cyclic imine, an effect which should increase with increasing ring size. "I-strain" was presumed to result from the change in co-ordination number (and, therefore, preferred bond angle) of the hetero-atom upon complex formation, an effect which should decrease with increasing ring size.

Investigation of the basicity of the cyclic imines and N-methyl cyclic imines by means of hydrogen bonding with methanol-d and by pK_a measurements in aqueous solution showed a basicity order of 5- ≥ 4- > 6- > 3-membered ring.[2] In that study "I-strain" was judged to be small in hydrogen bonding because of the

[1] H. C. BROWN and M. GERSTEIN, *J. Amer. Chem. Soc.* **72**, 2926 (1950).

[2] S. SEARLES, M. TAMRES, F. BLOCK and L. A. QUARTERMAN, *J. Amer. Chem. Soc.* **78**, 4917 (1956).

weakness of the interaction, and "F strain" was judged to be small in proton transfer because of the small size of the acceptor. The observed basicity order was ascribed to an alteration in electron distribution around the atoms in the ring which accompanies the change in geometric configuration.

In order to obtain quantitative thermodynamic data on the steric and inductive effect of the N-methyl group, the manometric investigation of the trimethylboron addition compounds of the N-methyl cyclic imines was undertaken, since these results could be compared directly with those of BROWN and GERSTEIN[1] for the corresponding unsubstituted cyclic imines. In the event that the steric factors were not too preponderant, there was also the possibility of obtaining some information on the variation of inductive effect with ring size. Proton magnetic resonance studies[3] on the N-methyl cyclic imines reveal small differences in the proton spectrum of the N-methyl groups, but these are so close to experimental error that the results are not conclusive.

EXPERIMENTAL

Materials. Trimethylboron was prepared by the method described by BROWN[4]. The vapour pressure observed for the purified material was 7·9 mm at $-96\cdot0°C$, 87·4 mm at $-63\cdot6°C$, and 247 mm at $-45\cdot3°C$.

The preparation and physical constants of the N-methyl cyclic imines have been reported previously[2]. The purity of the imines was verified by vapour phase chromatography, with any impurities having to be present to less than 0·01 per cent.

Apparatus. A constant temperature manostat was employed for the vapour phase study of the addition compounds. This apparatus has been described elsewhere[5]. The boiling liquid used in the lower temperature range (35–85°C) was 1-bromobutane, while that in the higher range (80–125°C) was chlorobenzene.

RESULTS AND DISCUSSION

All the N-methyl cyclic imines react with trimethylboron to form white, crystalline addition compounds of 1:1 composition and melt to yield colourless liquids. All were stable under the experimental conditions of this research. The N-methyl-pyrrolidine : trimethylboron and N-methylpiperidine : trimethylboron were observed to exhibit a marked tendency for the liquid to supercool below the freezing point, an observation also reported for piperidine : trimethylboron.[1] The melting points observed for the 3-, 4-, 5-, and 6-membered N-methyl cyclic imine : trimethylboron addition compounds are 94·2–94·4°C, 5–7°C, 45·4–46·4°C and 28–29°C, respectively. The melting points for the corresponding unsubstituted cyclic imine : trimethylboron addition compounds reported by BROWN and GERSTEIN[1] are 10–12°C, −9−−6°C, 43–44°C, and 81·5–82·5°C for the 3-, 4-, 5-, and 6-membered ring, respectively.

[3] R. L. RUTLEDGE. Thesis, University of Illinois (1958).
[4] H. C. BROWN, *J. Amer. Chem. Soc.* **67**, 374 (1945).
[5] D. E. McLAUGHLIN and M. TAMRES, *J. Amer. Chem. Soc.* **81**, 5618 (1960).

Numerical values for the saturation pressures of the 3-, 4-, 5-, and 6-member-ed ring N-methyl cyclic imine : trimethylboron addition compounds are given in Tables 1, 3, 5, and 7, respectively. The saturation pressure equation for each compound was obtained from a least squares treatment of the data. The equations are plotted in Fig. 1.
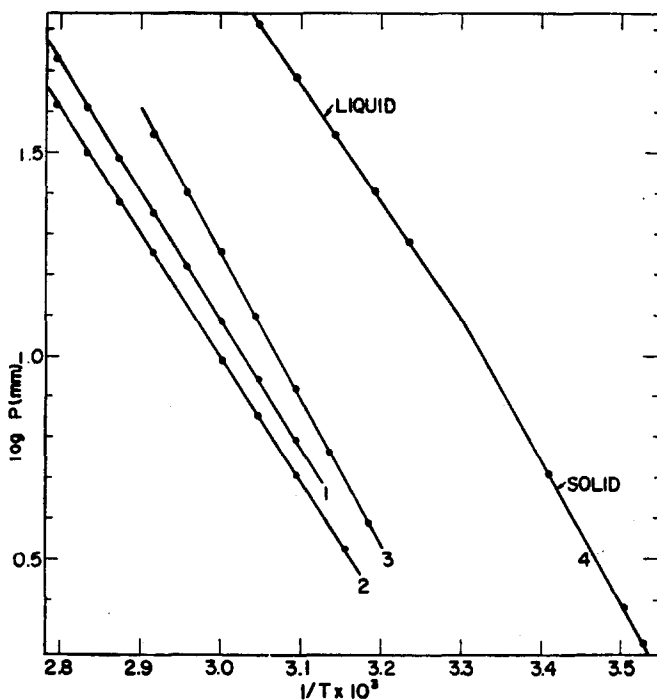

FIG. 1. — Saturation pressures of the N-methyl cyclic imine: trimethylboron addition compounds.
1. N-Methylethylenimine: $B(CH_3)_3$ (solid)
2. N-Methyltrimethylenimine: $B(CH_3)_3$ (liquid)
3. N-Methylpyrrolidine: $B(CH_3)_3$ (liquid)
4. N-Methylpiperidine: $B(CH_3)_3$ (solid and liquid).

Numerical data for the dissociation pressures are given in Tables 2, 4, 6 and 8. Although the data are listed in order of progressive increase in temperature, the individual points were taken in random fashion to avoid the possibility of systematic error. Plots of log K vs. $1/T$ are shown in Figs. 2, 3 and 4. The technique of initially measuring the pressure of each component separately was used in every determination. This was found preferable to using the "method of approximations"[6] because the latter method may give erratic results on occasion.[1] In one experiment on N-methyle-thylenimine : trimethylboron that happened to follow a study of a boron trifluoride etherate which left a slight polymeric deposit, it was found that the method of

[6] H. C. BROWN and M. GERSTEIN, *J. Amer. Chem. Soc.* **72**, 2923 (1950).

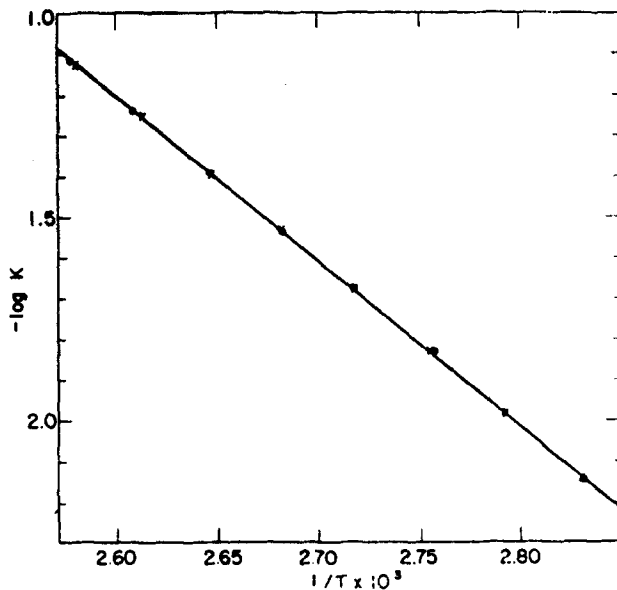FIG. 2. — Log K vs. $1/T$ for N-methylethylenimine:trimethylboron.
· 13·614 mm B(CH$_3$)$_3$ and 13·693 mm N-methylethylenimine
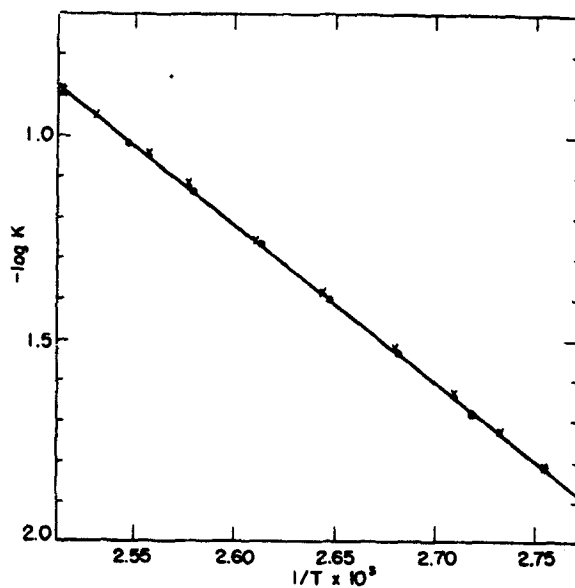x 14·176 mm B(CH$_3$)$_3$ and 13·682 mm N-methylethylenimine.

FIG. 3. — Log K vs. $1/T$ for N-methyltrimethylenimine:trimethylboron
· 14·299 mm B(CH$_3$)$_3$ and 14·099 mm N-methyltrimethylenimine
x 14·918 mm B(CH$_3$)$_3$ and 14·604 mm N-methyltrimethylenimine.

approximations still gave a straight line plot of log K vs. $1/T$ although slight adsorption effects made the results spurious.

The thermodynamic values of the trimethylboron addition compounds of the N-methyl cyclic imines are summarized in Table 9. These were calculated from a least squares determination of log K vs. $1/T$. For ease of comparison, the thermodynamic values of BROWN and GERSTEIN[1] for the corresponding unsubstituted cyclic imine : trimethylboron addition compounds are presented in Table 9 also. The stability order of the addition compounds which is observed for the series of N-methyl cyclic imines is 3- > 4- > 5- > 6- membered ring, whereas for the corresponding unsubstituted cyclic imines, the order reported by BROWN and GERSTEIN
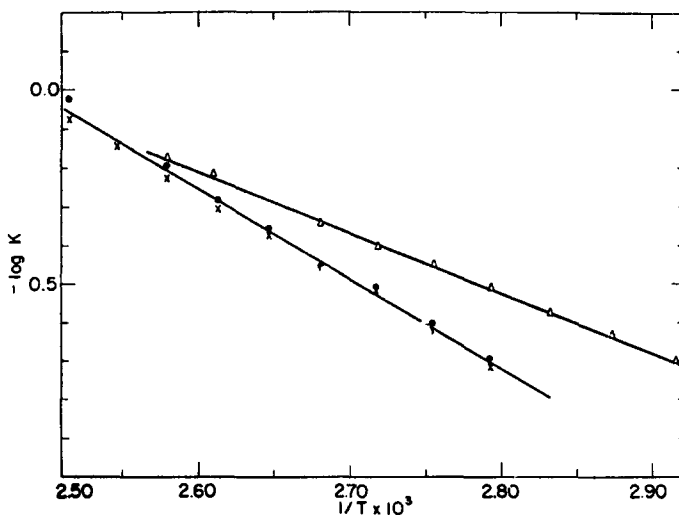
FIG. 4. — Log K vs. $1/T$ for N-methylpyrrolidine:trimethylboron and N-methylpiperidine:trimethylboron.

17·928 mm $B(CH_3)_3$ and 18·121 mm N-methylpyrrolidine

x 17·611 mm $B(CH_3)_3$ and 17·712 mm N-methylpyrrolidine

Δ 18·914 mm $B(CH_3)_3$ and 18·777 mm N-methylpiperidine.

TABLE 1.—SATURATION PRESSURES OF N-METHYLETHYLENIMINE :
TRIMETHYLBORON

Melting point: 94·2–94·4°C
Saturation pressure equation (solid):

$$\log P = \frac{-3121}{T} + 10\cdot451$$

Temperature (°C)	49·9	54·9	59·9	64·9	69·9
Pressure (mm)	6·17	8·75	12·20	16·64	22·63
Temperature (°C)	74·9	79·9	84·8		
Pressure (mm)	30·98	40·90	54·13		

is 4- > 5- > 6- > 3-membered ring. The complete reversal in the relative position of the 3-membered ring is sufficient evidence of a pronounced steric influence of N-methyl substitution upon the stability of the addition compound.

A more quantitative indication of the influence of the N-methyl group with increasing ring size is obtained from a comparison of the $\Delta H°$ values for the unsub-

TABLE 2.—DISSOCIATION DATA FOR N-METHYLETHYLENIMINE: TRIMETHYLBORON

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)
13·615 mm B(CH₃)₃ and 13·693 mm N-methylethylenimine at 0°C		

$$\log K = \frac{-4031}{T} + 9·276$$

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)
79·9	25·089	0·00714
84·8	26·480	0·0104
89·8	27·699	0·0147
94·6	29·218	0·0205
99·7	30·042	0·0291
104·7	32·119	0·0408
109·6	33·438	0·0580
114·8	34·742	0·0768

14·176 mm B(CH₃)₃ and 13·682 mm N-methylethylenimine at 0°C

$$\log K = \frac{-4063}{T} + 9·362$$

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)
80·1	25·577	0·00719
84·8	26·950	0·0104
89·8	28·383	0·0149
94·7	29·804	0·0208
99·7	31·339	0·0299
104·6	32·664	0·0403
109·5	34·077	0·0564
114·5	35·317	0·0754

TABLE 3.—SATURATION PRESSURES OF N-METHYLTRIMETHYLENIMINE: TRIMETHYLBORON

Melting point: 5–7°C

Saturation pressure equation (liquid):

$$\log P = \frac{-3006}{T} + 10·016$$

Temperature (°C)	43·4	49·9	54·9	59·9	69·9
Pressure (mm)	3·33	5·09	7·12	9·72	18·01
Temperature (°C)	74·9	79·9	84·8		
Pressure (mm)	24·13	31·71	41·22		

TABLE 4.—DISSOCIATION DATA FOR
N-METHYLTRIMETHYLENIMINE : TRIMETHYLBORON

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)

14·299 mm B(CH₃)₃ and 14·099 mm N-methyltrimethylenimine at 0°C

$$\log K = \frac{-3832}{T} + 8 \cdot 739$$

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)
89·8	28·862	0·0153
94·7	30·286	0·0206
99·7	31·772	0·0289
104·6	33·150	0·0393
109·5	34·530	0·0537
114·5	35·840	0·0726
119·5	37·013	0·0953
124·5	38·155	0·126

14·918 mm B(CH₃)₃ and 14·604 mm N-methyltrimethylenimine at 0°C

$$\log K = \frac{-3863}{T} + 8 \cdot 828$$

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)
89·9	29·975	0·0152
92·8	30·888	0·0188
95·9	31·856	0·0233
100·0	33·064	0·0301
105·1	34·557	0·0415
110·0	36·012	0·0551
115·0	37·348	0·0767
118·0	38·098	0·0906
122·0	39·040	0·112
124·7	39·675	0·131

TABLE 5.—SATURATION PRESSURES OF N-METHYLPYRROLIDINE : TRIMETHYLBORON

Melting point: 45·4–46·4°C

Saturation pressure equation (liquid):

$$\log P = \frac{-3541}{T} + 11 \cdot 376$$

Temperature (°C)	24·7	40·5	45·5	49·9	55·3
Pressure (mm)	0·85*	3·86†	5·74	8·29	12·52
Temperature (°C)	59·9	64·9	69·9		
Pressure (mm)	18·11	25·32	35·17		

* solid: † supercooled liquid.

Table 6.—Dissociation data for N-methylpyrrolidine:trimethylboron

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)

17·928 mm B(CH$_3$)$_3$ and 18·121 mm N-methylpyrrolidine at 0°C

$$\log K = \frac{-2397}{T} + 5·992$$

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)
84·9	44·433	0·203
89·8	45·458	0·250
94·7	46·122	0·298
94·8	46·475	0·313
99·7	47·251	0·347
104·6	48·223	0·441
109·5	49·052	0·519
114·5	49·938	0·645
124·4	51·572	0·957

17·611 mm B(CH$_3$)$_3$ and 17·712 mm N-methylpyrrolidine at 0°C

$$\log K = \frac{-2266}{T} + 5·620$$

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)
84·8	43·479	0·194
89·8	44·475	0·236
94·7	45·514	0·303
99·7	46·324	0·344
104·6	47·221	0·421
109·6	48·051	0·495
114·5	48·860	0·588
119·5	49·690	0·717
124·4	50·445	0·837

Table 7.—Saturation pressures of N-methylpiperidine:trimethylboron

Melting point: 28–29°C
Saturation pressure equation (liquid):

$$\log P = \frac{-2839}{T} + 10·472$$

Temperature (°C)	10·1	12·1	20·0	35·8	40·0
Pressure (mm)	1·97*	2·40*	5·10*	19·07	25·46
Temperature (°C)	44·9	49·9	55·0		
Pressure (mm)	35·11	48·51	65·54		

* solid.

TABLE 8. — DISSOCIATION DATA FOR N-METHYLPIPERIDINE:TRIMETHYLBORON

$$\log K = \frac{-1540}{T} + 3 \cdot 794$$

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)
18·914 mm $B(CH_3)_3$ and 18·777 mm N-methylpiperidine at 0°C		
69·9	44·494	0·201
74·9	45·483	0·239
79·9	46·351	0·269
84·8	47·250	0·313
89·8	48·117	0·357
94·7	48·916	0·396
100·0	49·799	0·451
110·0	51·505	0·607
114·5	52·213	0·670

stituted and the corresponding N-methyl cyclic imines of Table 9. In the absence of any steric effect, the inductive effect of the methyl group would be expected to increase the basicity of the imine, but only in the case of the 3-membered ring does methyl substitution on the nitrogen result in an increase in $\Delta H°$. For the

TABLE 9. — THERMODYNAMIC DISSOCIATION DATA FOR ADDITION COMPOUNDS OF N-METHYL CYCLIC IMINES WITH TRIMETHYLBORON

This research:	$\Delta H°$ (kcal/mole)	K_{100} (atm)	ΔF_{100} (cal/mole)	$\Delta S°$ (e. u.)
N-methylethylenimine: $B(CH_3)_3$	$18 \cdot 52 \pm 0 \cdot 2$	0·0300	2601 ± 15	$42 \cdot 7 \pm 0 \cdot 6$
N-methyltrimethylenimine: $B(CH_3)_3$	$17 \cdot 61 \pm 0 \cdot 2$	0·0298	2606 ± 15	$40 \cdot 2 \pm 0 \cdot 6$
N-methylpyrrolidine: $B(CH_3)_3$	$10 \cdot 67 \pm 0 \cdot 2$	0·363	752 ± 15	$26 \cdot 6 \pm 0 \cdot 6$
N-methylpiperidine: $B(CH_3)_3$	$7 \cdot 05 \pm 0 \cdot 2$	0·465	568 ± 15	$17 \cdot 4 \pm 0 \cdot 6$
BROWN and GERSTEIN[1]:				
Ethylenimine:$B(CH_3)_3$	$17 \cdot 59 \pm 0 \cdot 1$	0·0284	2640	40·1
Trimethylenimine:$B(CH_3)_3$	$22 \cdot 48 \pm 0 \cdot 5$	0·000322	5960	44·3
Pyrrolidine:$B(CH_3)_3$	$20 \cdot 43 \pm 0 \cdot 2$	0·00350	4190	43·5
Piperidine:$B(CH_3)_3$	$19 \cdot 65 \pm 0 \cdot 1$	0·0210	2864	45·0

other ring compounds, N-methyl substitution results in a decrease in $\Delta H°$, the decrease being smallest for trimethylenimine and largest for piperidine. The numerical changes in $\Delta H°$ upon N-methyl substitution in the various rings are as follows: 3-, $\Delta(\Delta H°) = 0 \cdot 9$ kcal/mole; 4-, $\Delta(\Delta H°) = -4 \cdot 9$ kcal/mole; 5-, $\Delta(\Delta H°) = -9 \cdot 8$ kcal/mole; 6-, $\Delta(\Delta H°) = -12 \cdot 6$ kcal/mole.

These differences could be attributed solely to steric factors providing that the inductive effect of the methyl group remains the same in all ring sizes. Inasmuch as the interaction between a substituent and the ring is surely mutual, the change in electron distribution of the ring atoms as the ring size changes perhaps results in a change in inductive effect. The proton magnetic resonanse spectra of the N-methyl protons in the N-methyl cyclic imines show small variations with ring size, but the data may be difficult to evaluate in terms of a single variable. Table 10 shows the proton magnetic resonance data obtained by RUTLEDGE[3] for the cyclic imines and the N-methyl cyclic imines. These data do not constitute proof that the inductive effect varies with ring size but are cited as an indication tbat this effect may exist. However, for the present study on the interaction with trimethylboron, the steric factor certainly predominates, so that the relative $\Delta(\Delta H°)$ values can be taken as a measure of the change in the steric influence of the N-methyl group with change in ring size.

TABLE 10.—PROTON MAGNETIC RESONANCE CHEMICAL SHIFTS IN THE
CYCLIC IMINES[3]

	Chemical shift		
	α-CH$_2$	β-CH$_2$	N-H
Ethylenimine	−0·35		−0·35
Trimethylenimine	(−0·26)*	(−0·18)*	−0·29
Pyrrolidine	−0·23	−0·33	−0·27
Piperidine	−0·26	−0·37†	−0·33
	α-CH$_2$	β-CH$_2$	N-CH$_3$
N-methylethylenimine	−0·37		−0·27
N-methyltrimethylenimine	−0·22	−0·32	−0·31
N-methylpyrrolidine	−0·28	−0·31	−0·28
N-methylpiperidine	−0·28	−0·28†	−0·28

* Trimethylenimine exhibits a very complex spectrum and the assignments are only tentative.
β- and γ-CH$_2$.

Futher evidence of this large steric interference in the trimethylboron addition compounds can be obtained from a comparison of the effect of N-methyl substitution in the cyclic imines using a less bulky reference acid. In hydrogen bonding studies[2] using CH_3OD as an electron acceptor, it was observed that N-methyl substitution causes an increase in donor ability for all ring sizes. Evidently, the inductive effect of the N-methyl group in the cyclic imines is quite marked, but even in hydrogen bonding there may be some steric interaction since the change in OD shift upon N-methyl substitution is 48, 34, 30 and 28 cm^{-1} for the 3-, 4-, 5- and 6-membered ring, respectively.

A case in which steric effects may be somewhat more important than in hydrogen bonding is the rate of quaternization[7] of the N-methyl cyclic imines with methyl iodide where a rate order of 4- > 5- > 6- > 3-membered ring was observed. If the rate of quaternization can be simply related to the electorn donor ability of the imine, then the order is slightly different from that found in the hydrogen bonding and proton transfer studies,[2] i.e. 5- > 4- > 6- > 3-membered ring. Perhaps, a greater steric factor in the 5- relative to the 4-membered ring in the rate study has caused the reversal of these two ring sizes. Some steric interaction of the N-methyl group with methyl iodide is not unreasonable in view of the very large steric effects observed toward trimethylboron. However, it may also be that solvation energies are influencing the results.

It seems to be true in a number of molecular addition compounds that a higher enthalpy of dissociation is associated with a higher entropy of dissociation. The linearity between the enthalpy and entropy of dissociation for a series of related complexes has been observed in several investigations, for example, in the complexes of iodine[8] and iodine monochloride[9] with substituted benzenes and in the iodine complexes of various ethers.[10, 11] An interpretation which has been offered is that the motion of the two components of the complex, relative to each other, becomes more restricted as the strength of the interaction or the enthalpy term increases.[8] In Fig. 5, the $\Delta H°$ versus the $\Delta S°$ values for the N-methyl cyclic imine : trimethylboron addition compounds of this investigation are plotted. As the figure shows, a linear relation exists, yet steric factors are obviously quite large. It seems that the steric factor is of a type which prevents the close approach of the trimethylboron molecule and, therefore, results in a lowering of the $\Delta H°$ term as well as the $\Delta S°$.

It has been proposed that saturation pressures could be used as a measure of relative stability of addition compounds if they are of similar structure and molecular weight.[12] Brown and Gerstein[1] extrapolated the saturation pressure data of the cyclic imine : trimethylboron addition compounds to obtain hypothetical "boiling points" of the addition compounds and found an order of "boiling points" of 4-(201·4°C)〉 5-(191·3°C)〉 6-(176·5°C)〉 3-(159·5°C) membered ring, which is the same as the order of relative stabilities. If the saturation pressure data for the N-methyl cyclic imine : trimethylboron addition compounds are extrapolated to obtain "boiling points", the order found is 4-(149°C)〉 5-(121°C)〉 6-(100°C) membered ring. No saturation pressure data for ethylenimine : trimethylboron was obtained for the liquid phase, but if the data for the solid are extrapolated to a pressure of 760 mm, a temperature of 139°C is found. It seems most probable that the value for the liquid would be enough higher than 139°C to

[7] S. Searles, F. Block and M. Tamres, Paper presented at Southwest Regional Amer. Chem. Soc. Meeting, Tulsa, Oklahoma, December, 1957.

[8] R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.* **77**, 2164 (1955).

[9] N. Ogimachi, L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.* **77**, 4202 (1955).

[10] Sister M. Brandon, M. Tamres and S. Searles, Jr., *J. Amer. Chem. Soc.* **82**, 2129 (1960).

[11] M. Tamres and Sister M. Brandon, *J. Amer. Chem. Soc.* **82**, 2134 (1960).

[12] H. C. Brown and H. Pearsall, *J. Amer. Chem. Soc.* **67**, 1765 (1945).

make it the highest of the series; and hence, the order is the same as the order of stabilities. The criterion of saturation pressures as a measure of relative stability applies, then, to the series of N-methyl cyclic imine addition compounds, and it
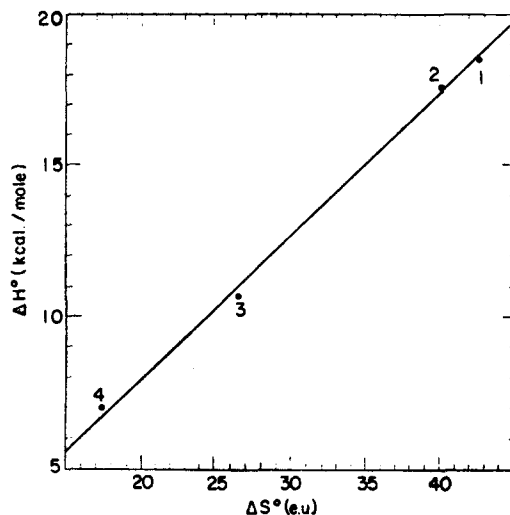

FIG. 5. — $\Delta H°$ vs. $\Delta S°$ for the N-methyl cyclic imine:trimethylboron addition compounds.
1. N-Methylethylenimine:B(CH$_3$)$_3$
2. N-Methyltrimethylenimine: B(CH$_3$)$_3$
3. N-Methylpyrrolidine:B(CH$_3$)$_3$
4. N-Methylpiperidine:B(CH$_3$)$_3$

applies further in the sense that the decrease in stability upon methyl substitution does lead to a decrease in "boiling point" of the addition compound.