# STRUCTURAL STUDIES BY NUCLEAR MAGNETIC RESONANCE—XVIII

## CONFORMATIONAL AND CONFIGURATIONAL ISOMERISM OF N-ALKYL IMINES<sup>1</sup>

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(Received in USA 1 December 1967; accepted for publication 8 December 1967)

Abstract—Conformations and configurations were assigned to several N-Me imines and N-alkyl acetaldimines from analyses of their 60-Mc NMR spectra. All aldimines exist exclusively in the syn configuration. Interpretation of the vicinal and long-range (across 4 and 5 bonds) spin—spin coupling constants of N-Me aldimines led to the conclusion that I and II are the minimum energy conformations of these compounds. The  $\Delta H^\circ$  values for I  $\rightleftharpoons$  II fall between those of aldehydes, which are usually negative, and those of oximes and their O-methyl ethers, which are positive. Interpretation of the long-range (across 4 and 5 bonds) spin—spin coupling constants of N-alkyl acetaldimines led to the conclusion that III is far more stable than IV.

The greater thermodynamic stabilities of the syn over the anti isomers of aldimines and III over IV have been explained in terms of nonbonded interactions across the C=N double bond. The results of some of these calculations are given.

ONE of the problems that we have investigated and commented on in recent publications<sup>2-6</sup> has been the effect of Z on the relative stabilities of rotamers I and II.



Thus, when Z is  $OMe^2$  or OH,  $^4 \Delta H^\circ$  for I  $\rightleftharpoons$  II is more positive than when Z is amino,  $^5$  N-methylamino,  $^6$  or N-methylanilino.  $^3$  To probe further into the relationship between  $\Delta H^\circ$  and Z, we have investigated the case where Z is an alkyl group, i.e. an appreciably less electronegative group than in the previously examined cases. The decision to study these compounds was further dictated by the expectation that N-alkyl imines will also be suitable models to study the conformational isomerism about the C---N single bond in terms of the relative stabilities of III and IV. Such information is presently unavailable.



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#### RESULTS

Chemical shifts. In Table 1 are summarized the chemical shifts and the syn/anti ratios of several representative N-Me imines. The notation used to distinguish the various protons is shown in V. Each proton is referred to as cis or trans with respect



to the N-Me group. The syn isomers of the aldimines are those having H<sub>1</sub> cis to the N-Me group; and of the ketimines, those having the  $\alpha$ -Me cis to it. Most chemical shifts are accurate to  $\pm 0.03$  ppm. Exceptions are those of  $\alpha$ -methine protons and of  $\alpha$ -methylene protons of Et groups; the reported values are the centers of multiplets. The syn/anti ratios of the ketimines were calculated from integrations of the  $\alpha$ -Me signals and are accurate to  $\pm 5\%$ .

All N-Me aldimines and N-alkyl acetaldimines that we examined existed exclusively in the syn configuration. Neither heat, nor treatment of the aldimines with acid or dimsyl sodium gave any detectable amount of the *anti* isomer. These results agree with the findings of other investigators.<sup>7-9</sup> The *anti* isomers of the anils of benzaldehyde have been detected after irradiation<sup>10, 11</sup> at  $-100^{\circ}$ , or flash photolysis<sup>12-14</sup> at 30°, of the corresponding syn isomers. The *anti* isomers, which rapidly collapsed to the syn isomers (half-lives of approximately 0.5 sec at 30°), were identified by UV spectroscopy. The detection of both isomers of N-Me ketimines is consonant with the findings of other investigators with the anils of aliphatic ketones<sup>7</sup> and benzophenones,<sup>7, 15</sup> with the N-alkyl imines of benzophenones,<sup>7, 15-19</sup> and with some double ketimines.<sup>8, 9</sup>

In Table 2 are summarized several  $\Delta v$  ( $v_{in C_6H_6} - v_{in CCL_4}$ ) values. A positive  $\Delta v$  means that resonance occurs at a higher field in benzene than in carbon tetrachloride; a negative the reverse. It is worth noting that the  $\Delta v$  values for *cis* protons are considerably more positive than those of the corresponding *trans*.

Spin-spin coupling. The temperature dependence of the vicinal spin-spin coupling constants,  $J_{H_1H_e}$ , whose accuracy is about  $\pm 0.03$ , of N-Me aldimines is shown in Table 3. One feature of the data is pertinent to subsequent discussion: Most  $J_{H_1H_e}$  decrease with increasing temperature, except (a) those of the N-Me imines of acetaldehyde, n-butyraldehyde, n-heptaldehyde, t-butylacetaldehyde and cyclohexane-carboxaldehyde which are temperature independent and (b) that of N-Me propionaldimine which increases with increasing temperature.

In Table 4 are listed the long-range spin-spin coupling constants between N-Me and  $H_1$  (4-bond coupling) and between N-Me and *trans*  $H_{\alpha}$  (5-bond coupling). Whereas the 4-bond coupling is independent of temperature and of the structure of substrate, the 5-bond coupling exhibits trends inverse to those of the vicinal coupling, i.e. it decreases whenever the 3-bond vicinal coupling increases. The 1-60 c/s value of the 4-bond coupling is the same as the 1-61 c/s value determined for  $J_{H_1CH_3}$  of N-Me formaldimine<sup>20</sup> (VI). From the published spectrum of N-Me formaldimine and the resolution observed in the  $H_1$  signals of the aldimines that we have investigated, the assignment<sup>20</sup> of the low field signal to  $H_1$  and of the high field signal to  $H_2$  is correct. Those assignments were based on the relative broadness of the signals.<sup>20</sup>

RıR	C=NCH		H,	¤(CH)	¤(C	H <sub>2</sub> )	a(CF	(,1	<b>B</b> (C	( <sup>8</sup> H	NCH <sub>3</sub>	syn°/anti
R,	R2	Solvent <sup>b</sup>	cis	trans	cis	trans	cis	trans	cis	trans		
н	Ā	CCI.	2.44					8.19			6.83	100/0
: =	M		2.7.2					8.34			96-9	100/0
: 1	E	Ncat	2.35			7.83				8-97	6-80	100/0
: 1	ίŭ	5	2.35			7.80				8.96	6-82	100/0
: #	រដ	C.H.				16-L				9:04	6.88	100/0
Ħ	Neopentvl	cci,	2.44			7-94					6.84	100/0
H	Neopentyl	CD	2.55			7-93					6-87	100/0
H	-F		2.52	7.65						8-97	6.84	100/0
H	- H	C.H.	·	7-80						9-03	6.89	100/0
H	3-Pentvl		2.47	8-024							6-75	100/0
H	sec-Bu	CC	2.58	7.87						<b>66</b> -8	6.83	100/0
Н	sec-Bu	C,D,	2·73	7-80						9-03	6.86	100/0
	C											
Н	$\sim$	ca.	2-57								6.83	100/0
	)(											9 9 9
Н	$\sim$	C,H,	v								6-87	0/001
Å	) <mark>,</mark>	Neat					8·22	8·10			7-06	
Me	Me	CCI					8·23	8·10			7-05	
Ň	Me	C.H.					8-64	8-07			7-05	
Me	E	CCI			7-83	7.83	8·27	8·13	<del>0</del> 06	<b>00</b> 6	7-03	86/14
Me	ដ	C,H,			8-06	16.7	8-66	8·14	9-24	8:9 <b>4</b>	10-2	86/14
Me		ççî,		7-62			8·29	8·18	10-6	10-6	7-02	96/4
Me	4	C.H.		7-70			8-64	8·19	9-17	8-97	7-07	96/4
Me	t-Bu	CC CC					8-26			8·99	7-00	100/0
Mc	t-Bu	C,H,					8-55			<b>06</b> .8	7-00	100/0
ш	ы	G			67-T	61·1			<b>0</b> 06	90 <u>6</u>	6·9	
Ē	H	C,H,			8.11	7-98			9-24	00-6	6-94	
sur is the i	isomer having R. c	is to the N-meth	vl group.	• 5% (V/V	) solns.	Solvent ir	iterference.	, Cente	r of multipl			
			•									

TABLE 1. CHEMICAL SHIFTS (T-VALUES) OF N-ME IMINES AND Sym<sup>2</sup>/anti ratios

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$\Delta v(B-CH_3)$ $\Delta v$	cis trans NCH3		9.C - P:3.H	0.74 <b>*</b> 04 <b>3.</b> 14		/7+ 9€+	13.7 13.7		227 214 bC4			+14-5			-2.9 +0.3	+15.5 _4.6 ±0.1
(гн	trans	+11.0	-								+ 4-4	+0.7		<b>7 1</b>		
-Ωλ(α-(	cis										+25.8	+23.4	+ 20-0		7./1+	
-CH <sub>1</sub> )	trans		+ 10-8	+ 8.4	+ 1-9	- 0-5						+2:7				+ 7-5
Δ <b>ψ</b> (α-	cis											+ 15-5				+ 19.6
Δψα-CH)	trans						+ 9.4	+0-2	+1·2	-0-5			+4.6			
<b>Δ</b> <sub>1</sub> (H <sub>1</sub> )	cis	+ 19-0		8.8 +		+ 6.7		+ 8.7	0-6 +	+ 12.6						
c=ncH₃	R2	Me	Et	n-Pr	i-Bu	Neopentyl	-1	CHEt <sub>2</sub>	sec-Bu	5-Etyl-pentyl	Mc	ŭ	- <b>-</b>	t. Bu		되
R , R 2(	R.	Н	Н	H	H	н	н	Н	Н	Н	Me	Mc	Mc	٩M		ជ

Table 2.  $v_{ia}\,c_{a}u_{a}^{--}v_{ia}\,cci_{a}\,(\Delta\nu)^{*}$  in c/s of N-Methyl imines

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• Positive values mean that resonance in benzene is at higher field; negative the reverse.

Hı	СН,					
$\rangle$	= N			$J_{H_1H_{\mathfrak{C}}}(c/s)$		
R <sub>1</sub> R <sub>2</sub> CH	_			• • •		
R <sub>1</sub>	R <sub>2</sub>	- 30°	05	+ 36°	+ 50°	+ 70°
н	н	4.78 (4.76)*	<b>4</b> ·78	4·76*		
н	Мс	3.09"	4·04*	4-07		
н	Et	4.28	4.30	4.32	4.28	4-31
н	n-Pentyl	4·23		4.29	4·28	4.28
н	i-Pr	4-62	4-58	4.52	4.53	4-46
н	t-Bu	5.46*	5-44*	5-48*	5·45*	5·44 <sup>6</sup>
Ме	Mc	<b>4</b> ·11		4-05	4-04	
Me	Et	<b>4</b> ·78	4.71	4.62	4.53	<b>4</b> ·52
Me	n-Pr	5-00	4.88	4.86	4·77	4.64
Et	Et	5-42		5.20	5.00	4 <del>.9</del> 6
Et	n-Bu	5.60	5.50	5-34	5.26	5·17 (5 <b>·</b> 04) <sup>∉</sup>
	$\rangle$	3.82	3.76	3.86	3.86	

TABLE 3. VICINAL SPIN-SPIN COUPLING CONSTANTS OF NEAT LIQUID N-Me ALDIMINES

Value at −15°.

5% soln (V/V) in CCl<sub>4</sub>.

• Values at +15°.

<sup>4</sup> Value at +90°.



In Table 5 is shown the effect of solvent polarity on the vicinal and long-range coupling constants. The pertinent observations are: (a) The 4-bond couplings,  $J_{H_1CH_2}$ , are independent of the polarity of solvent. (b) Most vicinal couplings are larger by about 10-20% in acetonitrile than in cyclohexane; those of N-Me acetaldimine and t-butylacetaldimine are larger only by about 2-3%. (c) The 5-bond couplings again exhibit trends opposite to those of the vicinal couplings.

In Table 6 are listed the long-range 5-bond couplings,  $J_{H_n-CH_3}$ , of the N-Me ketimines. The *trans* couplings are similar to the *trans* couplings of the aldimines. All the *cis* couplings involve a *cis* Me group and are, as expected, constant (about 0.79 c/s).

In order to assess the relative stabilities of III and IV we have studied the long-range coupling constants of N-alkyl acetaldimines. The data are summarized in Table 7. Both the 4-bond coupling,  $J_{H_1 \dots H_N}$ , and the 5-bond coupling,  $J_{CH_3 \dots H_N}$ , are sensitive to substitution on the N-alkyl group. They are all smaller than those of the N-Me acetaldimine ( $H_{H_1H_N} = 1.60 \text{ c/s}$  and  $J_{CH_3 \dots H_N} = 1.42 \text{ c/s}$ ), they behave irregularly with temperature, and are very small when the N-alkyl group is alkyl disubstituted ( $R_2CH$ —). In all cases the vicinal coupling,  $J_{H_1H_N}$ , is constant and has a value of about 4.74 c/s.

		+ 70°			1-28	1-17	-0 <b>4</b> -		1·15		0-77	0-87	
		+ 50°			1·26	1.18	1-02	1-23	1-05	1-01	0-76	0-74	1-23
	J <sub>Нс</sub> сн <sub>3</sub> (c/s)	+36°	1-43*	1-47	1-26	1.15	1-04	1-24	1-06	10-1	0-74	0-70	1.16
		°0			1-26	1-22	1-03	1·23	101	94	0-71	0-62	1.16
		– 30°			1-31	1-17	<b>-6</b> 6-0	1-23	0-95	0.89	0.66		
		+ 70°			1-55	1·58			1·59		1.59	1·59	
		+ 50°			1-60	1-58		1-59	1-59	1-59	1-60	1·60	1:57
	J <sub>Н1-СН3</sub> (с/s)	+36°	-99-1	1-60	1-57	1.58	1-62*	1-58	1.58	1-59	1-57	1-57	1-60
		°0		99 99	1-58	1-59	1·58°	1-57	1-60	1.60	1.58	1·58	1.57
		- 30°		1-60	1-55	1.55	1-65	1·59	1-61	1-55	1·55	1·55	
CH,		R,	н	Mc	Ēt	i-Pr	t-Bu	Mc	ы Ш	<u>-</u> Р	Ē	n-Bu	•
л н	R₁R₂CΉ <b>.</b>	R,	H	н	Н	Н	н	Mc	Me	Me	ш	۵ ۵	$\bigcirc$

TABLE 4. LONG-RANGE SPIN-SPIN COUPLING CONSTANTS OF NEAT LIQUID N-METHYL ALDIMINES

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5% soln (V/V) in CCl4.

H <sub>1</sub>	CH	l,	cyclohexane <sup>s</sup>			acetonitrile <sup>b</sup>	
$R_1R_2CH_{e}$ $R_1$	R <sub>2</sub>	J <sub>H1He</sub>	J <sub>не—сн</sub> ,	J <sub>н1</sub> сн <sub>3</sub>	$J_{\rm H_1H_R}$	J <sub>Не—СН</sub> ,	J <sub>н1—СН3</sub>
н	н	4.71	1.42	1.60	4.78	1.38	1.60
н	Et	4-09	1.29	1.60	4.57	1.27	1.57
н	t-Bu	5.45	0.94	1.60	5.61	1.03	1.60
Me	Et	4.56	1-01	1.58	4.88	0.91	1.62
Et	Et	5.10	0.70	1.59	5.57	0-60	1.60
Et	n-Bu	5.24	0.74	1.58	5·79	0.65	1.61
$\langle$	$\rangle$	3.18	1.19	1.62	4-06	1.08	1.57

TABLE 5. EFFECT OF SOLVENT POLARITY ON THE COUPLING CONSTANTS<sup>4</sup> OF N-METHYL ALDIMINES

" Values at 36° and in c/s.

\* 5-10% solns (V/V).

	CH,				
$R_1R_2CH_{\mu}$ –	└└─ CH <sub>a</sub> R ₃	R4			
trans	cıs			J <sub>Ha</sub> _C	н, (c/s) <sup>#</sup>
Ri	R 2	R 3	R <sub>4</sub>	cis	trans
н	н	н	н	0.79	1.33
н	Мс	н	Н	0.77	1.32
н	н	н	Me		1.35
Me	Me	н	н	0.79	0-82
н	н	Me	Me		1.29
R <sub>1</sub> R <sub>2</sub> C	$H_{a} = t - Bu$	н	н	0.77	

TABLE 6. LONG-RANGE SPIN-SPIN COUPLING CONSTANTS OF NEAT LIQUID N-METHYL KETIMINES

<sup>4</sup> Values were determined in the temperature range  $-15^{\circ}$  to  $+90^{\circ}$ . Within this temperature range they all remained constant to  $\pm 0.03$  c/s.

#### DISCUSSION

Conformations of aldimines along the carbon  $(sp)^3$ -carbon $(sp^2)$  bond. The vicinal coupling data (Table 3) are consonant with the idea that the minimum energy conformations of the syn isomers along the C  $(sp^3)$ -C $(sp^2)$  bond are eclipsing (I and II). From the reasonable assumption that  $J_t > J_g$ , where  $J_t$  is the trans coupling and  $J_g$  the gauche, the vicinal coupling  $J_{H_1H_g}$  of monosubstituted acetaldehyde derivatives should be temperature independent if VIIa, VIIb and VIII are energetically equivalent. If VIIa is more stable than VIII, the coupling should decrease with increase in tem-

	+ 110°							1.15	(1-09)					
	μ (c/s) + 90°					1.11		1.13						
	, сн <i>у</i> -н + 70°				1.10	1.10	1.12	1-19						
	+ 40°	1.42	1-08 <b>0</b>	1·10	1.12	1.10	1.13	1.15		< 0.4	<0.4	< 0.4		
	+ 110°							1-40	(1·39) <sup>c</sup>			0.73		
(v) (v)	(1/2) + 90°					1·36		1-34				0.73	I	Values at 140°
-	+ 70°				1-42	1.38	1-38	1-42			0:50	0.70		s at 20°. '
	+40°	1.60	1-35 <sup>b</sup>	1·36	1·39	1.36	1-40	1·39		0-59	0.56	0-52		Value
CH <sub>N</sub> R <sub>1</sub> R <sub>2</sub>	R,	Н	Mc	Ē	n-Pr	n-Bu	i-Pr	Рћ		Me	Et	$\frown$		(V/V) in CCl.
H, H,	R	Н	н	H	Н	Н	Н	н		Me	E	$\smile$		" 10% solt

TABLE 7. LONG-RANGE SPIN-SPIN COUPLING CONSTANTS OF NEAT LIQUID N-ALKYL ACETALDIMINES

Values at 20°. 10% soln (V/V) in CCI. perature; and if less stable, it should increase. Similarly, for the disubstituted acetaldehyde derivatives the coupling should be temperature independent if IX, Xa and Xb are energetically equivalent. If IX is more stable than Xa, the coupling should decrease with increase in temperature; and if less stable, it should increase. From the data



listed in Table 3 we conclude: (a) For the N-Me imines of monosubstituted acetaldehydes, when R is Me, VIII is more stable than VIIa; when R is Et or n-amyl, VIIa, and VIII are energetically equivalent; and, when R is isopropyl or t-butyl, VIIa



is more stable than VIII. (b) For the N-Me imines of disubstituted acetaldehydes, when  $R_1$  and  $R_2$  are the methylene groups of the cyclohexyl ring, IX and Xa are energetically equivalent; and, when  $R_1$  and  $R_2$  are Me or larger groups, IX is more stable than Xa.

The method of calculating rotamer populations and enthalpy differences,  $\Delta H^{\circ}$ , has been previously discussed.<sup>2, 21</sup> From Eqs (1) and (2), which

$$J_{\text{obs}} = \frac{1}{3}(J_t + 2J_g) \tag{1}$$

$$J_{obs} + 0.4 = \frac{1}{2}(J_r + J_g)$$
(2)

express the average coupling constants of N-Me acetaldimine and N-Me t-butylacetaldime, respectively, the values of  $J_t$  and  $J_g$  needed to calculate rotamer populations can be obtained; they are  $J_t = 9.65$  c/s and  $J_g = 2.35$  c/s. The term 0.4 c/s in Eq. (2) is the alkyl correction factor<sup>21</sup> for monosubstituted derivatives; for disubstituted derivatives it is 0.8 c/s. The present results (Table 3) demonstrate again the general applicability of these factors. For example, in the three cases where Eq. (1) applies, i.e. where the coupling constants are independent of temperature, N-Me acetaldimine, N-Me butyraldimine and heptaldimine, and N-Me cyclohexanecarboxaldimine, the coupling constants are about 4.76, 4.30 and 3.88 c/s, respectively. Furthermore, a plot of temperature vs the vicinal coupling constants of monosubstituted acetaldimines—except that of t-butylacetaldimine which exists primarily in conformation VII—shows convergence towards a value of about 4.3 c/s.

Rotamer populations can be now calculated from Eqs (3) and (4),

$$J_{obs} = p(J_t + J_g)/2 + (1 - p)J_g$$
(3)

$$J_{\text{obs}} = pJ_t + (1-p)J_g \tag{4}$$

which apply to monosubstituted and disubstituted N-Me acetaldimines, respectively, and where p is the fractional population of VII and of IX and (1 - p) that of VIII and of X. In Table 8 is shown the effect that the polarity of the solvent produces on the populations of a few N-Me aldimines. This effect, as well as the related increase of the vicinal  $J_{H_1H_{\alpha}}$  couplings (Table 5) in going from cyclohexane to acetonitrile, can be explained—as was done with the aldehydes<sup>21</sup>—in terms of XI and XII. The ratio



XI/XII will be larger in the more polar solvent acetonitrile than in the less polar solvent cyclohexane. Since  $J_t > J_g$ , the observed vicinal coupling constants will also be larger in acetonitrile than in cyclohexane.

		۲ ا	CH <sub>3</sub>	
R₁R₂CHO	CH=NCH	$R_1 R_1$	Н	
D	R,	cyclohexane	ncat	acetonitrile
R <sub>1</sub>	•			
 Н	Et	63	65	72
H Me	Et Et	63 41	65 42	72 48
H Me Et	Et Et Et	63 41 49	65 42 50	72 48 55
H Me Et Et	Et Et Et n-Bu	63 41 49 51	65 42 50 52	72 48 55 58

" Values at 36°.

In Table 9 are listed the enthalpy differences,  $\Delta H^{\circ}$ , which were calculated from reasonably linear plots of log K vs. 1/T. The equilibrium constants for monosubstituted and disubstituted acetaldimines were calculated from Eqs (5) and (6), respectively.

$$K_{eq}(\text{mono}) = 2(1 - p)/p$$
 (5)

$$K_{eq}(di) - (1 - p)/2p$$
 (6)

The  $\Delta H^{\circ}$  values are considerably less positive than those of hydrazones,<sup>5</sup> N-substituted hydrazones,<sup>3,6</sup> oximes<sup>4</sup> and oxime O-Me ethers.<sup>2</sup> In fact, they fall between those of the aldehydes<sup>21</sup> and those of the above mentioned compounds. N-Me propionaldimine is the only compound of the type  $R_1R_2C=NZ$  where rotamer II





is favored (enthalpy-wise) over rotamer I. From the  $\Delta H^{\circ}$  values of N-Me propionaldimine (-200 cal/mole), propionaldehyde hydrazone and N-substituted hydrazones (+100 to +400), and propionaldoxime and its O-Me ether (+400 to +500), it appears that  $\Delta H^{\circ}$  becomes more positive as the electronegativity of Z increases. Nonbonded interactions, therefore, between the Me group and the lone electron pair on the nitrogen are apparently ruled out as the main factor controlling the relative stabilities of the two rotamers, unless these nonbonded interactions are strongly



dependent on the polarizabilities of the lone electron pairs, or unless the structures of the molecules differ substantially.

In Table 10 are summarized the  $H_1$  chemical shifts and the vicinal spin-spin coupling constants,  $J_{H_1H_2}$ , of aldimines in 5% solutions in acetonitrile before and after addition of trifluoroacetic acid. These spectra displayed no four-bond coupling<sup>22</sup> and showed new peaks that gradually increased in size at the expense of the aldimine peaks, until the spectra of the aldimines eventually disappeared. Attempts to take the spectrum of the N-Me acetaldimine failed, as the reaction between trifluoroacetic acid and aldimine was too fast. While the spectra of N-t-octyl acetaldimine in 5% solutions to which trifluoroacetic acid had been added were unsatisfactory, reproducible spectra, which disappeared within five to ten minutes after acid addition, were

		acetonitrile	:	aceton	itrile + CF	,CO2H
Aldimine	$\dot{\delta_{H_1}}$	$\delta_{\rm NCH_3}$	$J_{H_1H_2}$	$\delta_{H_1}$	$\delta_{\rm NCH_3}$	$J_{H_1H_0}$
$CH_3CH = N - t - C_8H_{17}$	2.54		4.72	2.53		4·78
$CH_3(CH_2)_2CH = NCH_3$	2.35	6.82	4.57	2.48	6.91	4.67
(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> CH=NCH <sub>3</sub>	2.45	6.81	5.61	2.24	6.90	5.68
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> CHCH=NCH <sub>3</sub>	2.53	6.78	5.79	2.30	6.72	7-04
(CH <sub>3</sub> CH <sub>2</sub> )CH <sub>3</sub> CHCH=NCH <sub>3</sub>	2.47	6.83	5.02	2.28	6·79	6.06

Table 10. Chemical shifts (t-values) and vicinal coupling constants,  $J_{HH^*}$  (c/s) of aldimines<sup>4</sup> in acetonitrile and acetonitrile + trifluoroacetic acid

" All values at 36°.

obtained in 20% solutions. The salient features of the data are: (a) The coupling constants of N-t-octyl acetaldimine, which exists in a single conformation, and N-Me t-butylacetaldimine, which exists primarily in conformation VII, increase only slightly on protonation. (b) The coupling constants of the other compounds increase more. Increase of the coupling constants means increase of the ratio 1/11. On protonation of the lone electron pair, therefore,  $\Delta H^{\circ}$  becomes more positive. We attribute this change, as we did in oximes,<sup>4</sup> hydrazones<sup>5</sup> and N-methylhydrazones,<sup>6</sup> to increased nonbonded repulsions between alkyl and hydrogen over alkyl and lone electron pair.

Long-range coupling and conformations about the carbon( $sp^3$ )-nitrogen ( $sp^2$ ) bond. From the now available knowledge of the populations of the various rotamers about the C( $sp^2$ )-C( $sp^3$ ) bond and the data listed in Table 4, it is possible to elucidate the stereo-dependence of the 5-bond coupling,  $J_{H_aCH_3}$ . Analogous treatment of the data (Table 4) of the 5-bond coupling to that used to calculate the vicinal  $J_t$  and  $J_g$  values



leads to 2.1 c/s and 0.2 c/s for  $J_{H_a-NCH_3}$  and  $J_{H_b-NCH_3}$  (XVI), respectively. It is worth noting that, whereas  $|J_{H_a-NCH_3}|$  is greater than  $|J_{H_b-NCH_3}|$ ,  $|J_{H_a-H_1}|$  is smaller than  $|J_{H_bH_1}|$ .

The data on the long-range 4-bond and 5-bond couplings of N-alkyl acetaldimines (Table 7) can be treated so as to provide useful information about the relative stabilities of rotamers III and IV. It has been established,<sup>23, 24</sup> that the four bond allylic coupling  $|J_{H_nH}|$  is greater than  $|J_{H_nH}|$  (XVII). By analogy,  $|J_{H_nH}|$  of XVIII should be greater than



 $|J_{H_bH}|$ . From this reasonable assumption and the data listed in Table 7, we can readily conclude that rotamer XIX is far more stable than rotamer XX. We can also conclude



that the 5-bond coupling  $|J_{H_n-CH_3}|$  is greater than  $|J_{H_b-CH_3}|$  (XXI). Their values appear to be similar with those of the other 5-bond couplings (XVI). From these we further conclude that  $|J_{H_nH_n}|$  (XXII) is greater than  $|J_{H_bH_b}|$  (XXII).



From the preceding discussion the conclusion can be drawn that the ratio XIX/XX is appreciably greater than the analogous ratio XXIV/XXV of the corresponding alkenes.<sup>23</sup> This difference is best rationalized in terms of greater nonbonded repulsions



between R and H in XX than in XXV, on account of the C=N bond being shorter than the C=C bond. By use of the nonbonded potential functions given by Bartell,<sup>25</sup> the 1,6-hydrogen-hydrogen nonbounded interaction energy in XXVI is about +3.5



Kcal/mole when X is nitrogen and +1 Kcal/mole when X is carbon. The difference in this interaction energy increases rapidly on rotation of the methyl group about the C-C bond and reaches a maximum when H<sub>6</sub> is in the plane of the molecule.<sup>26</sup> Configurational isomerism. As pointed out, the syn/anti ratios observed in this investigation agree well with those observed by previous investigators.<sup>7-9, 15, 16</sup> Of particular interest is the observation that, whereas  $\Delta G^{\circ}$  for 7 is greater than +2.2 Kcal/mole,  $\Delta G^{\circ}$  for the analogous isomerization 8 is less than +1.0 Kcal/mole.<sup>27</sup>

From the relative stabilities of I and II of the aldimines and the 1-alkenes, the reasonable conclusion may be drawn that the Me-lone electron pair nonbonded interactions in the *trans* isomer of the imine are less repulsive than the Me-proton interactions in the *trans* isomer of 2-butene. This effect would make  $\Delta G^{\circ}$  for 7 more positive than  $\Delta G^{\circ}$  for 8. A second source leading to the same effect would be the more repulsive Me-Me nonbonded interactions in the *cis* isomer of the imine than in that of 2-butene, on account of the C=N bond being shorter than the C=C bond. To test this effect we have calculated<sup>25</sup> the nonbounded interaction energies between the Me-Me protons and summarized the results in Table 11. The structures of propene<sup>28</sup> and N-Me formaldimine<sup>29</sup> were used as models for the structures of 2-butene and N-Me acetaldimine.<sup>26</sup>

As structures 4 and 5, rather than 1 and 2 in which the 1,3-proton-proton eclipsing interactions have not been taken into account, probably represent the minimum energy conformations of the compounds, it is clear from the data that the nonbonded interactions in the *cis*-N-Me acetaldimine are more repulsive than those in the *cis*-2-butene by about 1.4 Kcal/mole.

Interpretation of solvent effects. The considerably larger upfield shift of the resonances of the *cis* protons over those of the corresponding *trans* (Table 2) on dilution with benzene suggests specific orientation of benzene by interaction with the solute. The data are adequately accommodated in terms of XXVII, whereby the benzene is



attracted by the partial positive charge on the sp<sup>2</sup>-hybridized carbon and is closer to the *cis* group  $R_1$  than to the *trans* group  $R_2$  on account of repulsion between the  $\pi$ -electrons of benzene and the lone electron pair on the nitrogen.<sup>30</sup>

No.	Structure	$r_{\mathrm{H_1H_6}}(\mathrm{\AA})$	E(Kcal/mole)
1	H, H, H, H,	2.884	– 0•03/H₁ ↔ H <sub>6</sub>
2	H H <sub>1</sub> H <sub>1</sub> H <sub>6</sub> H <sub>6</sub>	3-151	–0•03/H₁ ↔ H <sub>6</sub>
3		2-068	+08/H₁↔H <sub>6</sub>
4	H, H, H, H, H,	2052	$+0.8/H_1 \leftrightarrow H_6$
5	H H <sub>1</sub> H <sub>1</sub> H <sub>6</sub> H	2.400	+0·09/H₁↔H <sub>6</sub>
6	H. H. H. H. H.	1.405	+ 14•0/H 1 ↔ H6
7	H, H, H, H	1.799	+ 2·6/H <sub>1</sub> ↔ H <sub>6</sub>

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 TABLE 11. 1,6-PROTON – PROTON NONBONDED INTERACTION ENERGIES, E,

 POR cis-N-METHYL ACETALDIMINE AND cis-2-BUTENE

#### EXPERIMENTAL

Preparation of imines. The various N-alkyl imines were prepared according to established procedures. <sup>31-35</sup> The following is a typical example. To approximately 2 g (0.06 mole) MeNH<sub>2</sub> maintained at  $-30^{\circ}$ , was added dropwise with stirring 2.33 g (0.02 mole) cyclohexanecarboxaldehyde. The mixture was warmed to  $0^{\circ}$  and to it was added approximately 3 g KOH. After gas evolution ceased, the organic liquid was decanted into a bottle containing molecular sieves, type 4-a, and left overnight. The aldimine was suitable for use without further purification. In most cases the imines were purified by distillation under reduced press or by VPC with a Perkin-Elmer Vapor Fractometer equipped with a 9 ft 20 % SF-30 Silicon preparative column.

NMR spectra were determined at 60-Mc. on a Model A-60 spectrometer (Varian Associates, Palo Alto, Calif.). Undegassed solns were used with TMS as internal reference.

Acknowledgement—We thank the Petroleum Research Fund, administered by the American Chemical Society, for partial financial support (2722-A1,4).

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