STRUCTURAL STUDIES BY NUCLEAR MAGNETIC RESONANCE—XIX

N,N-DIMETHYLHYDRAZONES¹ AND GENERAL COMMENTS ON CONFIGURATIONAL AND CONFORMATIONAL ISOMERISM

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Abstract—Configurations and conformations were assigned to several aldehyde and ketone N,Ndimethylhydrazones from analyses of their 60-Mc NMR spectra. Aldehyde, but not ketone, N,Ndimethylhydrazones exist exclusively in the *syn* configuration. Interpretation of the vicinal spin-spin coupling constants, $J_{H_1H_n}$, led to the conclusion that II and III are the minimum energy conformations of these compounds. The ΔH^0 values for II = III were found to be more positive than those of N-Me imines (Z = Me) but less positive than those of oximes (Z = OH) and their O-methyl ethers (Z = Me).

General comments are made on several aspects of configurational and conformational isomerism about single, double and partial double bonds, and on the usefulness and limitations of NMR in studying various problems associated with such isomerism.

IN RECENT years we have investigated by NMR spectroscopy and commented¹ on various problems arising from restricted rotation about single, double and partial double bonds. Of particular interest have been the questions of configurational isomerism about the C—N double bond of system I, the relative stabilities of rotamers II and III, the conformational preferences of group Z, the anisotropic



effects of the C—N double bond and the association between I and various solvents. In this paper we wish to present results from our NMR studies of N,N-dimethylhydrazones ($Z = NMe_2$) that are relevant to these problems. We will also take the opportunity to summarize our conclusions on these problems and to make some general comments on the uses and limitations of NMR in this particular area of research.

RESULTS

In Table 1 are summarized the chemical shifts, whose accuracy is about ± 0.03 ppm, and the syn/anti ratios of a few representative N,N-dimethylhydrazones. The

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R1R2	C=NN(CH ₃) ₂			111)5		ſ	· · ·	<i>.</i> .			
Ŗ	R,	Solvent ^a	cis	trans	trans	cis	trans	cis	trans		
н	Me	Neat	3-47				8-20			7-38	100/0
Н	Me	CCI	3-51				8.17			7-36	100/0
H	Me	C,H,	3.66				8·20			7-48	100/0
Ŧ	Et	Ncat	3:48		7-83				10-6	7.37	100/0
т	Ē	cci	3-53		7-87				8-98	7.36	100/0
Ŧ	Ē	C ₆ H	3-60		7-88				10-6	7:46	100/0
T	Neopentyl	Ncat	3-46		7-94					7.35	100/0
Ŧ	Neopentyl	cci ,	3-50		7-95					7:34	100/0
m	Neopentyl	C,H	3.50		7-84					7:45	100/0
	i-Pr	Ncat	3-57	7-67					6 6 -8	7-38	100/0
Ŧ	i-Pr	ca	3-64	7-64					8-97	7-37	100/0
T	i-Pr	C,H,	3.64	7-67					8-96	7:46	100/0
Ŧ	3-Pentyl	Neat	3.69	19-T						7.35	100/0
т	3-Pentyl	с СО	3-71	7-93						7-35	100/0
	3-Pentyl	C,H	3-75	7.88						7-46	100/0
Ŧ	\bigcirc	Ncat	3-64							7.39	100/0
-	\bigcirc	CCI,	3.66							7.38	100/0
Ŧ	\bigcirc	C,H,	3.64							7-46	100/0
ĥ	Me	Ncat				60- 8	8.16			7-67	
Чc	Mc	ប្ដី				8·12	8·16			7-67	
٨	Mc	C,H,				8·28	8·28			7.61	
٨e	Ē	Neat			7.87	8-14	8·20		66-8	7-69	82/18
Ř	Et	លី			7-86	8·14	8.17		8-96	7.69	82/184
Mc	Et	C,H,			7-94	8·25	8·28	9.16	9-02	7-60	82/18
Ϋ́	j-Pr	Ncat		7-63		8-17	8·27	9-04 20-04	66-8	7-69	93/74
Me	i-Pr	CCI.		7.61 7-61		8.18	8-27	10-6	8.97	7-69	p1/26
Me	i-Pr	C,H,		7-62		8-25	8.31	9.16	00-6	7-60	93/7

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protons.

¢ cis proton.

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	N(CH ₃) ₂	+ 7:2	+ -	+ 5.4 + 6.6	+ 4.8	- 3-6	- 5.4	- 5-4
сН ₃)	trans	+ - 8	-	- 0-0			+ 3-6	+1.8
₿(C	cis						+ 12-0	0-6+
H ₃)	(rans	+ 1.8				+ 7·2	+ 6·6	+ 2.4
a(C)	cis					+ 9.6	+ 6.6	+4·2
α(CH ₂)	trans	¥	- 0 .0				+4.8	
a(CH)	trans		-	+ 1.8 30				9 0+
Ч	cis	+ 9-0 + 4-2	8	0-0 + 2:4	- 1·2			
=NN(CH ₃) ₂	R2	Me Et	Neopentyl	3-Pentyl	\bigcirc	Mc	ы	i-Pr
RIRIC	R,	н	HB	L H	Н	Me	Me	Me

Table 2. $v_{in\,C_{a}H_a} - v_{in\,CCI_a} (\Delta v)^a$ in c/s of N,N-dimethylhydrazones

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

notation used to distinguish the various protons is shown in IV. Each proton is referred to or *cis* or *trans* with respect to the N,N-dimethylamino group.



As in N-methylphenylhydrazones³ ($Z = NCH_3C_6H_5$)—but not in hydrazones,⁴ N-methylhydrazones,⁵ phenylhydrazones,⁶ ring substituted phenylhydrazones,⁷⁻⁹ semicarbazones^{8.9} and thiosemicarbazones⁸—aldehyde N,N-dimethylhydrazones exist only in the *syn* configuration (H_1 *cis* to N,N-dimethylamino group). Neither heat nor treatment with acid gave evidence for the presence of the *anti* isomer. In contrast, the ketone derivatives exist in both the *syn* and the *anti* configurations. The presence, therefore, of at least one hydrogen on the amino nitrogen is a necessary condition for the *anti* isomers of the aldehydes to be sufficiently stable with respect to the *syn* so as to be detectable by NMR.

In sharp contrast to all our previous findings,²⁻¹³ the α -Me protons resonate at lower, rather than higher, magnetic fields when *cis* than when *trans* to $Z(Z = NMe_2)$. Furthermore, the *cis* α -methine proton resonates lower than the corresponding *trans* by about 1.4 ppm, rather than by the usually observed values of 0.5 to 0.8 ppm.

In Table 2 are summarized several $\Delta v(v_{in CCl_4}-v_{in CCl_4})$ values. Two features of the data are pertinent to subsequent discussion: (a) Benzene shifts the resonances of *cis* protons to higher fields than does those of the corresponding *trans*. In the case of acetone N,N-dimethylhydrazone the two signals coalesce and eventually cross over when the concentration of the hydrazone in benzene becomes less than 10%. (b) Whereas the resonances of the N,N-dimethylamino protons of the aldehyde derivatives are shifted upfield by benzene, those of the corresponding protons of the ketone derivatives are shifted downfield. The same effect was observed with N-methyl-hydrazones.

The representative UV spectra in Table 3 show additional differences between the

R ₁	R ₂	Solvent	λ _{max} (mμ)	$\varepsilon \times 10^{-1}$
н	Мс	cyclohexane	240-8	6.8
н	Ме	95% ethanol	239-0	5.7
н	Мс	water	231-0	1.2
Me	Mc	cyclohexane	266-0	0-60
Me	Me	95% ethanol	265-0	0.76
Me	Me	water	256-0	0.39
Ме	Et	cyclohexane	274-0	0-82
Me	Et	95% ethanol	268-0	0.82
Me	Et	water	253-0	0-78

TABLE 3. UV SPECTRA OF SOME N, N-DIMETHYLHYDRAZONES

atdehyde and the ketone N,N-dimethylhydrazones. Whereas the maximum absorption of the aldehyde derivatives occurs at about 240 mµ, that of the ketone derivatives is bathochromically shifted to about 265 mµ. This shift is accompanied by a decrease in intensity. As pointed out,^{3, 14} this is probably the $\eta \rightarrow \pi^{*}$ transition involving the lone electron pair of the amino nitrogen. In this respect, again, N,N-dimethylhydrazones behave similarly to N-methylphenylhydrazones and not to hydrazones and compounds that have at least one hydrogen on the amino nitrogen.⁵

In Table 4 is shown the effect of temperature on the vicinal spin-spin coupling constants, $J_{H_1H_2}$, whose accuracy is about ± 0.03 c/s, of the syn isomers of aldehyde N,N-dimethylhydrazones. All couplings decrease with increasing solvent polarity (Table 5). By the usual treatment of the data,² the enthalpy differences, ΔH° , between

R ₂ CH ₄ —C	$H_1 = NN(CH_3)_2$		J _{H,H}	(c/s)	
R ₁	R ₂	- 30 °	0 °	+ 44 °	+ 70°
н	н	5.33	5-31	5.32	5.28
н	Ме	5-16	5.12	5.10	5-00
Н	t-Bu	6.24	6-24	6-22	6-11
Ме	Ме	5-35	5-25	5.12	5.08
Et	Et	6.82	6-52	6.33	6 ∙10
\langle	$\overline{}$	5-24	5-16	5.00	4.77

TABLE 4. SPIN-SPIN COUPLING CONSTANTS OF THE *syn* isomers of neat liquid N,N-dimethylhydrazones

TABLE 5. EFFECT OF SOLVENT POLARITY ON $J_{H,H_{\bullet}}$ of the sym isomers of N,N-dimethylhydrazones

R ₁ R ₂ CH _e —Cl	H ₁ =NN(CH ₃) ₂	$J_{\rm H_1H_{e}}$ (c/s) at 43°			
R _i	R ₂	cyclohexane	acetonitrile"		
Н	н	5.30	5.36		
н	Me	5-00	5.30		
н	t-Bu	6.10	6.25		
Мс	Мс	4.96	5-50		
Et	Et	6.24	6.80		
\langle	\supset	4.80	5.50		

* 10% solutions.

rotamers have been calculated and summarized in Table 6. The calculated spin-spin coupling constants, $J_t = 10.6$ c/s and $J_g = 2.7$ c/s, are similar to those calculated for N-methylhydrazones ($J_t = 10.5$ and $J_g = 2.8$ c/s)⁵ and for hydrazones ($J_t = 10.0$ and $J_g = 3.0$ c/s).⁴





DISCUSSION

Chemical shifts and anisotropic effects. A sufficient amount of information on the chemical shifts of syn and anti isomers has now been accumulated that some general comments about the degree of reliability with which configurational and conformational assignments may be made and about the anisotropic effects of the C=N double bond are feasible. As an aid to our discussion, we have summarized in Table 7 the chemical shift differences in nonaromatic solvents between *cis* and *trans* protons for a variety of compounds with restricted rotation. The positive sign means that protons *cis* to Z resonate at higher fields than the corresponding protons that are *trans* to it; a negative sign means the reverse.

The least reliable chemical shifts in assigning syn and anti configurations are those of β -protons and α -methylenes. They depend on the type of compound, i.e. on the nature of X, Y and Z, and quite often on the structure of R₁ and R₂. The $\Delta\delta$ differences are usually small (± 0.07 ppm), except those of nitrosamines¹¹ where they range from +0.2 (β -Me) to +0.6 ppm (α -methylene).

Somewhat more reliable are the chemical shifts of α -Me groups. These too, however, depend on the nature of X, Y and Z. The $\Delta\delta$ values are positive and large (about +0.75 ppm) for the α -Me protons of nitrosamines, somewhat less positive for most compounds, about zero for oximes¹² and their O-methyl ethers¹³ and small but *negative* for N,N-dimethylhydrazones.

The most reliable chemical shifts in assigning syn and anti configurations are those of α -methine and H₁ protons. Regardless of the structure of compound—with the notable and significant exception of protonated diisopropyl ketone¹⁵—or solvent, α -methine protons resonate at lower magnetic fields when *cis* than when *trans*. The $\Delta\delta$ values are large and negative for most compounds, about -0.2 to -0.6 ppm, more negative for oximes and their O-methyl ethers (about -0.8 ppm) and significantly more negative, -1.35 ppm, for the N,N-dimethylhydrazone of methyl isopropyl ketone. Similarly, the $\Delta\delta$ values for H₁ are also negative and large, ranging from about -0.3 to about -1.0 ppm. There are two significant exceptions, however;

Compound	H	α(CH)	α(CH ₂)	∞(CH₃)	β(CH ₃)	Ref.
R,R,C=-ÔH	+	~0		~0	_	15, 16
$R_1R_2C = NR$ (alkyl)	_	5	~0	+	~0	2, 20
$R_1R_2C = NNH_2$	—		~0	+	±	4
$R_1R_2C = NNHCH_3$	_	5	b	+	0→+	5
$R_1R_2C = NNHC_6H_3$	_		+	+	+	6
$R_1R_2C = NNHC_6H_4X(p)$	_		+	+	0→±	8, 9
$(X = CH_3, C1, NO_2)$						
$R_1R_2C = NNHC_6H_3(NO_2)_2$	—		+	+	0→±	7
R ₁ R ₂ C=NNHCONH ₂	_	_	0→+	+	0→±	8, 9
$R_1R_2C = NNHCSNH_2$	—	٠	0→+	+	0→ <u>+</u>	9
R ₁ R ₂ C=NNCH ₃ C ₆ H ₅	¢	٠	ь	+	+	3
$R_1R_2C = NN(CH_3)_2$	ć		ь	-	+	r
$\mathbf{R}_1\mathbf{R}_2\mathbf{C}$ =NOH		_		0→ -	0	12
$R_1R_1C = NOCH_3$	—			0→+	+	13
$R_1R_2 N = N\bar{O}$	4	_	+	+	+	11
$R_1R_2\dot{N} = CR\bar{O}$	+	_		+	±	17, 18, 23
RÔ=NŌ	4	_	+	+		s

TABLE 7. $\delta_{cis} - \delta_{trans} (\Delta \delta)^{s}$ of $R_1 R_2 X = YZ$ in nonaromatic solvents

^a A positive $\Delta \delta$ means that protons *cis* to Z resonate at higher fields than those that are *trans*; a negative the reverse.

^b The resonances of both cis and trans protons have not been established.

' Only the syn isomer of the aldehyde derivatives is detectable.

- ⁴ No H₁ protons in these compounds.
- * This work.
- ^f From W. D. Phillips, C. E. Looney and C. P. Spoeth, J. Mol. Spectry. 1, 35 (1957).

 $\Delta\delta$ for the H₁ of protonated formaldehyde¹⁶ and formamide^{16, 18} are smaller but *positive*.

On the basis of the aforementioned observations and the information available²⁻¹⁴ on the conformations of groups R_1 and R_2 , it is now possible to elucidate the aniso-tropic effects of the group X = YZ. Let us examine first positions A(V) and B(V)



that are in the plane of the molecule. In all compounds where H(A) resonates at lower fields than H(B) atom Y has a lone electron pair in an sp²-hybridized orbital and Z possesses one or more lone electron pairs. In cases where H(A) resonates at higher magnetic fields than H(B) one of these two features is absent. For example,



in protonated formaldehyde (VI) Z has no lone electron pair; in formamide (VII), Y does not. Formamide may be a special case, as the anisotropy of the group might be better approximated by that of the carbonyl. If so, H(A) should resonate at a higher¹⁹ field than H(B). Since H(A) of N-methylformaldimine (VIII), where Z has



no lone electron pair, resonates at a lower field^{20,2} by about 0.34 ppm than H(B), reliable conclusions on the relative contributions of the two features in determining the difference in the anisotropic effects at positions A and B cannot be drawn.

The $\Delta\delta$ differences of the chemical shifts of α -methine protons permit us to estimate the relative anisotropic screening effects at positions A and B (both in the plane of the molecule) of IX. The experimentally determined $\Delta\delta$ values express only



minimum differences between $\delta_{H(A)}$ and $\delta_{H(B)}$, for the following reasons. As shown in previous publications in the series, the predominant conformation of the R₂CHgroup when *cis* to Z is the one where the C—H(A) bond is almost in the plane of the molecule, as shown in IX. As the population of this conformation increases by increasing the sizes of the alkyl groups on R₂CH—, the *cis* α -methine resonance shifts downfield. The true chemical shift of the *cis* α -methine when in position A is, therefore, lower than the experimentally measured ones. The chemical shifts of the *trans* α -methine protons are weighted averages of the chemical shifts in positions B(X) and B'(XI). As shown in previous publications in this series, the chemical shifts of the *trans* α -methine protons move to higher fields as the concentration of rotamer X increases, i.e. position B (in the plane of the double bond) is shielded with respect to position B'. The true chemical shift of the *trans* α -methine when in position B is, therefore, higher than the experimentally measured ones. We estimate that H(A) should resonate at lower fields than H(B) by about 2-4 ppm. Apparently the main source of this difference is the anisotropy of the lone electron pairs on Z. In the only compound,



protonated diisopropyl ketone,¹⁵ where Z has no lone electron pairs, the *cis* and *trans* α -methine resonances where indistinguishable. Not only are the lone electron pairs responsible for the bulk of this difference, but their orientation with respect to the C—H(A) bond is also important. For example, in compounds such as XII,



where the orbital of the lone electron pair is about perpendicular to the plane of the molecule and overlaps with the π -orbital of the double bond, $\Delta\delta$ is about -0.5 ppm; in oximes and their O-methyl ethers (XIII), $\Delta\delta$ is about -0.8 ppm; and in N,N-dimethylhydrazones, where the orbital of the lone electron pair is near, or in, the plane of the molecule (XIV), *vide infra*, and orthogonal to the π -orbital of the double bond, $\Delta\delta$ is about -1.35 ppm. We attribute the finding that $\Delta\delta$ of α -Me protons is positive in XII, about zero in XIII, and negative in XIV to such differences in the orientation of the lone electron pair orbitals. We, therefore, conclude that the anisotropy of the lone electron pair on Y is not, as suggested for oximes,²¹ the controlling factor.

On the basis of the above discussion and from the conformations²⁻¹⁴ of groups R_1 and R_2 (I) it is now easy to understand why the chemical shifts of α -methylene and β -Me protons behave irregularly. As pointed out, ¹² both conformations XV and XVI



are significantly populated. Similarly, both conformations II and III of the *trans* RCH₂-groups are important, their ratio varying with R. The experimental *cis* and *trans* chemical shifts, therefore, are weighted averages of the chemical shifts of protons

from several positions at which the anisotropic screening constants are unknown and can be quite different.

From the finding that the $cis\alpha$ -Me protons resonate at higher magnetic fields than the corresponding *trans*, and by considering XVII, we conclude that position A'



is shielded with respect to position B'. The reverse, of course, is true with positions A and B.

The aforementioned arguments and conclusions could be very well extended to predict the relative chemical shifts of other compounds. For example, the methine proton of XVIII (X = halogen, alkoxy) should resonate by 0.5 to 1.5 ppm lower than the methine of XIX.



Interpretation of solvent effects on chemical shifts. A valuable compliment to chemical shifts in assigning syn and anti configurations is the specific and predictable effect that an aromatic solvent, such as benzene, has on these chemicals shifts. In practically all compounds studied the effect of benzene on the chemical shifts of the corresponding cis and trans protons is different and depends, primarily, on the nature of Y and Z. As has been discussed by us and by other investigators,^{22,23} these effects require stereospecific orientation of benzene by interaction with a positive center(s) on the substrate. The bulk of the available data on the chemical shifts of R_1 and R_2 can be readily rationalized in terms of three types of orientation complexes, $XX^{10-13,22,23} XXI^2$ and $XXII.^{4-10}$ Model XX produces larger upfield shifts of the



resonances of the *trans* (R_2) than of the *cis* (R_1) protons. Some *cis* protons are shifted downfield. Models XXI and XXII produce the reverse effect. Mode. XX applies to the following classes of compounds: amides, nitrosamines, oximes and oxime O-methyl

ethers. Model XXI applies to N-alkylimines and to N,N-dimethylhydrazones. Model XXII applies to hydrazone-type compounds bearing at least one hydrogen on the amino nitrogen.

Since model XXII is self-explanatory, we will discuss the features on Y and Z that determine whether XX or XXI will apply. The controlling factor is apparently the repulsion between the π -electrons of benzene and the lone electron pairs on Y and Z. If only Z has a lone electron pair, then model XX applies, as illustrated by amides (XXIII). If only Y has a lone electron pair, then model XXI applies, as illustrated by



N-methylimines (XXIV). On this basis we can predict that XX will apply to vinyl halides and vinyl ethers.

If both Y and Z have lone electron pairs, model XX applies, as illustrated by nitrosamines (XXV). Model XXI will apply, as illustrated by N,N-dimethylhydrazones (XXVI), when the lone electron pair on Z is in the plane of the molecule and, therefore,



orthogonal to the π -orbital of the oriented benzene molecule. The benzene molecule, thus, by being oriented between the two (in plane) lone electron pairs finds itself closer to the cis (\mathbf{R}_1) than to the trans (\mathbf{R}_2) groups.

The effect of an aromatic solvent is often strong enough to cause crossing over of the resonances of *cis* and *trans* protons, as in amides²³ and oxime O-methyl ethers¹³ (model XX), and as in N,N-dimethylhydrazones (model XXI). In general, model XX shifts the resonance of the *cis* α -methine protons downfield; model XXI does so to that of the *trans* α -methine protons.

Conformations of the Z groups. The absence of detectable configurational isomerism about the C=N double bond of the aldehyde, but not of the ketone, N,N-dimethylhydrazones may be rationalized, as was done with N-methylphenylhydrazones,³ in terms of rotational isomerism about the N-N single bond. For example, whereas in the syn isomer XXVII the lone electron pair orbital on the N,N-dimethylamino nitrogen is parallel to and overlaps with the π -orbitals of the carbon-nitrogen double bond, in the anti isomer XXVIII it is orthogonal to the π -orbitals as a result of the nonbonded repulsions between R and N-Me. The ensuing loss of resonance stabilization in XXVIII is therefore responsible for the presence of only syn isomers. In contrast to the aldehyde N,N-dimethylhydrazone isomers, both isomers of the ketone derivatives will suffer loss of overlap and, thus, will be detectable. The correctness of this explanation is cogently supported by the UV spectra¹⁴ (Table 3) and by the effect of benzene dilution on the chemical shifts of the N,N-dimethyl protons.³



The conformations of the various Z groups may now be summarized as follows: For hydrazone-type compounds that contain at least one proton on the amino nitrogen, the conformation of Z for both aldehyde and ketone derivatives is as in XXIX,



where the lone pair electron orbital on the amino nitrogen is parallel to and overlaps with the π -orbital of the double bond. For compounds without a hydrogen on the amino nitrogen the conformation of the aldehyde derivatives is XXX, i.e. the same as XXIX, and of the ketone derivatives it is XXXI. For oximes and their O-methyl ethers, it is XXXII.

Conformations of the alkyl groups of the syn isomers. The evidence accumulated in recent years is consonant with II and III being the minimum energy conformations about the relevant sp²-sp³ C—C bonds. A sufficient number of data is now available to, at least, gain some understanding of the effects of Y and Z on the relative stabilities of II and III. In Table 8 are summarized ΔH° values for XXXIII \rightleftharpoons XXXIV along with



the *trans* and *gauche* coupling constants of the various systems. From the ΔH° values of propionaldehyde²⁴ (-800 cal/mole), N-methyl propionaldimine² (-200 cal/mole) and 1-butene[†] (+400 cal/mole), it appears that these values depend on the electro-

†This value was estimated by us from data of the coupling constants of propene and 1-butene and from J_t and J_e of the olefins.²⁵

Some J_i , J_g values and ΔH° for H	H X CH,	••	CH, X H H
Compound	J_i (c/s)	J _e (c/s)	ΔH° (cal/mole)
EtH	7.6	05	- 800
Et H	9.7	2.4	- 200
Et H	10-0	3-0	ca. + 400
Et H	10.5	2.8	+ 500
Et H	10-6	2.7	+ 250
Et H	10-3	2·4	ca. +100
Et H	10-4	3-0	ca. +100

 Some J_i , J_g values and ΔH° for	H CH,		сн, х
 Compound	J, (c/s)	J _g (c/s)	ΔH° (cal/mole)
	13-0	2.4	+ 500
	11-3	3.2	+ 400
	11.6	3.7	ca. +400

TABLE 8—continued

negativity of Y, i.e. they become more negative as the positive charge on the sp²-hybridized carbon increases. On the basis of the reported¹⁶ vicinal couplings of protonated acetaldehyde (J = 3.5 c/s) and protonated propionaldehyde (J < 0.4 c/s), the conclusion may be drawn that ΔH° for the protonated propionaldehyde is appreciably more negative than the -800 cal/mole for the unprotonated species. This, of course, is consonant with the statement that we have just made. From the values of N-Me propionaldimine, those of N,N-dimethyl-(+250 cal/mole), N-methyl-phenyl- (+100 cal/mole) and 2,4-dinitrophenylhydrazones (+100 cal/mole), and that of propionaldoxime O-methyl ether (+400 cal/mole), it appears that these values become more positive as the electronegativity of Z increases.† The causes for these trends are presently not well understood. Nonbonded interactions will certainly influence these values, but it is evident from the results that they are not the controlling factor. Furthermore, by using Bartell's procedure²⁶ and the nonbonded potential functions of Scott and Scheraga,²⁷ ΔH° for propionaldehyde is calculated²⁸ to be only -170 cal/mole.

EXPERIMENTAL

Preparation of N,N-dimethylhydrazones. The following illustrates the general procedure used to prepare N,N-dimethylhydrazones. Into a 25 ml, 2-necked, round-bottomed flask equipped with a reflux condenser, drying tube and rubber syringe cap was added 50 g (003 mole) BaO, and a solution of 10 g (001 mole) 3,3-dimethylbutyraldehyde in 10 ml of EtOH. To the cooled solution was added with a hypodermic

† The values for the oxime, hydrazone and N-methylhydrazone derivatives are not included in the correlation, as these values are too positive on account of strong intermolecular hydrogen bonding.^{12, 4, 5}

syringe 1-0 g (0-016 mole) 1,1-dimethylhydrazine. After the initial exothermic reaction had subsided, the reaction mixture was refluxed for 1 hr. The material was then cooled, filtered, extracted with additional EtOH and dried over MgSO₄. Fractionation yielded 0-80 g (56%) of 3,3-dimethylbutyraldehyde N,N-dimethylhydrazone as a colorless liquid, b.p. 65° at 50 mm of Hg.

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.

UV spectra were taken with a Cary 14 recording spectrophorometer.

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