NUCLEAR MAGNETIC RESONANCE STUDIES OF HYDRAZONES

Thesis for the Degree of M. S.

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Carol Elizabeth Osborne

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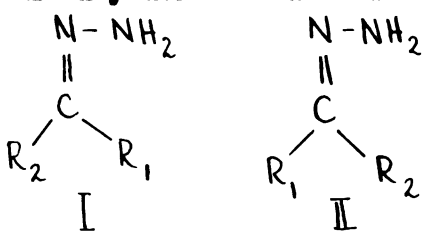
ABSTRACT

NUCLEAR MAGNETIC RESONANCE STUDIES OF HYDRAZONES

by Carol Elizabeth Osborne

The nuclear magnetic resonance spectra of thirteen hydrazones were examined to determine configurations, conformations, syn/anti ratios and solvent effects.

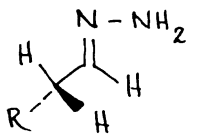
The assignment of configurations was based on two points. Sterically it is resonable to expect that configuration I should be thermodynamically more stable than II when R_1 is smaller



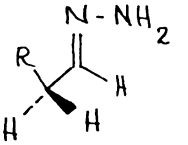
than R_2. Secondly, due to steriospecific association of benzene with the substrate the chemical shift of <u>cis</u> protons to higher magnetic fields is greater than that of the <u>trans</u> protons. Using these two principles it was possible to make configurational assignments to the syn and anti isomers of various hydrazones. For example, in all cases the cis aldehydic proton of aldehydic hydrazones is found to resonate at lower magnetic fields than the trans aldehydic proton.

From the spin-spin coupling constants it was possible to determine which conformations were the more stable for the hydrazones. For example, the coupling constant for syn pro-

pionaldehyde hydrazone $J_{H_1H_\alpha}$ = 5.52 c.p.s., while for syn isovaleraldehyde hydrazone $J_{H_1H_\alpha}$ = 5.60 c.p.s. This indicates that for the syn aldehydic hydrazones conformation III



III



IV

becomes more stable than conformation IV as the R group increases in size. Conformation III involves a trans coupling and a gauche coupling and conformation IV two gauche couplings. Since $J_t > J_g$ conformation III would have the larger coupling constant.

The relationship between conformations and chemical shifts was also examined. It was found that a proton in the plane of the carbon-nitrogen bond is shielded with respect to a proton above or below the plane.

THE

NUCLEAR MAGNETIC RESONANCE STUDIES OF HYDRAZINES

By

Carol Elizabeth Osborne

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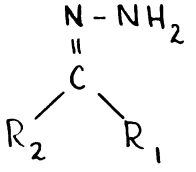
TABLE OF CONTENTS

LIST OF TABLES

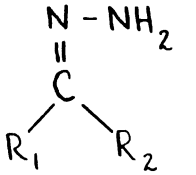
LIST OF FIGURES

INTRODUCTION

Nuclear magnetic resonance spectroscopy has been a very useful method for studying problems arising from restricted rotation about a carbon-nitrogen double bond. The hydrogens in the neighborhood of the anisotropic group serve as a probe for detecting asymmetry around the double bond; e.g. I and II.



I



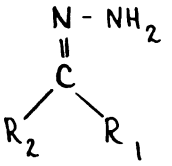
II

Many workers have used n.m.r. to study the isomers of compounds containing a carbon-nitrogen double bond. In 1958, Phillips (1) showed the existence of syn-anti isomers of aliphatic aldoximes. Later Lustig observed separate peaks for the syn-anti isomers of ketoximes in the presence of aromatic solvents (2). Studies of 2,4-dinitrophenylhydrazones and semicarbazones were made by Karabatsos, Graham and Vane (3). Karabatsos and Taller (4,5) made similar studies of nitrosamines, phenylhydrazones and p-tolylhydrazones.

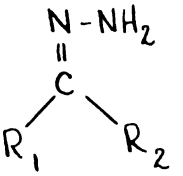
The purpose of this research was to study by n.m.r. configurational and conformational isomerism of hydrazones; e.g. syn and anti assignments to isomers, syn/anti ratios, and conformations of the alkyl groups attached to the carbon-nitrogen double bond.

The assignment of configurations is based on steric considerations. For example, the ratio III/IV should increase

when R_1 is kept constant and R_2 is changed from ethyl to isopropyl.

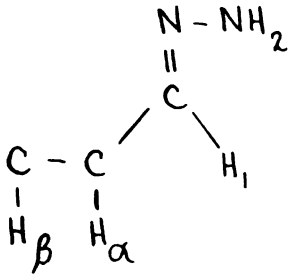


III



IV

Throughout the thesis the isomer with the amino group cis to the smaller R group will be regarded as the syn isomer. The hydrogens of the R groups are numbered as indicated in V and are designated as cis or trans to the amino group.



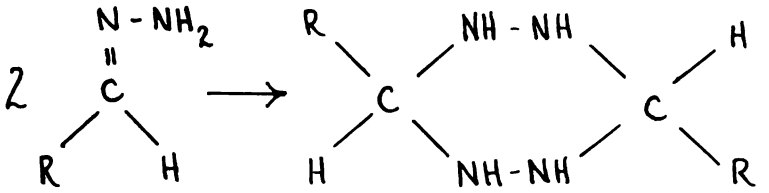
V

RESULTS AND DISCUSSION

Chemical Shifts

Table I summarizes the chemical shifts of several hydrazones. The more intense signals were assigned to the configuration with the smallest group cis to the amino group. In many instances azine was present in the product or was forming from hydrazone as the spectra were taken. Figure 1 shows the spectrum of a freshly distilled sample of acetone hydrazone with a small amount of azine present. After letting the acetone hydrazone sit at room temperature for a few hours the spectrum was taken again showing evidence of more azine, as seen in figure 2. In order to confirm the hydrazone peaks a small amount of the corresponding aldehyde or ketone was added to the hydrazone sample after the spectra were run and the sample was re-examined to see which peaks decreased in intensity.

The aldehydic hydrazones dimerize at room temperature (reaction one) to give crystalline 3,6-dialkylhexahydro-



(1)

s-tetrazine (6). Figure 3 shows the spectrum of acetaldehyde hydrazone with peaks which presumably are those of the dimer. Immediately after this spectrum was run the sample crystallized in the n.m.r. tube.

Table I

Chemical Shifts of Hydrazones in τ

$R_1 \diagdown C = N-NH_2 \diagup R_2$	Solvent	$H_\alpha(CH_3)$ cis	$H_\alpha(CH_3)$ trans	$H_\alpha(CH_2)$ cis	$H_\alpha(CH_2)$ trans	$H_\alpha(CH)$ trans	$H_\beta(CH_3)$ cis	$H_\beta(CH_3)$ trans	C_6H_5 cis	C_6H_5 trans	NH_2
$R_1 = R_2 = CH_3$	Neat	8.35	8.20								5.05
	CCl_4	8.33	8.18								
	Benzene	8.64	8.22								
$R_1 = CH_3$	Neat	8.34	8.21	7.84	7.87		8.92	9.01			4.67
$R_2 = CH_2CH_3$	CCl_4	8.34	8.21	-	7.85		-	8.97			5.25
	Benzene	8.67	8.23	-	7.92		-	8.98			5.42
$R_1 = CH_3$	Neat	8.38	8.28			7.61	8.90	9.00			4.91
$R_2 = CH(CH_3)_2$	CCl_4	8.37	8.28			7.61	9.00	8.98			5.26
	Benzene	8.65	8.28			7.62	9.21	8.97			5.32
$R_1 = CH_3$	Neat	8.32						8.93			
$R_2 = C(CH_3)_3$	CCl_4	8.34						8.93			
	Benzene	8.63						8.93			
$R_1 = CH_3$	Neat	8.47	8.22	-	6.56				-	2.80	5.16
$R_2 = CH_2C_6H_5$	CCl_4	8.45	8.18	6.55	6.61				2.74	2.84	
	Benzene	8.77	8.22	6.84	6.88						

Table I (cont.)

Chemical Shifts of Hydrazones in τ

$R_1 \diagdown C=N-NH_2 \diagup R_2$	Solvent	H_1		$H_\alpha(CH_3)$		$H_\alpha(CH_2)$		$H_\alpha(CH)$	$H_\beta(CH_3)$		$H_\beta(CH_2)$	$H_\gamma(CH_3)$
		cis	trans	cis	trans	cis	trans	trans	cis	trans	trans	trans
R_1 = H R_2 = CH_3	Neat Benzene	2.88	3.42	8.32 8.77	8.23 8.39							
R_1 = H R_2 = CH_2CH_3	Neat	2.93	3.61				7.92		8.90	9.02		
R_1 = H R_2 = CH_2i-Pr	Neat CCl_4 Benzene	2.96 3.08 3.30	3.56				7.98					
R_1 = H R_2 = i-Pr	Neat CCl_4 Benzene	2.97 3.08 3.40	3.75					7.67		8.97 8.98 9.04		
R_1 = H R_2 = $CH(Et)_2$	Neat CCl_4 Benzene	3.05 3.25 3.43	3.73 3.76					8.05 8.05 8.03			8.63 8.60 8.71	9.12 9.10 9.13
R_1 = H R_2 = $CH_2C_6H_5$	Neat CCl_4	3.02 2.96	3.40			6.35	6.63 6.55					
R_1 = H R_2 = CH(i-Pr)$_2$	Neat* CCl_4	2.87 3.13	3.66					8.49				
R_1 = H R_2 = CH_2(t-Bu)	Neat*	2.85	3.45				7.99					9.07

* Some EtOH present

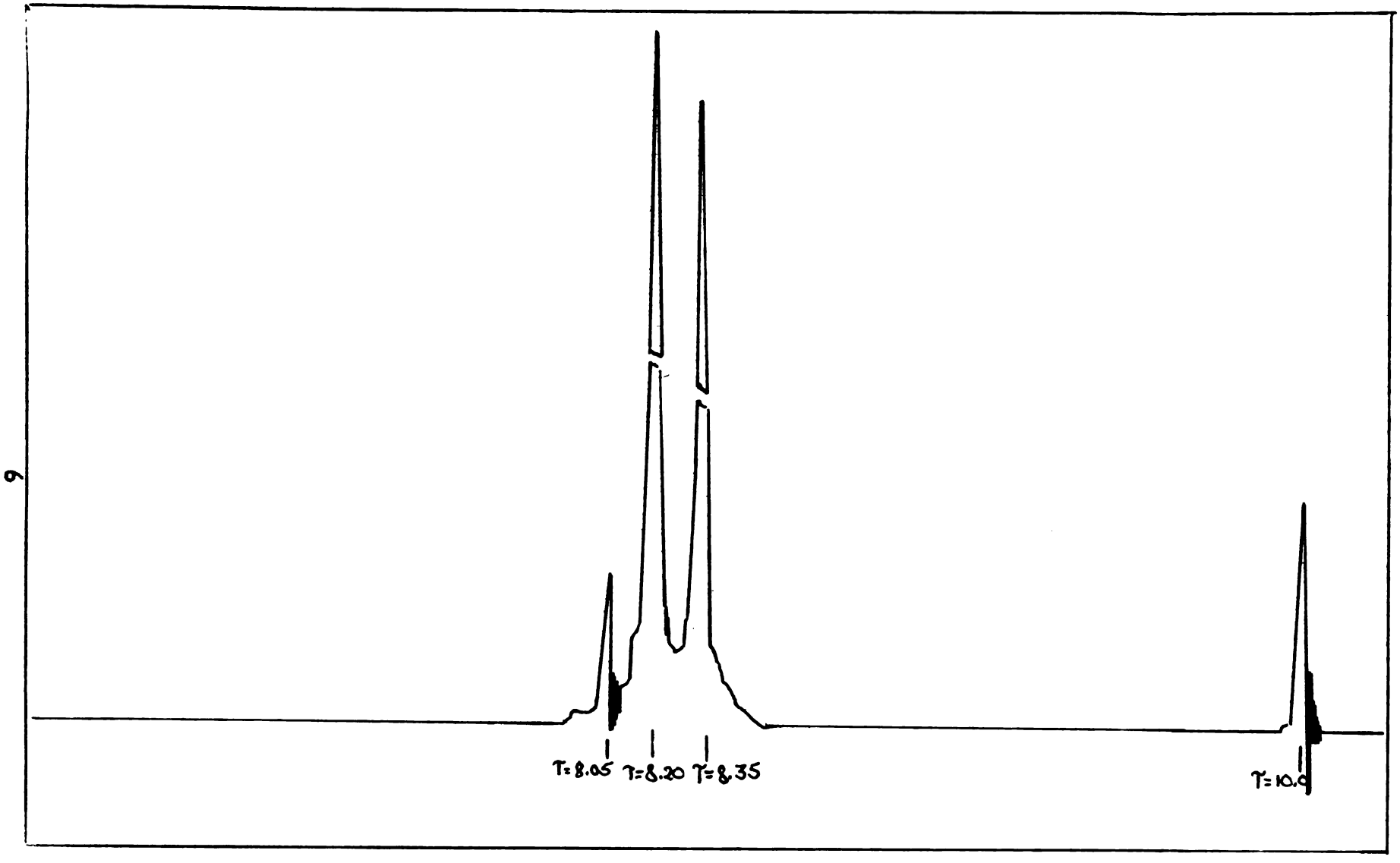


Fig.1.—N.m.r. spectrum of acetone hydrazone with small amount of azine present.

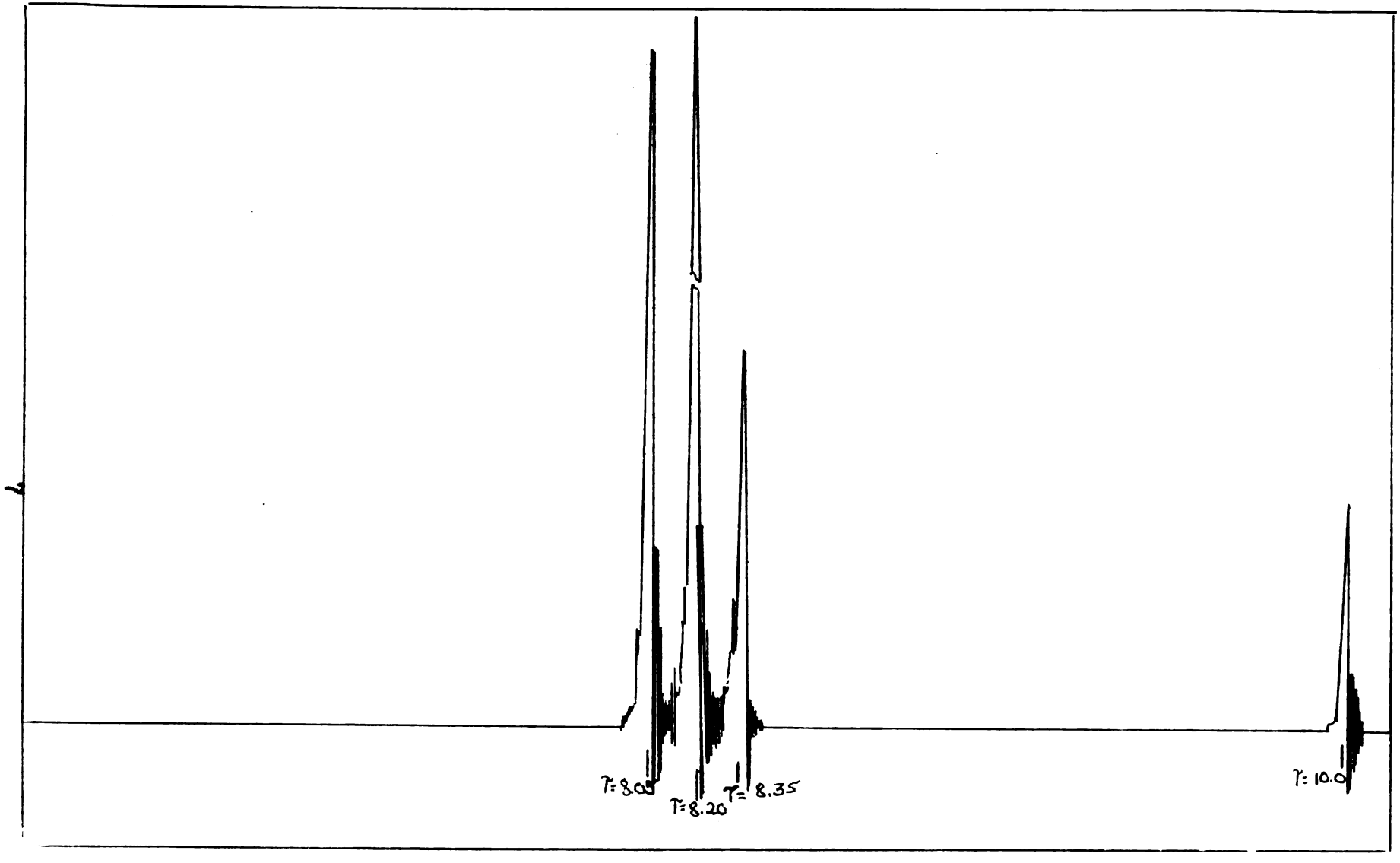


Fig.2.—N.m.r. spectrum of acetone hydrazone with considerable azine present.

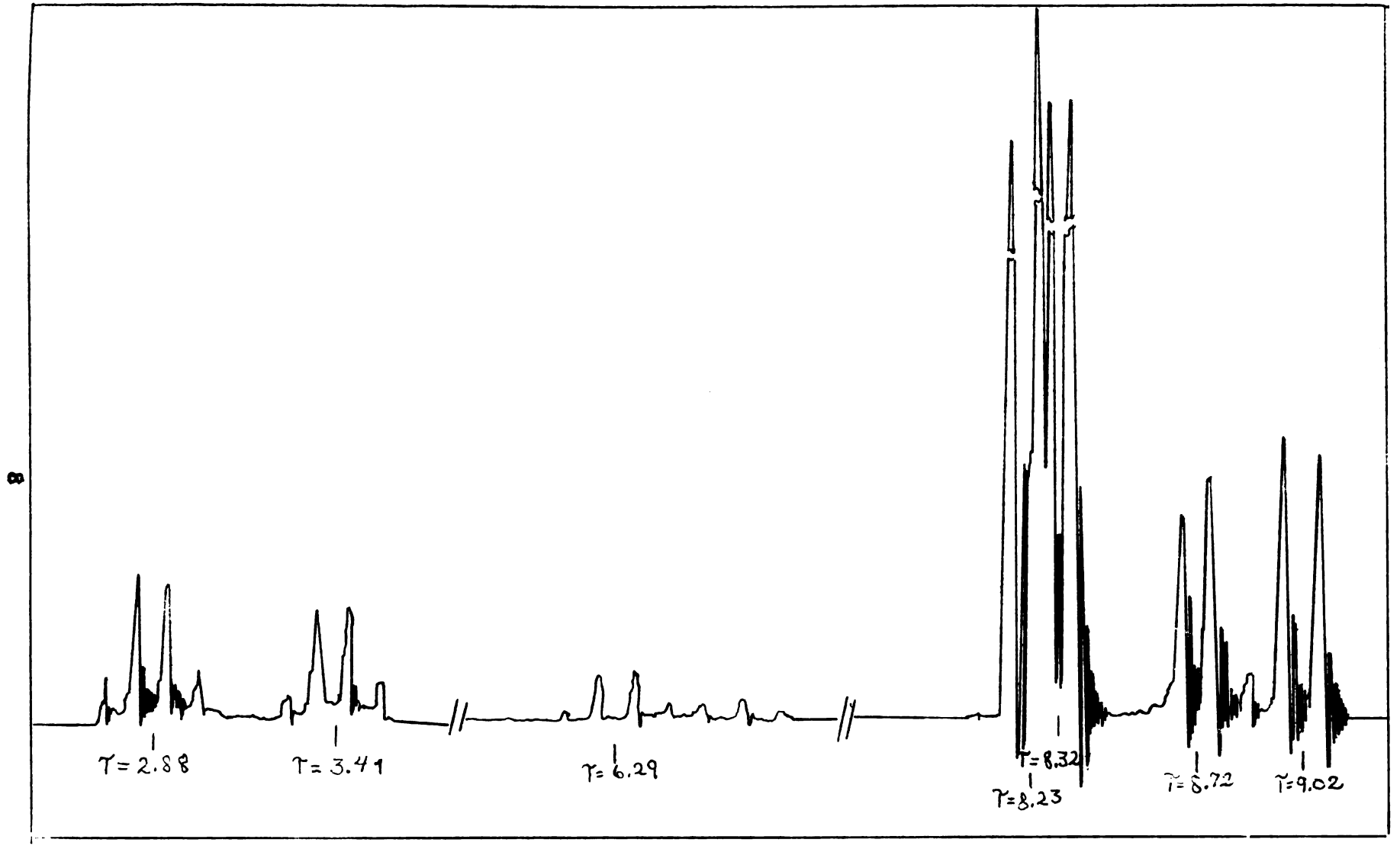
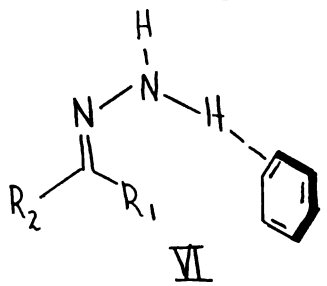


Fig.3.—N.m.r. spectrum of acetaldehyde hydrazone showing peaks assumed to be those of the dimer.

From Table I it can be seen that α-methyl protons always appear at higher fields when cis to the amino group than when trans. In contrast, the aldehydic proton, H_1, and β-methyl protons resonate at lower fields when cis than when trans. Although in only a few cases could cis α-methylene protons be detected, it appears that they are deshielded (lower fields) with respect to trans α-methylene protons. It was not possible to detect the resonance of the cis α-methine protons.

Solvent Effects

The effect of solvent on the chemical shifts can also be seen by looking at Table I. The solutions shown in Table I are all 10% hydrazone - 90% solvent, by volume. In carbon tetrachloride there is little effect on the chemical shifts for either the syn or the anti isomers. But when benzene is used as the solvent the cis hydrogens are shifted upfield more than the trans hydrogens. A hydrogen bonded complex of conformation VI explains this behavior. Since



VI

R_1 is closer to the center of the benzene ring than R_2 $\Delta\nu$(cis) > $\Delta\nu$ (trans). The behavior of hydrazones in benzene is similar to that of other compounds of the type $R_1R_2C{=}NZ$ (3,4,7).

Figure 4 shows the effect of dilution studies on acetone hydrazone. Curve I, which is concave upward, represents the cis α-methyl hydrogens of acetone hydrazone in benzene. Curve II, also concave upward with a slight shift towards lower magnetic fields with low concentrations of the solvent, is the trans α-methyl hydrogens in benzene. Curve III is the cis α-methyl hydrogens in carbon tetrachloride and Curve IV the trans α-methyl hydrogens in carbon tetrachloride. The chemical shifts in carbon tetrachloride are quite insensitive to dilution.

Coupling Constants

Table II summarizes the coupling constants, accurate to ±0.05 c.p.s., between H_1 and the α-protons of the aldehydic hydrazones. The probe temperature was maintained at about 36°.

Conformations of the syn Isomers

Many instrumental methods have shown that the stable conformation of a tetrahedral carbon bonded to a trigonal carbon has a single bond eclipsing the double bond (8-22). If VII is the conformation of acetaldehyde hydrazone, then its coupling constant may be expressed as:

$$J_{HH} = (2J_g + J_t)/3$$

where J_g is the gauche coupling and J_t the trans coupling.

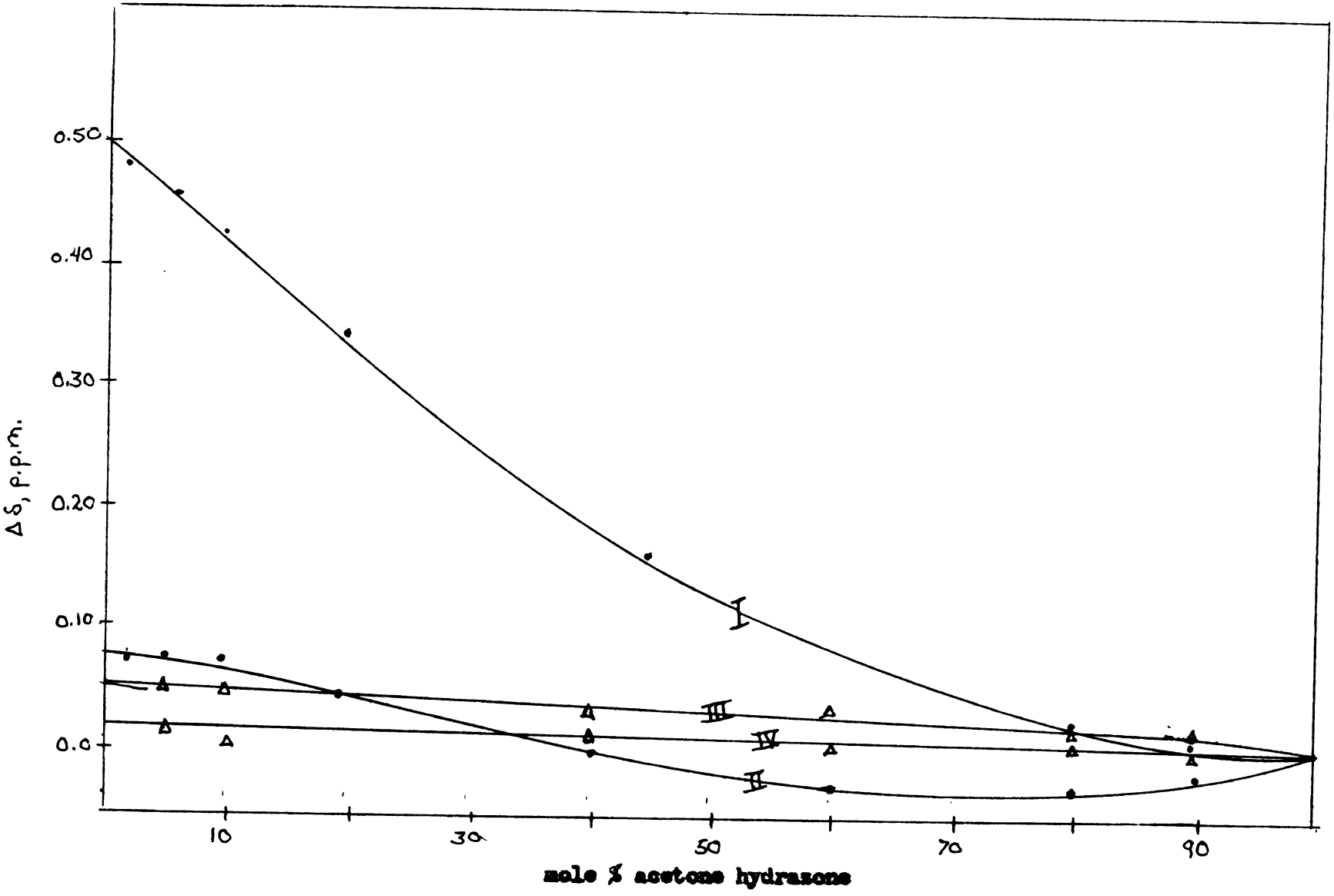


Fig. 4.—Effect of dilution on the chemical shifts of acetone hydrazone: I, cis, α-methyl in benzene; II, trans, α-methyl in benzene; III, cis, α-methyl in carbon tetrachloride; IV, trans, α-methyl in carbon tetrachloride.

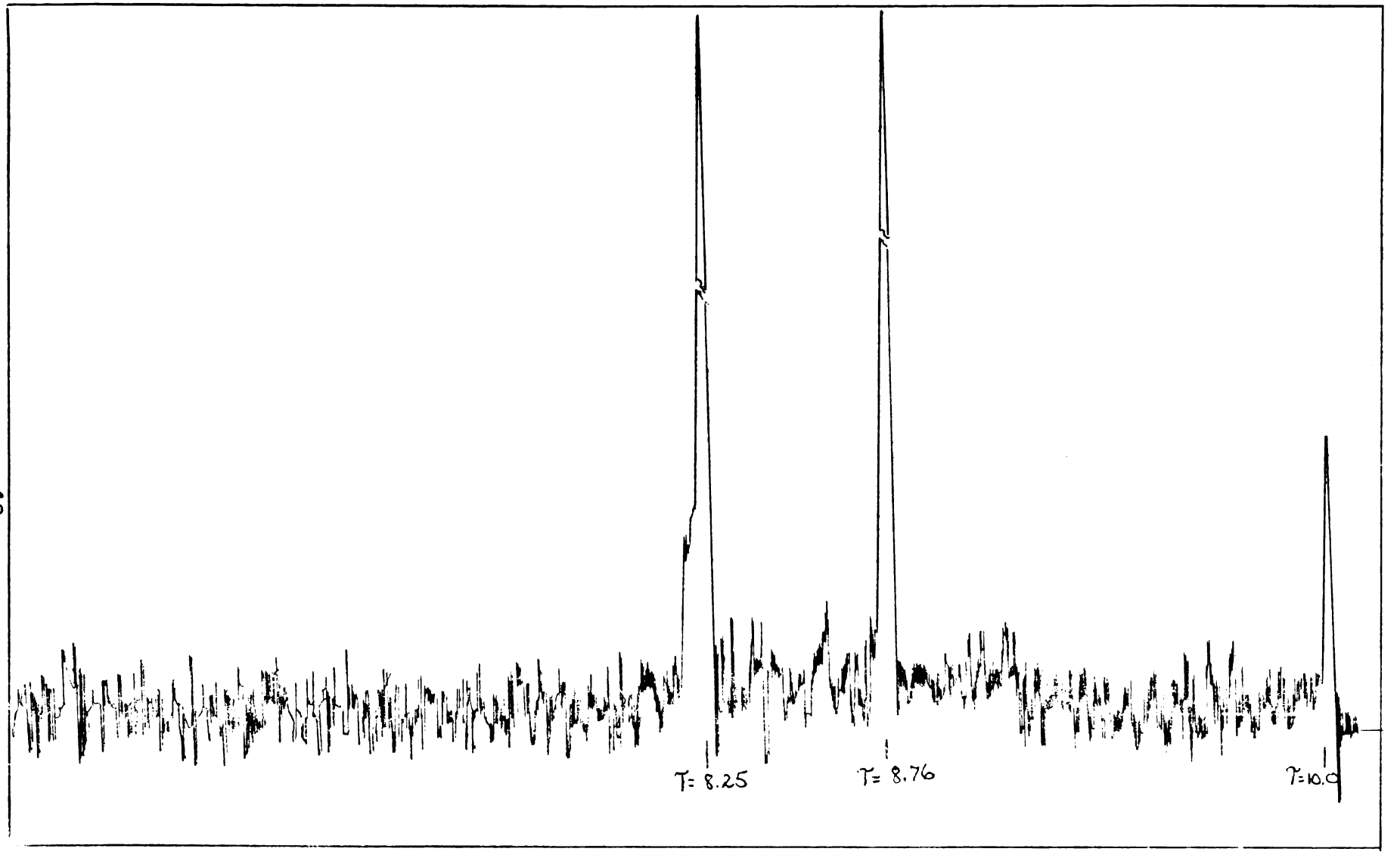


Fig. 5.—N.m.r. spectrum of acetone hydrazone, 2 mole % in benzene.

Table II

Spin-Spin Coupling Constants of Hydrazones

$R_1 \diagdown C = N - NH_2$ $R_2 \diagup$	Solvent	$J_{H_1 H_\alpha}$ (c.p.s.) cis	trans
$R_1 = H$ $R_2 = CH_3$	Neat	5.40	5.50
$R_1 = H$ $R_2 = CH_2CH_3$	Neat	5.52	5.45
$R_1 = H$ $R_2 = CH_2$i-Pr	Neat	5.60	4.93
	CCl_4	5.50	
	Benzene	5.53	
$R_1 = H$ $R_2 = CH_2C_6H_5$	Neat	5.77	5.07
	CCl_4	5.77	
$R_1 = H$ $R_2 = CH_2$t-Bu	EtOH	6.23	5.35
$R_1 = H$ $R_2 =$ i-Pr	Neat	5.18	7.18
$R_1 = H$ $R_2 = CH(Et)_2$	Neat	6.32	8.10
	CCl_4	6.26	7.68
	Benzene	6.32	
$R_1 = H$ $R_2 = CH$(i-Pr)$_2$	EtOH	6.58	8.43

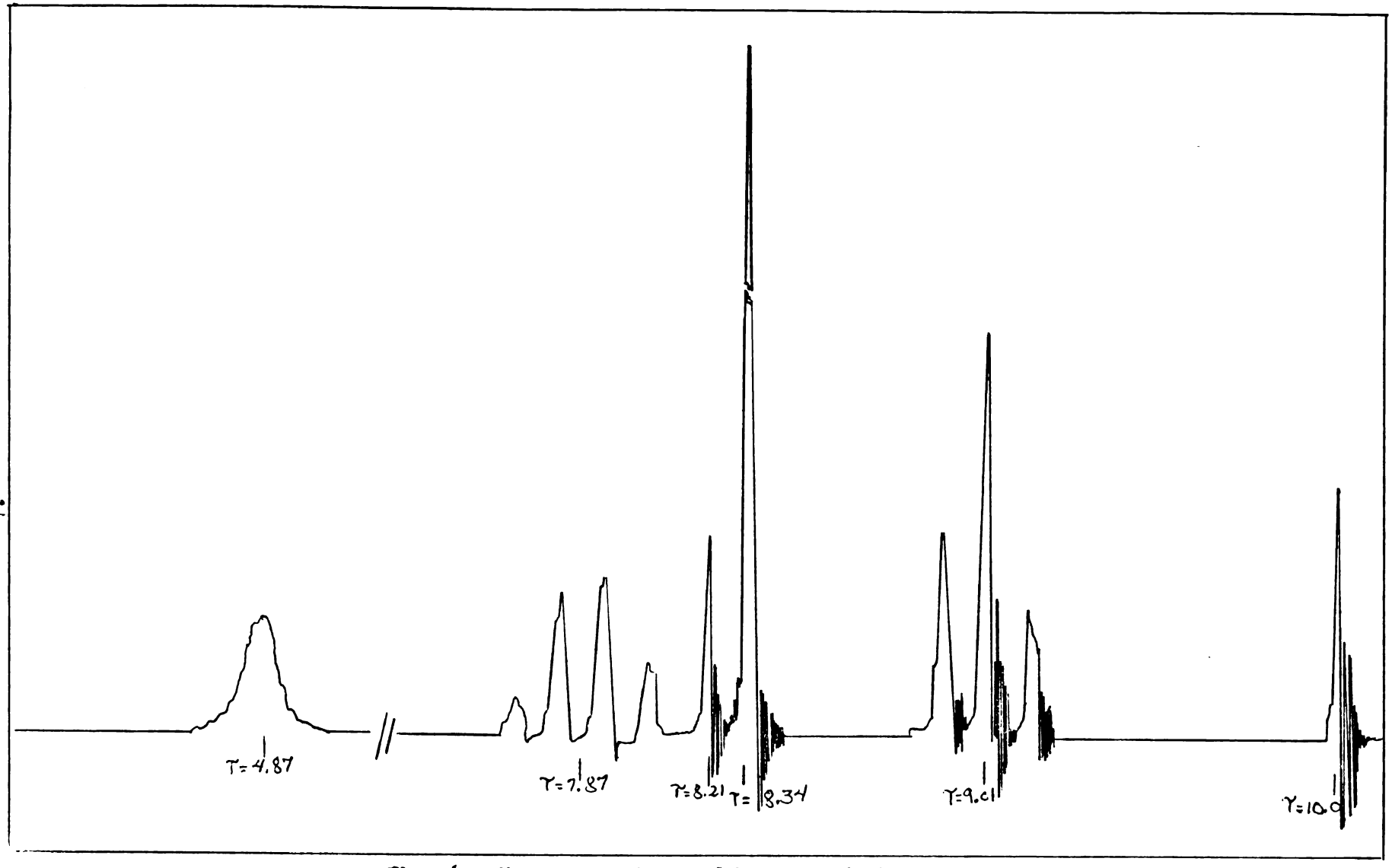
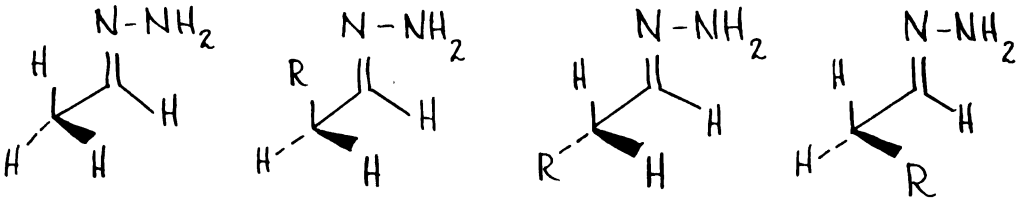


Fig. 6.—N.m.r. spectrum of butanone hydrazone.



VII VIII IXa IXb

If VIII and IX_a are energetically equivalent then the coupling constant for a monosubstituted aldehydic hydrazone should be the same as that for acetaldehyde hydrazone (5.40 c.p.s.). However, the substitution of an alkyl group probably decreases the coupling by about 0.4-0.7 c.p.s. per alkyl substituent (23-25). (For example, $J_{CH_3CH_2X}$ is 8.0 c.p.s. (X = H), 7.26 c.p.s. (X = CH_3) and 6.8 c.p.s. for isobutane.) From steric considerations one would expect IX to be more favorable than VIII, in which case the coupling constant of monosubstituted acetaldehyde hydrazone would be larger than that of acetaldehyde hydrazone since $J_t > J_g$. Also, as R gets larger $J_{H_1H_\alpha}$ should get larger because more of the compound would be in conformation IX. From the data it can be concluded that this is the case; e.g. $J_{H_1H_\alpha}$ for methylacetaldehyde hydrazone is 5.52 c.p.s., for isopropylacetaldehyde hydrazone 5.60 c.p.s., and for t-butylacetaldehyde hydrazone 6.23 c.p.s.

For the disubstituted aldehydic hydrazones there are three possible conformations with a single bond (C - H) eclipsing the carbon-nitrogen double bond. As the R groups get larger more of the compound should be in conformation X rather than XI and the coupling constant should increase. The data

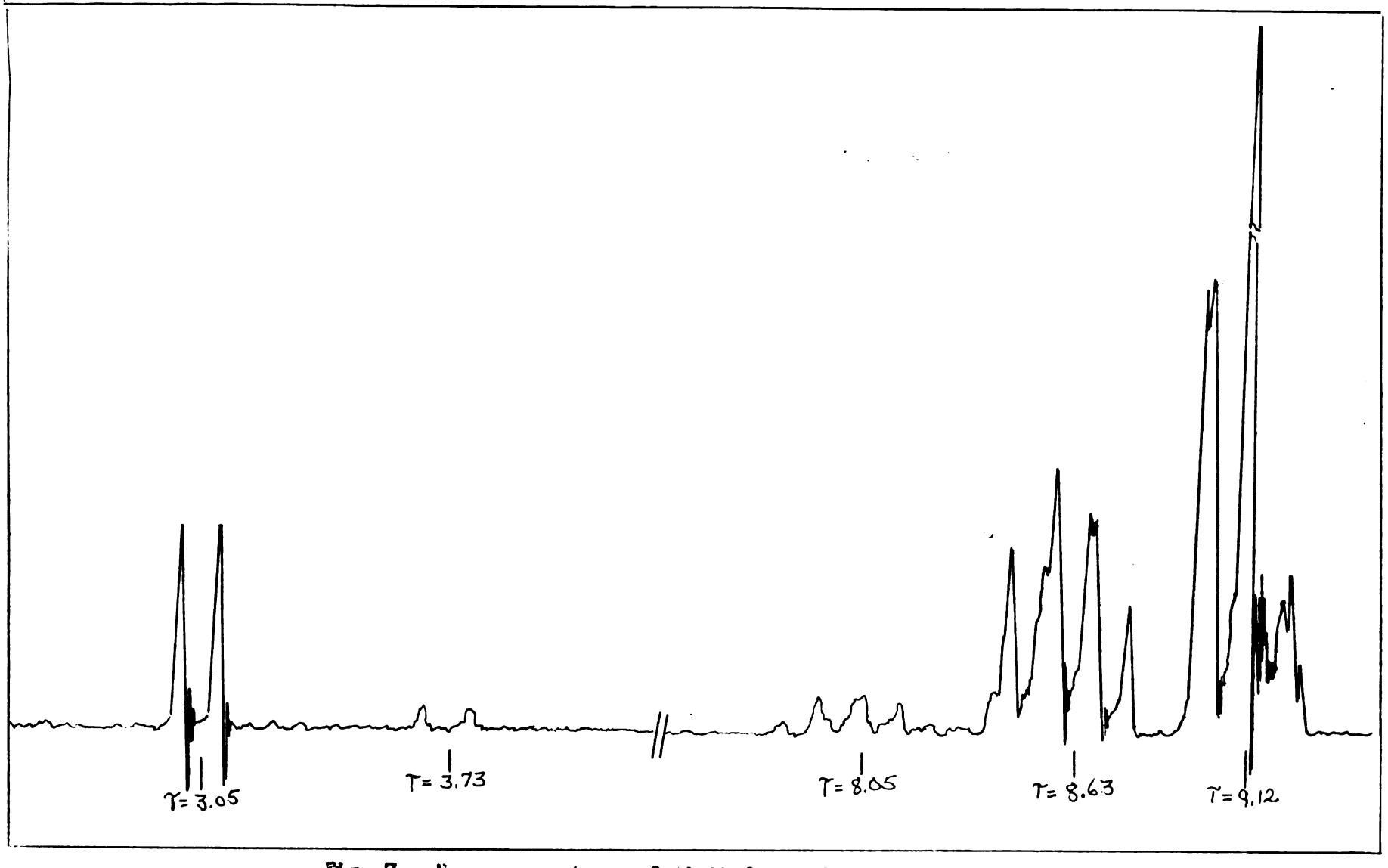
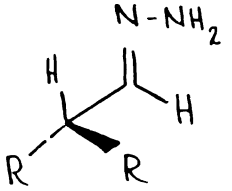
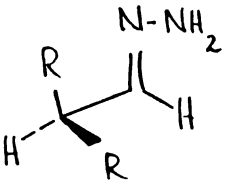


Fig. 7.—N.m.r. spectrum of diethylacetaldehyde hydrazone.

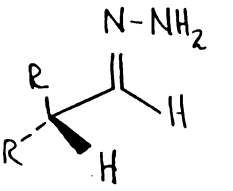
indicate that this is true, conformation X is more stable



X



XIa



XIb

than conformation XI. For example, when both R groups are methyl J = 5.18 c.p.s.; when they are isopropyls J = 6.58 c.p.s.

If it is assumed that t-butylacetaldehyde hydrazone exists solely in conformation IX then its coupling constant may be expressed as:

$$J_{HH_{exp.}} + \text{correction} = \frac{J_g + J_t}{2}$$

where the correction factor arises from the substitution of an alkyl group for a hydrogen. By using the above expression and the one previously given for $J_{H_\beta H_\alpha}$ of acetaldehyde hydrazone it is possible to calculate J_g and J_t. When 0.3 per alkyl substituent is used as the correction factor J_g = 3.14 c.p.s., J_t = 9.92 c.p.s.; with 0.5 as the correction J_g = 2.74 c.p.s., J_t = 10.72 c.p.s.; using 0.7, J_g = 2.34 c.p.s., J_t = 11.52 c.p.s. These values are comparable to those which Bothner-By found for olefins; J_g = 3.7 c.p.s., J_t = 11.5 c.p.s. (10).

The values calculated for J_g and J_t may then be used to determine the percentages of the different conformers. For the monosubstituted acetaldehyde hydrazones the expression for determining the percentages of the two is:

$$J_{HH_{exp.}} + \text{correction} = \frac{x(J_g + J_t)}{2} + (1 - x)J_g$$

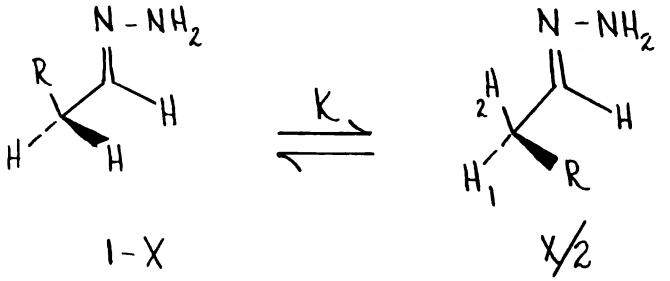
where x is the amount of the compound in conformation IX_a + IX_b, and (1 - x) the amount in conformation VIII. Table III shows the percentages obtained by this method.

For the disubstituted acetaldehyde hydrazones the expression for calculating the amounts of conformers X and XI_a + XI_b is:

$$J_{III_{exp.}} + 2(\text{correction}) = xJ_t + (1 - x)J_g$$

where x is the amount of conformer X and (1 - x) the amount of conformer XI_a + XI_b. The percentages thus obtained for the different conformations of the disubstituted acetaldehyde hydrazones are also shown in Table III.

The percentages of different conformations at equilibrium may then be used to find ΔF^o, the standard free energy



1-X X/2

change between the two conformations. The expression for ΔF^o is:

$$\Delta F^o = -RT\ln K$$

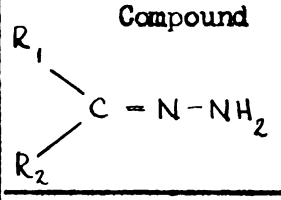
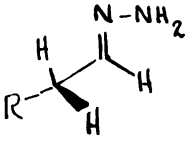
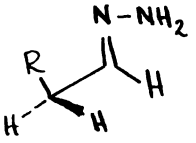
or

$$\Delta F^o = -RT\ln\frac{x/2}{1 - x}$$

The values found for ΔF^o are shown in Table IV.

Table III

Conformer Percentages of Syn Aldehydic Hydrazones

Monosubstituted aldehydic hydrazones	Conformation					
Compound 	 IX$_a$ + IX$_b$			 VIII		
	Correction per alkyl substituent					
	.3	.5	.7	.3	.5	.7
R_1 = H R_2 = CH_2CH_3	79%	82%	85%	21%	18%	15%
R_1 = H R_2 = CH_2i-Pr	82%	84%	86%	18%	16%	14%
R_1 = H R_2 = $CH_2C_6H_5$	86%	89%	90%	14%	11%	10%

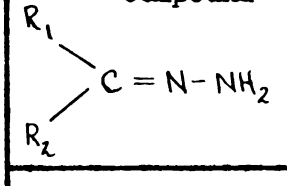
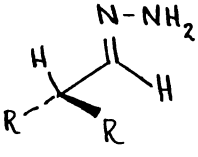
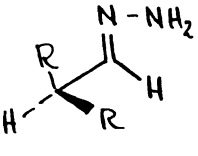
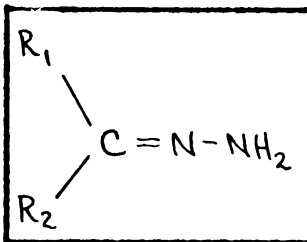
Disubstituted aldehydic hydrazones	Conformation					
Compound 	 X			 XIa + XI$_b$		
	Correction per alkyl substituent					
	.3	.5	.7	.3	.5	.7
R_1 = H R_2 = i-Pr	39%	43%	46%	61%	57%	54%
R_1 = H R_2 = $CH(Et)_2$	56%	57%	59%	44%	43%	41%
R_1 = H R_2 = CH(i-Pr)$_2$	60%	61%	61%	40%	39%	39%

Table IV

ΔF° Values for the Conformations of Syn Aldehydic Hydrazones

	ΔF° cal. mole^{-1}		
	Correction used in determing K		
	.3	.5	.7
$R_1 = H \quad R_2 = CH_2CH_3$	-388	-519	-636
$R_1 = H \quad R_2 = CH_2$i-Pr	-506	-595	-688
$R_1 = H \quad R_2 = CH_2C_6H_5$	-688	-856	-923
$R_1 = H \quad R_2 =$ i-Pr	-150	-252	-328
$R_1 = H \quad R_2 = CH(Et)_2$	-583	-597	-648
$R_1 = H \quad R_2 = CH($i-Pr$)_2$	-675	-701	-701

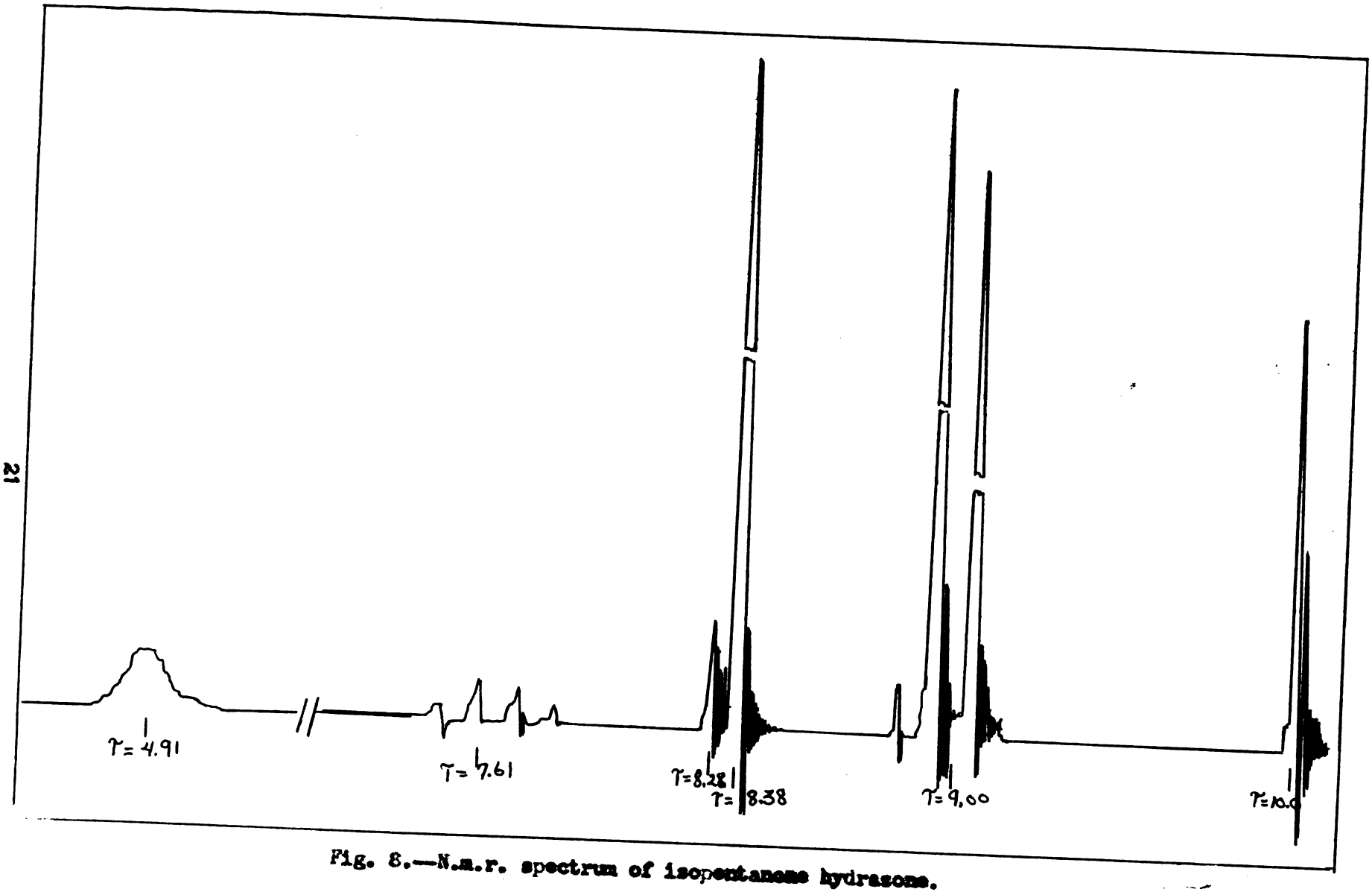


Fig. 8.—N.m.r. spectrum of isopentanone hydrazone.

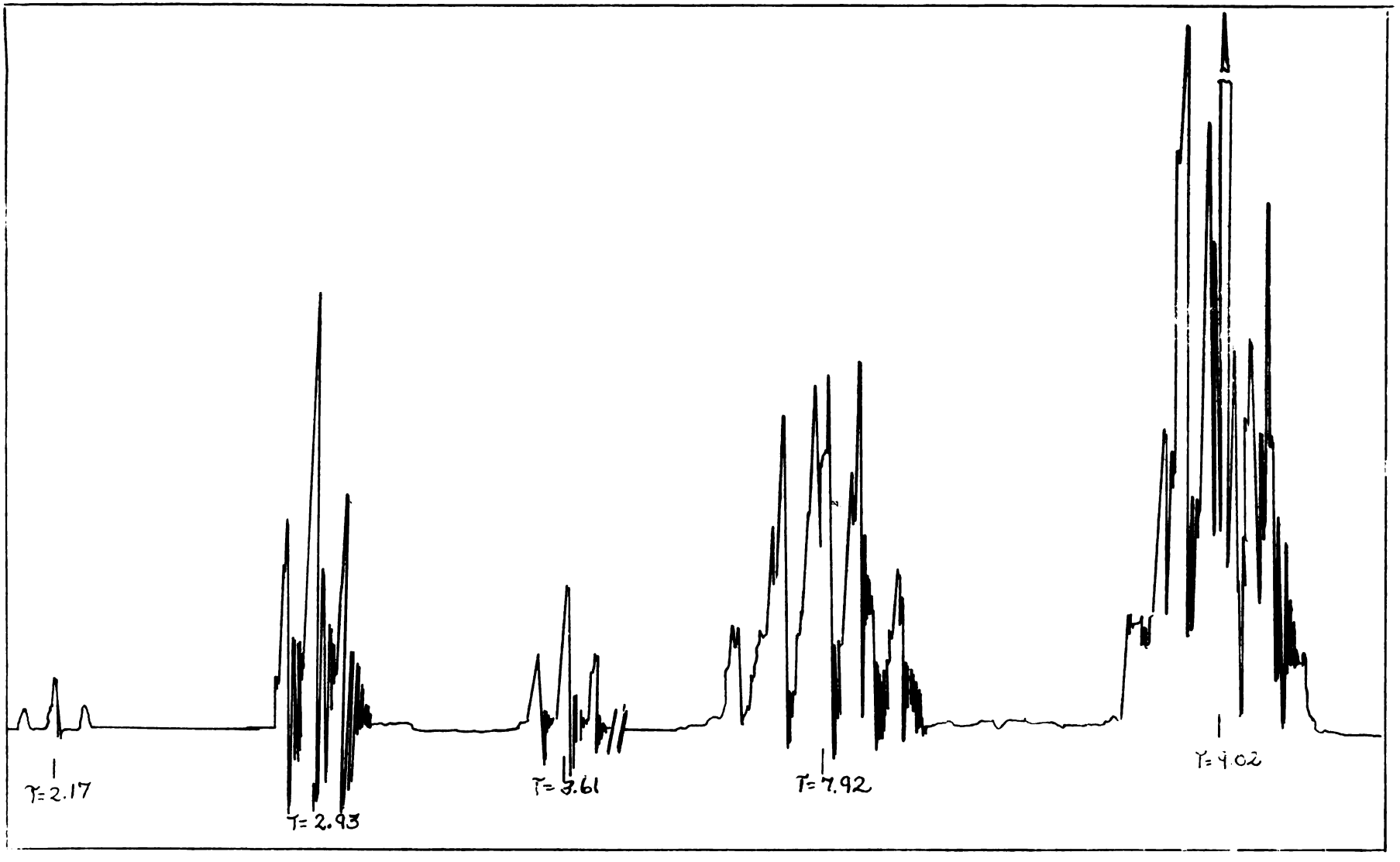
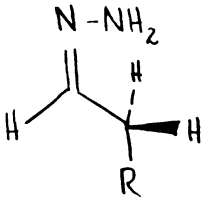


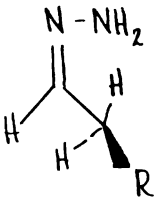
Fig. 9.—N.m.r. spectrum of propionaldehyde hydrazone, small triplet downfield is from azine.

Conformations of the anti Isomers

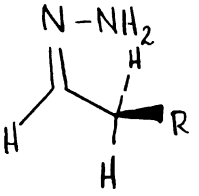
It can be observed from Table II that for the monosubstituted aldehydic hydrazones the trans coupling constant in each case is less than the cis coupling constant; e.g. $J_{H_1H_\alpha}$ = 5.60 c.p.s. for the syn form of isopropylacetaldehyde hydrazone and for the anti form $J_{H_1H_\alpha}$ = 4.93 c.p.s. This would seem to indicate that for the anti monosubstituted acetaldehyde hydrazones conformation XII is more stable than conformation XIII, since conformation XII has two gauche couplings



XII



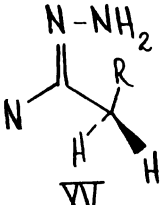
XIII



XIV

whereas XIII has one gauche and one trans coupling. Conformation XIV would have approximately the same coupling constant as XIII and would not explain the decrease.

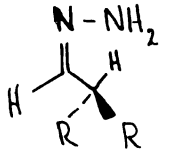
Another explanation for the decrease could be that the more stable conformation for the anti forms of the monosubstituted acetaldehyde hydrazones is conformation XV. This seems



XV

unreasonable since there would be considerable steric interaction between the alkyl group and the amino group in this conformation.

When the disubstituted anti aldehydic hydrazones are compared with the syn disubstituted aldehydic hydrazones it can be seen that they have much larger coupling constants; e.g. J_{H_1H} = 6.32 c.p.s. for diethylacetaldehyde hydrazones in the syn form, while for the anti form J_{H_1H} = 8.10 c.p.s.



XVI

Conformation XVI then is the more stable conformation for the anti disubstituted acetaldehyde hydrazones.

Half-Widths

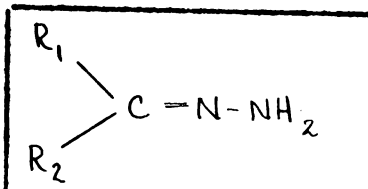
Table V shows the half-widths of the aldehydic protons, H_1, and the α-methyl protons of several hydrazones. They were measured in an effort to determine if coupling was occurring with the protons of the amino group. Although some of the half-widths are larger than would be expected for no coupling, there are no specific trends. From these data it is impossible to make any definite statements regarding coupling between the amino protons and the α-methyl protons or the aldehydic protons, H_1, of these hydrazones.

Anisotropic Effects of the Carbon-Nitrogen Double Bond

It was shown from the coupling constants that for the

Table V

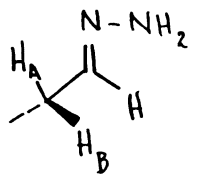
Half-Widths of α-methyl Protons and Aldehydic Protons

	Half-width of α-CH_3 (c.p.s.)		Half-width of H_1 (c.p.s.)	
	cis	trans	cis	trans
$R_1 = CH_3$ $R_2 = CH_2CH_3$	1.20	1.0		
$R_1 = CH_3$ $R_2 = t\text{-Bu}$	.50			
$R_1 = CH_3$ $R_2 = CH_2C_6H_5$	.70	.70		
$R_1 = H$ $R_2 = CH_3$	.55	.70	.71	1.10
$R_1 = H$ $R_2 = CH_2CH_3$			.74	1.07
$R_1 = H$ $R_2 = CH_2\text{i-Pr}$			.63	.93
$R_1 = H$ $R_2 = CH_2C_6H_5$			.84	.97
$R_1 = H$ $R_2 = CH_2t\text{-Bu}$			.80	.98
$R_1 = H$ $R_2 = CH(Et)_2$			.65	.70
$R_1 = H$ $R_2 = CH(\text{i-Pr})_2$			.89	.70
$R_1 = H$ $R_2 = \text{i-Pr}$			.61	.78

syn-hydrazones, when R is changed from methyl to isopropyl to t-butyl, conformation IX is more stable than conformation VIII. Similarly for the disubstituted acetaldehyde hydrazones, conformation X becomes more stable than conformation XI as the R groups increase in size.

Table VI shows what this change in conformation does to the chemical shifts. The chemical shifts, accurate to ± 1 c.p.s., are expressed in c.p.s. downfield from tetramethyl silane (0 c.p.s.). From the table it can be seen that as the α-proton spends more time in the plane of the carbon-nitrogen double bond the resonance shifts to higher magnetic fields; e.g. the α-methine proton of dimethylacetaldehyde hydrazone resonates at 140 c.p.s., whereas the α-methine proton of diisopropylacetaldehyde hydrazone resonates at 90.6 c.p.s. That is, a proton in the plane of the carbon-nitrogen double bond is shielded with respect to one above or below the plane. This behavior is opposite to that generally accepted for carbonyl compounds (26).

The difference between $\nu_{H(A)}$ and $\nu_{H(B)}$ may be due to

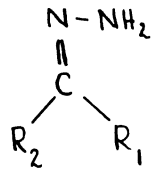


the anisotropy of the carbon-nitrogen double bond or hyperconjugation which can occur with protons in position (B), but not in position (A).

Table VI

Chemical Shifts, in c.p.s., of the

Syn Aldehyde and Syn Ketone Hydrazones

	ν (α-CH_3)	ν(α-CH_2)	ν(α-CH)
R_1 = H R_2 = CH_3	101.5		
R_1 = H R_2 = CH_2CH_3		125	
R_1 = H R_2 = CH_2i-Pr		121	
R_1 = H R_2 = CH_2t-Bu*		120.5	
R_1 = H R_2 = $CH_2C_6H_5$		201	
R_1 = H R_2 = CH(Me)$_2$			140
R_1 = H R_2 = CH(Et)$_2$			117
R_1 = H R_2 = CH(i-Pr)$_2$			90.5
R_1 = CH_3 R_2 = CH_3	108		
R_1 = CH_3 R_2 = CH_2CH_3		128	
R_1 = CH_3 R_2 = $CH_2C_6H_5$		206.5	
R_1 = CH_3 R_2 = CH(Me)$_2$			143.5

All spectra are neat solutions run at 60 Mc and 36° except those indicated by *, the latter were run in EtOH.

This behavior has also been demonstrated for carbonyl compounds and other carbonyl derivatives (27).

Syn/Anti Ratios

The percentages of the syn and anti isomers of various hydrazones are shown in Table VII. The values were determined from integration of peak areas and are accurate to $\pm$ 5%. In all cases the disubstituted aldehyde hydrazones and the α,α-disubstituted ketone hydrazones show a larger percentage of syn isomer than any of the monosubstituted hydrazones. It is interesting to note that for the disubstituted acetaldehyde hydrazones the percentage of the anti form increases as R changes from methyl to ethyl to isopropyl. It would seem from steric considerations, that the trend would be the other way.

Table VII

Syn/Anti Composition of Hydrazones; Neat

$R_1 \diagdown C-N-NH_2 \diagup R_2$	% syn	% anti
R_1 = Me R_2 = Et	77.8%	22.2%
R_1 = Me R_2 = i-Pr	93.1%	6.9%
R_1 = Me R_2 = $CH_2C_6H_5$	78.5%	21.5%
R_1 = Me R_2 = t-Bu	100%	
R_1 = H R_2 = Me	51.2%	48.7%
R_1 = H R_2 = i-Pr	90.7%	9.3%
R_1 = H R_2 = $CH(Et)_2$*	86.9%	13.1%
R_1 = H R_2 = $CH(i\text{-}Pr)_2$[a]	83.7%	16.3%
R_1 = H R_2 = $CH_2(t\text{-}Bu)$[a]	72.5%	27.5%

[a] Some EtOH present

* Value may be slightly in error due to small azine peak underneath the cis proton peak.

EXPERIMENTAL

Apparatus

The reactions were carried out in a 100 ml. round bottom flask equipped with a condenser. To the top of the condenser was added a small separatory funnel for the addition of the aldehyde or ketone.

Reaction Procedure

A 4 gram sample (3.88 ml. or 0.08 moles) of 100% hydrazine hydrate, 5 ml. of ethyl alcohol, and 15.3 g. (0.10 moles) of barium oxide were placed in a 100 ml. round bottom flask and cooled to 0° with an ice bath. To the magnetically stirred solution was added, over a period of a half hour, a solution containing 4.53 g. (.078 moles or 5.73 mls.) of acetone in 5 ml. of ethyl alcohol. After the addition was completed the reaction was allowed to stir for 10 minutes. The reaction mixture was then cooled and shaken with ether. After filtration the ether-hydrazone mixture was distilled under vacuum. The material boiling from 115-120° was collected.

The above procedure was followed for the other compounds with variations in time and reaction temperature. For example, all ketone hydrazone derivatives, except acetone hydrazone, were allowed to stir for three hours at room temperature after addition of the ketone.

N.M.R. Spectra

A Varian A-60 n.m.r. spectrometer operating at approximately 36° was used to obtain all spectra. The undegassed samples were run in thin-walled A-60 sample tubes. Tetramethylsilane was used as an internal reference standard (τ = 10.00). The chemical shifts were measured from sweep widths of 500 c.p.s. and 250 c.p.s. Spin-spin coupling were obtained from a sweep width of 50 c.p.s.

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