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The Correlation of Spectra and Steric Effects in Alkyl and Aryl Hydrazones

Dennis J. Weber

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THE CORRELATION OF SPECTRA AND STERIC EFFECTS IN
ALKYL AND ARYL HYDRAZONES

A Thesis
Presented to
The Faculty of the School of Graduate Studies
Western Michigan University

In partial fulfillment
of the requirement for
the degree of Master of Arts
in Chemistry

by
Dennis J. Weber
Kalamazoo, Michigan
August, 1962

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ACKNOWLEDGMENT

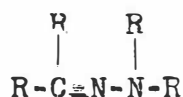
The author wishes to express his appreciation to Dr. Don C. Iffland for his excellent guidance and for the freedom granted in the preparation of this thesis.

Acknowledgment is also hereby given to the Upjohn Company for financial assistance towards the Master of Arts degree and especially the Department of Physical and Analytical Chemistry for the use of equipment and some material and time for this project.

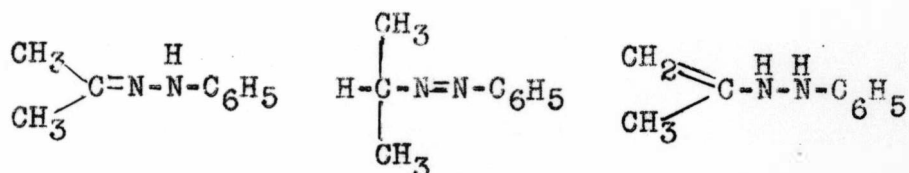
I also express my sincere thanks to Mr. Forrest MacKeller for his assistance in preparing and interpreting the NMR spectra, to Mrs. Betty Zimmer for her patience and time in helping obtain the ultraviolet absorption curves and to Mr. Arthur Crowley for his aid in the interpretation of the infrared spectra.

INTRODUCTION

The correlation of spectra, especially ultraviolet spectra, of hydrazones with their structure has resulted in considerable confusion because of the variations in spectra obtained from apparently the same basic chromophore. This chromophore is usually written as

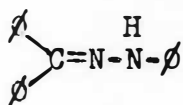


where R may be an alkyl or aryl group. Thus, P. Grammaticakis (9-13) prepared a large number of substituted hydrazones, recorded their ultraviolet spectra and concluded from the data that fresh solutions of the hydrazones were in the form as usually written and not in the azo or ene-hydrazine form. The possible related hydrazone, azo, and ene-hydrazine tautomeric structures for the case of acetone phenylhydrazone are illustrated.

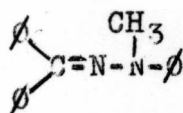


O'Connor (19) using nuclear magnetic resonance techniques concurred with the conclusion obtained by Grammaticakis. Ramart-Lucas (20-22) also noted the variations in ultraviolet spectra of substituted phenylhydrazones but was not able to explain the basic reason for the differences observed. Ramart-Lucas (21) makes the statement that the changes in ultraviolet spectra may be due to "deformations

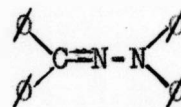
of valence angles". It is not stated which of the angles of the chromophore are deformed or what kind of deformation is involved. Dr. D. C. Iffland of these laboratories noted marked differences in the ultraviolet spectra of the following compounds



benzophenone
phenylhydrazone



benzophenone methyl
phenylhydrazone



benzophenone
diphenylhydrazone

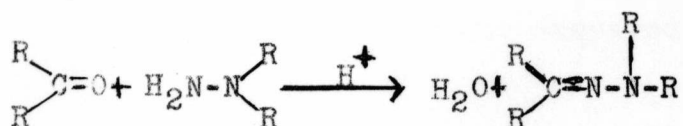
and proposed that possibly the preparation of a sufficient number of N-substituted and N,N-disubstituted hydrazones and determination of their spectra might permit a rationalization of the spectra observed. With this objective in mind the work described in this thesis was begun.

EXPERIMENTAL

In the following experimental section all melting points and boiling points are uncorrected. All temperatures are expressed in degrees centigrade.

A. Preparation of Hydrazones

All of the hydrazones were prepared by reaction of a ketone or aldehyde with the appropriate substituted hydrazine to give the desired product according to the general equation:



The necessary aldehydes, ketones and hydrazines were available commercially or previously prepared in this laboratory. Since the preparative procedures for all the hydrazones were nearly identical and differ only in details of purification a single example is given which is representative:

Acetophenone Phenylhydrazone. - Acetophenone (2.28 g., 0.019 mole), was condensed with phenylhydrazine (2.06 g., 0.019 mole) in 25 ml. of absolute ethanol containing 0.5 ml. of acetic acid. After heating on a steam bath for one hour the reaction mixture was mixed with water. White needles formed and were recrystallized from EtOH to obtain 3.6 g. (90% yield) of hydrazone, M. p. 105°. Literature value: 105° (4)

All of the liquid hydrazones were dried with an appropriate drying agent (anhydrous sodium sulfate, molecular

sieve, etc.) and distilled (under vacuum if necessary).

The infrared spectra of all the prepared hydrazones were determined on a Perkin-Elmer Model 221 prism-grating recording spectrophotometer and in all cases the expected absorption bands were present. In the case of the monosubstituted hydrazones the 3300 cm^{-1} N-H absorption band was present, and in the case of the disubstituted hydrazones it was absent. Whenever possible the spectra were compared to the published spectra of an authentic sample of the compound.

The physical characteristics of the prepared hydrazones are included in Table I.

B. Determination of Ultraviolet Spectra

The ultraviolet spectra were determined on a Cary recording spectrophotometer (Model 14) using matched one centimeter cells. All samples were dissolved in 95% ethanol. The spectra of the protonated hydrazones were measured in 6N alcoholic HCl. Examples of the spectra obtained are in Figures 3-5 and a compilation of the ultraviolet data is in Table II. The Cary spectrophotometer records the change in absorbance (ordinate) with the change in wavelength in millimicrons (abscissa). The curves are analysed by calculating the molar absorptivity (ϵ) for the peaks from the equation $A = \epsilon bc$, where b is the length of light path through the sample, c is the concentration in moles/liter, and A is the observed absorbance.

C. Determination of Nuclear Magnetic Resonance Spectra

The NMR spectra of all the hydrazones were determined on a 60 megacycle Varian A60 NMR spectrometer. All data are reported in c.p.s. downfield from tetramethyl silane (less than 2% concentration by volume). The samples were prepared for analysis by dissolving in a suitable non-hydrogen containing solvent (e.g. CCl_4) or in deuterated solvents (e.g. CDCl_3 , etc.). The specific solvents used are listed in the tabulation of NMR data in Table III. All of the samples were run using tetramethyl silane (Anderson Chemical Co.) as an internal standard. The Varian A60 instrument contains an automatic integrating mechanism to determine the number of hydrogens present. By using the number of hydrogens found, the splitting patterns of the spectrum, and their relative positions on the frequency scale, assignments of structure were made consistent with the peaks in the spectrum. A tabulation of peak frequencies and their associated partial structures are included in Table III.

TABLE I

Properties of Hydrazones

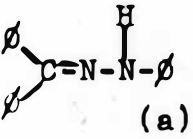
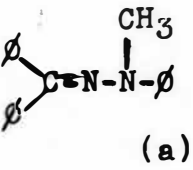
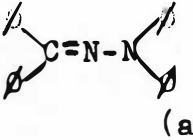
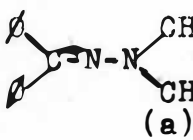
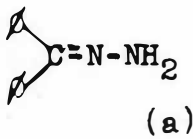
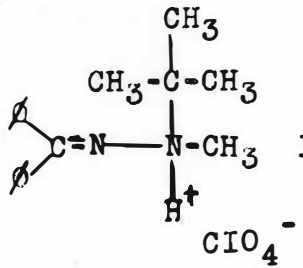
Structure of Compound	M.p.	B.p.	Mm.	Analysis		
	$^{\circ}\text{C}$	$^{\circ}\text{C}$		C	H	N
 (b) (a)	137			83.84% 83.79*	5.88% 5.92	
 (c) (a)	79			84.03 83.88	6.18 6.33	
 (d) (a)	147					8.20% 8.04
 (e) (a)	183		15	80.68 80.51	6.84 7.20	
 (f) (a)	99			79.44 79.60	6.45 6.17	
 (g) (a)	149					7.78 7.64

TABLE I

Properties of Hydrazones (cont'd)

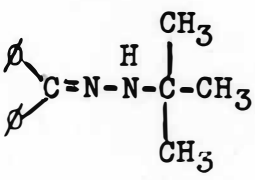
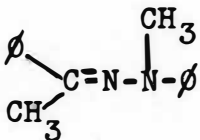
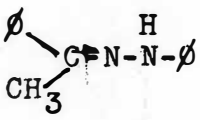
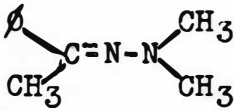
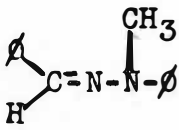
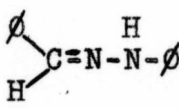

Structure of Compound	M.p.	B.p.	Mm.	Analysis		
	<u>°C</u>	<u>°C</u>		<u>C</u>	<u>H</u>	<u>N</u>
 (a)	(h) 77					
 (i)	47			80.5 80.5	7.16 7.20	
 (j)	104			79.9 80.0	3.67 6.72	
 (k)		78	1	74.1 74.1	8.92 8.70	
 (l)	105			79.9 79.9	6.61 6.71	
 (m)	158			79.3 79.6	6.39 6.17	
 (n)		120	5	72.7 72.9	7.70 8.16	

TABLE I
Properties of Hydrazones (cont'd)

Structure of Compound	W.p.	B.p.	Mm.	Analysis		
	<u>°C</u>	<u>°C</u>		<u>C</u>	<u>H</u>	<u>N</u>
$\begin{array}{c} \text{H} \\ \diagup \\ \text{C}=\text{N}-\text{N}-\text{CH}_3 \\ \diagdown \\ \text{H} \end{array}$		(o) 162	18			20.67 20.90
$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{N}-\text{N}-\phi \\ \diagdown \\ \text{CH}_3 \end{array}$	(p) 24					18.43 18.90
$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{N}-\text{N}-\phi \\ \diagdown \\ \text{CH}_3 \end{array}$		(q) 94-95	3			17.2 17.2
$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{N}-\text{N} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{array} \\ \diagdown \\ \text{CH}_3 \end{array}$	94		atm. press.	(r) 58.29 59.94	11.74 12.07	27.32 28.02
$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{N}-\text{N}-\text{CH}_3 \\ \diagdown \\ \text{CH}_3 \end{array}$	115		atm. press.	(s) 54.10 55.70	11.20 11.28	31.58 32.50
$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{N}-\text{NH}_2 \\ \diagdown \\ \text{CH}_3 \end{array}$	124		(t) atm. press.			
(a)						

Footnotes for Table I

- (a) Sample was received from Dr. D. Iffland
- (b) Literature value m.p. 137-138° (14)
- (c) Literature value m.p. 81-82° (4)
- (d) Literature value m.p. 145.5° (4)
- (e) Prepared by L. Salisbury, Analysis, Calculated for $C_{15}H_{16}N_2$: N, 12.51; found: N, 12.47
- (f) Literature value m.p. 97-98 (1)
- (g) Prepared by Dr. D. Iffland, Analysis, Calculated for $C_{18}H_{23}O_4NCl$: eq.wt., 366.8; found: eq.wt. 365.2
- (h) Literature value m.p. 73.5-78.5 (25)
- (i) Literature value m.p. 50° (21)
- (j) Literature value m.p. 104° (4)
- (k) Literature stated only that liquid did not crystallize at -15° (26)
- (l) Literature value m.p. 104° (13)
- (m) Literature value m.p. 158° (14)
- (n) Literature value b.p. 100° at 3mm, (32)
- (o) Literature value b.p. 81° at 8mm, (31)
- (p) Literature value m.p. 26.6° (18)
Infrared spectrum identical to curve of authentic sample (23)
- (q) Literature value b.p. 94-102 at 9mm. (19)
- (r) This compound contains 2.42% water by Karl Fischer titration. Recalculation of percent nitrogen, carbon and hydrogen allowing for water gives: found: N28.00, C59.72, H11.74. No previous preparation reported.
- (s) This compound contains 2.72% water by Karl Fischer titration. Recalculation of percent nitrogen, carbon and hydrogen allowing for water content gives: found: N, 32.46 C, 55.36 H, 11.20. No previous preparation reported.
- (t) Literature value b.p. 56-58 at 61mm (15)
- (*) Second value is theory calculated for structure indicated.

TABLE II

Ultraviolet Absorption Data of Hydrazones

Compound	Solvent	λ max. mu	ϵ	λ max. mu	ϵ	λ max. mu	ϵ	λ max. mu	ϵ
ϕ ϕ -C=N-N- ϕ	95 Alc.	237	18,590	298	11,360	340	20,560		
	Alc. HCl	228	12,100	272	14,100	384	3,100		
ϕ - ϕ -CH ₃ C=N-N- ϕ	95 Alc.	254	22,350	290 sh.	4,905	364	7,404		
	Alc. HCl	231	12,700	285	17,750			429	3,000
ϕ - ϕ - ϕ C=N-N- ϕ	95 Alc.	250	21,740	300	8,501	364	6,926		
ϕ - ϕ -CH ₃ C=N-N-CH ₃	95 Alc.	239	13,300	320	3,750				

Ultraviolet Absorption Data of Hydrazones (cont.)

Compound	Solvent	λ max.	ϵ	λ max.	ϵ	λ max.	ϵ	λ max.	ϵ
$\phi - \overset{\overset{\text{H}}{ }}{\underset{\underset{\text{N}-\text{N}-\text{H}}{ }}{\text{C}}}=\text{N}$	95 Alc.			272	11,650				
	Alc. HCl			258	16,800				
$\phi - \overset{\overset{\text{CH}_3\text{CH}_3}{ \quad }}{\underset{\underset{\text{N}-\text{N}-\text{C}-\text{CH}_3}{ \quad }}{\text{C}}}=\text{N}$	95 Alc.			248 sh.	12,100			332	4,100
$\phi - \overset{\overset{\text{H}^+ \quad \text{CH}_3}{ \quad }}{\underset{\underset{\text{N}-\text{N}-\text{C}-\text{CH}_3}{ \quad }}{\text{C}}}=\text{N}$ Alc. KOH ClO_4^-	.01 Molar Alc. KOH	236	12,900	250 sh.	11,500			330	4,100
$\phi - \overset{\overset{\text{H} \quad \text{CH}_3}{ \quad }}{\underset{\underset{\text{N}-\text{N}-\text{C}-\text{CH}_3}{ \quad }}{\text{C}}}=\text{N}$	95 Alc.	222 sh.	12,600			288	12,900		
	Alc. HCl	208	End Ab- sorption			255	16,250		
$\text{CH}_3 - \overset{\overset{\phi}{ }}{\underset{\underset{\text{N}-\text{N}-\phi}{ \quad }}{\text{C}}}=\text{N}$	95 Alc.			250	20,900	288	2,650	347	3,850
	Alc. HCl			244	14,450	278 sh.	2,000	358	195

TABLE II

Ultraviolet Absorption Data of Hydrazones (cont.)

<u>Compound</u>	<u>Solvent</u>	<u>λ max.</u>	<u>ϵ</u>	<u>λ max.</u>	<u>ϵ</u>	<u>λ max.</u>	<u>ϵ</u>	<u>λ max.</u>	<u>ϵ</u>
$\text{CH}_3 - \underset{\text{H}}{\overset{\phi}{\text{C}}} = \text{N} - \text{N} - \phi$	95 Alc.	232	12,850	244 sh.	11,500	302 sh.	13,750	330	19,900
	Alc. HCl	230	11,958	247	11,573	276 sh.	3,880	346	1,450
$\text{CH}_3 - \underset{\text{CH}_3}{\overset{\phi}{\text{C}}} = \text{N} - \text{N} - \text{CH}_3$	95 Alc.	228	13,050			308	2,100		
	Alc. HCl	247	11,700			280 sh.	1,400		
$\text{H} - \underset{\text{CH}_3}{\overset{\phi}{\text{C}}} = \text{N} - \text{N} - \phi$	95 Alc.	236	15,950	244 sh.	13,400	304 sh.	12,650	334	26,200
	Alc. HCl			250	13,250	286 sh.	2,000	342	311
$\text{H} - \underset{\text{H}}{\overset{\phi}{\text{C}}} = \text{N} - \text{N} - \phi$	95 Alc.	237	14,300	243 sh.	13,750	302	11,100	344	24,100
	Alc. HCl	232	10,450	250	2,300	292 sh.	1,400	364	55

TABLE II

Ultraviolet Absorption Data of Hydrazones (cont.)

<u>Compound</u>	<u>Solvent</u>	<u>λ max.</u>	<u>ϵ</u>	<u>λ max.</u>	<u>ϵ</u>	<u>λ max.</u>	<u>ϵ</u>	<u>λ max.</u>	<u>ϵ</u>
$\begin{array}{c} \phi \quad \text{CH}_3 \\ \quad \\ \text{H}-\text{C}=\text{N}-\text{N}-\text{CH}_3 \end{array}$	95 Alc.	222	8,700			295	17,300		
$\begin{array}{c} \phi \quad \text{H} \\ \quad \\ \text{H}-\text{C}=\text{N}-\text{N}-\text{CH}_3 \end{array}$	95 Alc.	218	9,450			284	15,600		
	Alc. HCl			250	13,350	282 sh.	1,550		
$\begin{array}{c} \text{CH}_3 \quad \text{H} \\ \quad \\ \text{CH}_3-\text{C}=\text{N}-\text{N}-\phi \end{array}$	95 Alc.	End Absorption				270	16,800		
	Alc. HCl	222	14,450			273	3,050		
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3-\text{C}=\text{N}-\text{N}-\phi \end{array}$	95 Alc.			249	10,900	283	3,350		
	Alc. HCl	229	6,550			270	710		

TABLE II

Ultraviolet Absorption Data of Hydrazones (cont.)

<u>Compound</u>	<u>Solvent</u>	<u>λ max.</u>	<u>ϵ</u>	<u>λ max.</u>	<u>ϵ</u>	<u>λ max.</u>	<u>ϵ</u>	<u>λ max.</u>	<u>ϵ</u>
$\text{CH}_3 - \overset{\text{CH}_3}{\underset{ }{\text{C}}} = \text{N} - \overset{\text{CH}_3}{\underset{ }{\text{N}}} - \text{CH}_3$	95 Alc.			266	950 ^(b)				
	Alc. HCl			No Apparent Absorption					
$\text{CH}_3 - \overset{\text{CH}_3}{\underset{ }{\text{C}}} = \text{N} - \overset{\text{H}}{\underset{ }{\text{N}}} - \text{CH}_3$	95 Alc.	227	4,460 ^(b)						
	Alc. HCl			242	80				
$\text{CH}_3 - \overset{\text{CH}_3}{\underset{ }{\text{C}}} = \text{N} - \text{NH}$	95 Alc.	212 sh.	3,850						
	Alc. HCl	No Apparent Absorption							

(a) Principle absorption bands are tabulated approximately in order of increasing wavelength. Bands indicated in the same column may not arise from corresponding excitation.

(b) Concentration corrected for water content in calculating ϵ .

TABLE III

NMR Absorption of Hydrazones

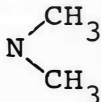
<u>Compound</u>	<u>Absorption Frequency (c.p.s.)</u>	<u>Number of Hydrogens Found</u>	<u>Partial Structure Indicated</u>
Benzophenone phenylhydrazone (a)	-537	1	NH
	-397 to -467	15	Ø
Benzophenone methylphenyl- hydrazone (a)	-171	3	N-CH ₃
	-460 to -400	15	Ø
Benzophenone diphenyl- hydrazone (a)	-470 to -400	20	Ø
Benzophenone dimethyl- hydrazone (a)	-153	6	
	-460 to -435	10	Ø
Benzophenone hydrazone (a)	-460 to -425	10	Ø
	-325	2	NH ₂
Benzophenone methyl-tert. butyl hydrazone- perchlorate salt (a)	-475 to -440	10	Ø
	-180	3	N-CH ₃
	-87	9	t-butyl
Benzophenone tert. butyl- hydrazone (a)	-425 to -468	10	Ø
	-308	1	N-H
	-72	9	t-butyl
Acetophenone methylphenyl- hydrazone (a)	-186	3	N-CH ₃
	-131	3	N=C-CH ₃
	-480 to -405	10	Ø

TABLE III

NMR Absorption of Hydrazones (Cont'd)

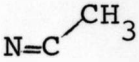
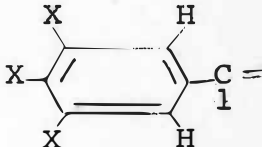
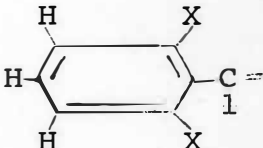
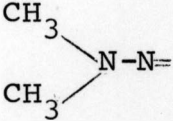
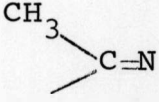
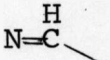
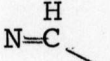
<u>Compound</u>	<u>Absorption Frequency (c.p.s.)</u>	<u>Number of Hydrogens Found</u>	<u>Partial Structure Indicated</u>
Acetophenone phenylhydrazone (a)	-137	3	
	-561	1	NH
	-475 to -400	10	∅
Acetophenone dimethyl- hydrazone (a)	-463	2	
	-430 to -445	3	
	-153	6	
	-138	3	
Benzaldehyde methylphenyl- hydrazone (b)	-205	3	N-CH ₃
	-462	1	
	-470 to -410	10	∅
Benzaldehyde phenyl- hydrazone (b)	-478	1	
	-716	1	N-H
	-470 to -400	10	∅

TABLE III

NMR Absorption of Hydrazones (Cont'd)

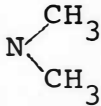
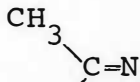
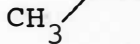
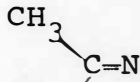
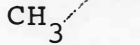
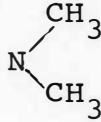
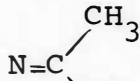
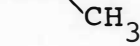
<u>Compound</u>	<u>Absorption Frequency (c.p.s.)</u>	<u>Number of Hydrogens Found</u>	<u>Partial Structure Indicated</u>
Benzaldehyde dimethyl- hydrazone (a)	-171	6	
	-460 to -432	6	$\text{O}-\underset{\text{H}}{\text{C}}=\text{N}$
Benzaldehyde methyl- hydrazone (a)	-425 to -460	6	$\text{O}-\overset{\text{H}}{\text{C}}=$
	-333	1	-NH
	-169	3	N-CH ₃
Acetone phenyl- hydrazone (a)	-395 to -445	6	$\text{O}-\overset{\text{H}}{\text{N}}-$
	-101	3	
	-117	3	
Acetone methyl- phenyl hydrazone (a)	-400 to -445	5	O
	-176	3	N-CH ₃
	-113	3	
	-123	3	
Acetone dimethyl- hydrazone (a)	-144	6	
	-117	3	
	-114	3	

TABLE III

NMR Absorption of Hydrazones (Cont'd)

<u>Compound</u>	<u>Absorption Frequency (c.p.s.)</u>	<u>Number of Hydrogens Found</u>	<u>Partial Structure Indicated</u>
Acetone methyl- hydrazone (a)	-273	1	N-H
	-172	3	N-CH ₃
	-114	3	CH ₃
	-103	3	$ \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \\ \text{CH}_3 \end{array} $
Acetone hydrazone (a)	-105 and -114	3	methyl
	-110 and -120	3	methyl
	-285	2	N-NH ₂

Footnotes to Table III

(a) solvent used was CDCl₃(b) solvent used was D₇DMF (Deuterodimethylformamide)

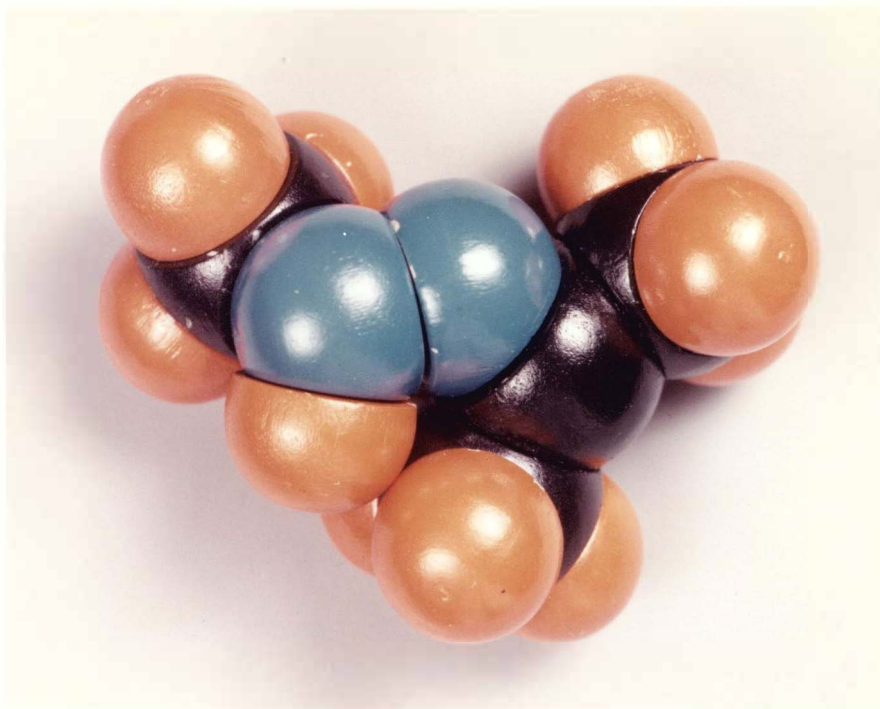


Fig. I Molecular Model of Acetonemethylhydrazone



Fig. II Molecular Model of Acetonedimethylhydrazone

Ultraviolet Absorption Curves
Benzophenone Hydrazones

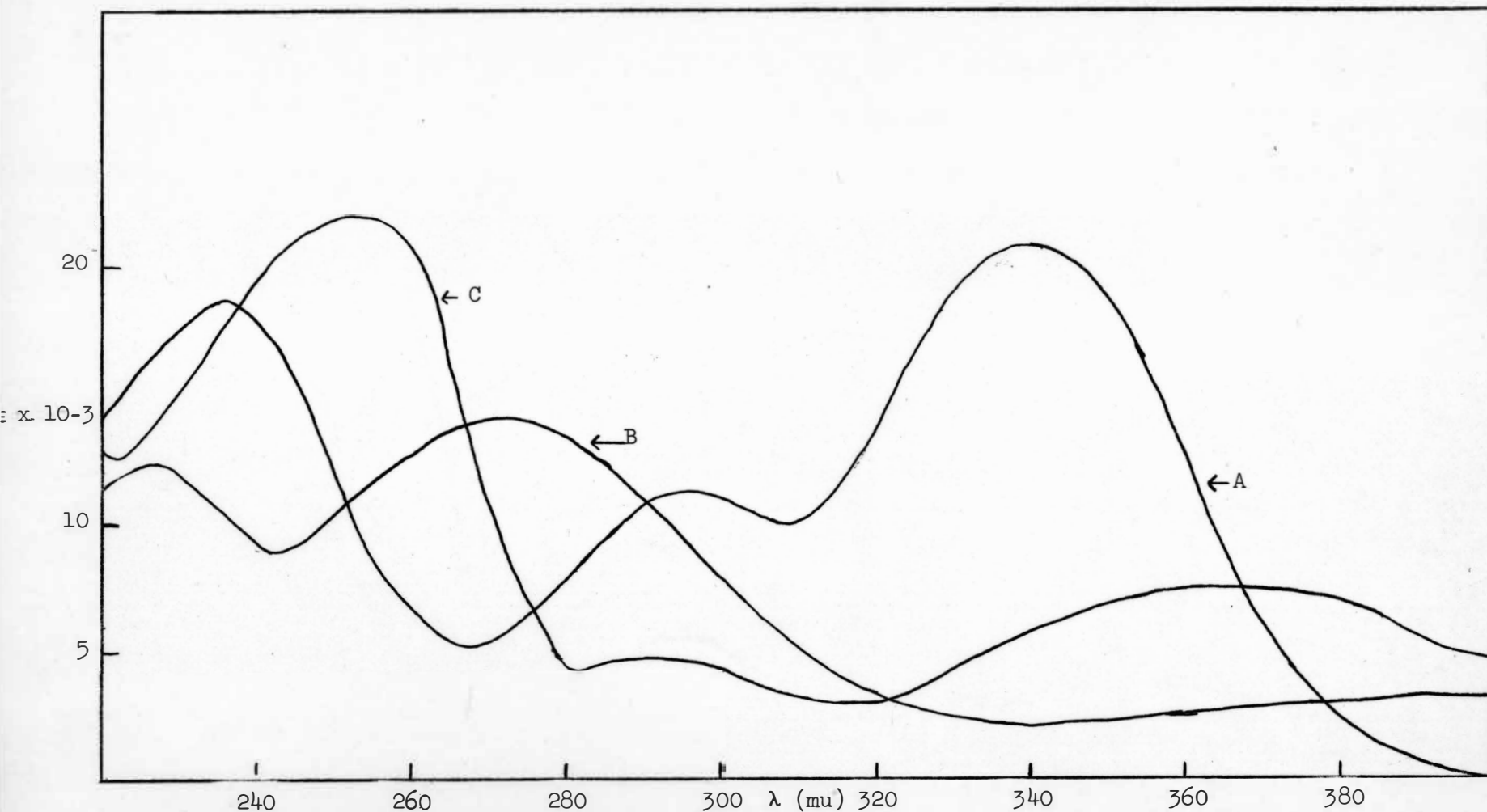


Figure III

- A - Benzophenonephenylhydrazone in Ethanol
- B - Benzophenonephenylhydrazone in Ethanolic HCl
- C - Benzophenonemethylphenylhydrazone in Ethanol

Ultraviolet Absorption Curves
Acetophenone Hydrazones

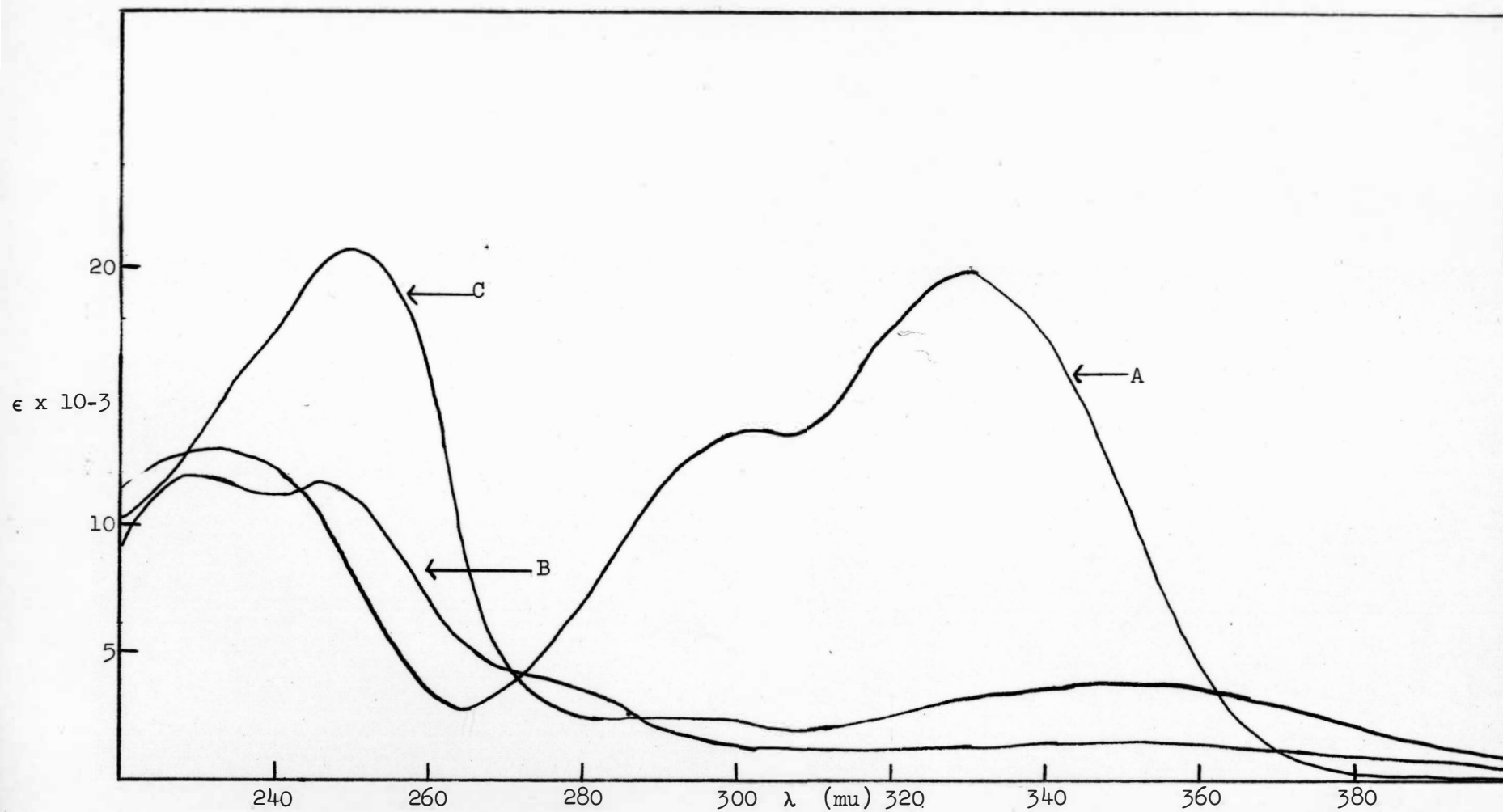


Figure IV

- A - Acetophenonephenylhydrazone in Ethanol
- B - Acetophenonephenylhydrazone in Ethanolic HCl
- C - Acetophenonemethylphenylhydrazone in Ethanol

Ultraviolet Absorption Curves
Benzaldehyde Hydrazones

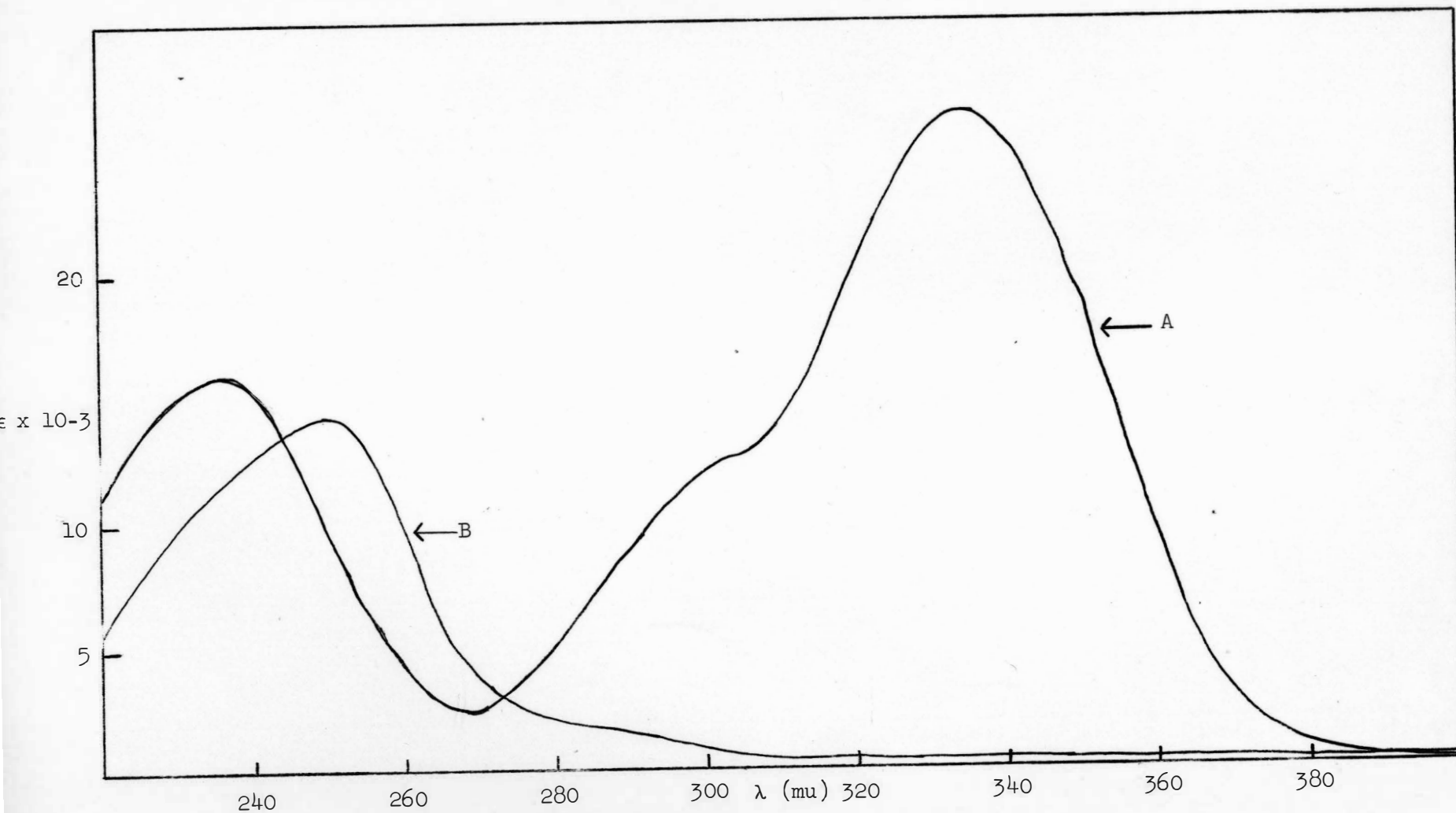


Figure V

A - Benzaldehydemethylphenylhydrazone in Ethanol

B - Benzaldehydemethylphenylhydrazone in Ethanolic HCl

Ultraviolet Absorption Curves

Acetone Hydrazones

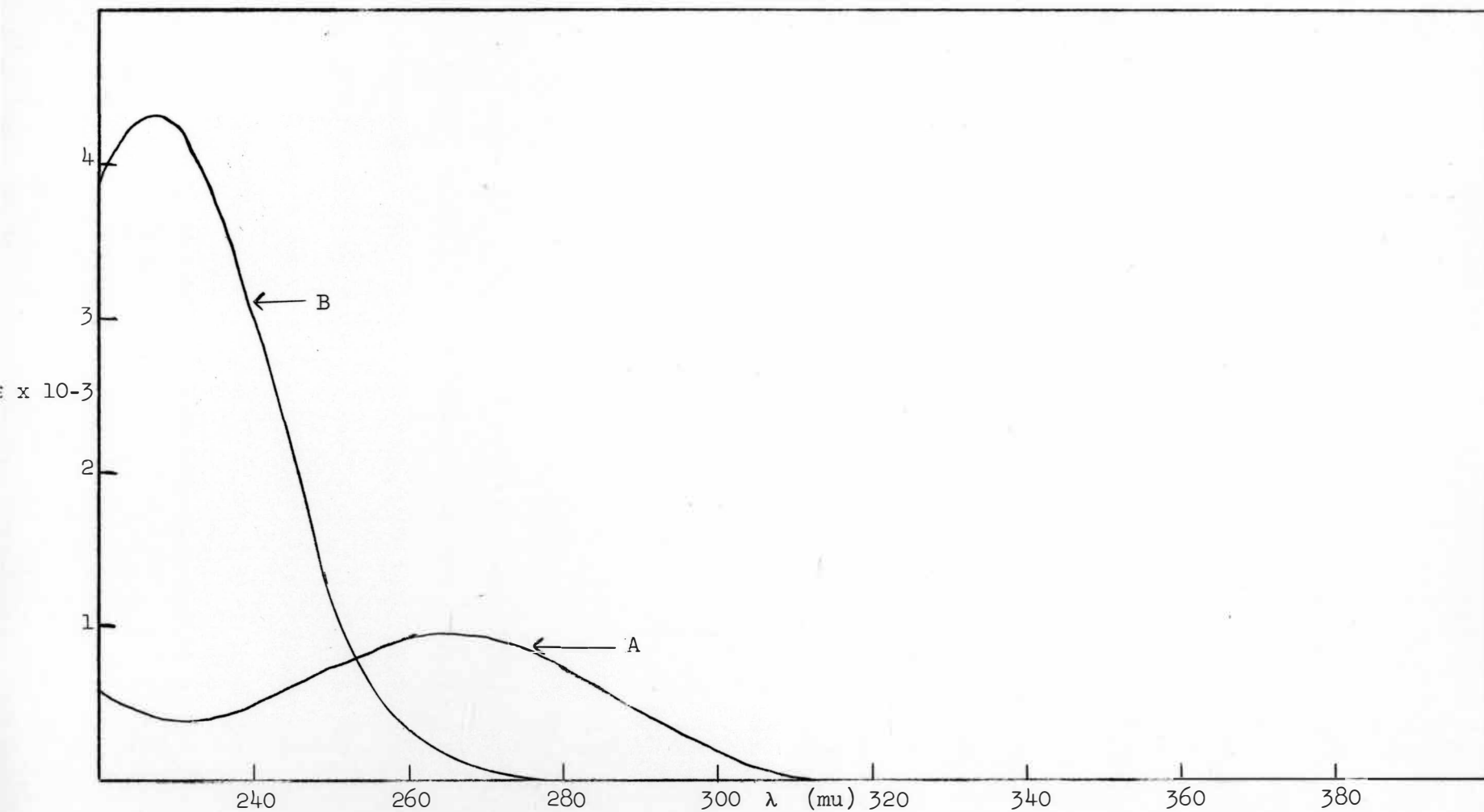


Figure VI

A - Acetonedimethylhydrazone in Ethanol

B - Acetonemethylhydrazone in Ethanol

DISCUSSION OF EXPERIMENTAL RESULTS

A. Ultraviolet Spectra1.) Phenylhydrazones of Aromatic Ketones and Aldehydes

The ultraviolet spectra of the phenylhydrazones of benzophenone, acetophenone and benzaldehyde are remarkably similar as can be seen from the data in Table II and from the UV curves in Fig. III-V. In all cases an exceptionally large absorbance occurs at about 340 mμ, a somewhat smaller absorbance, frequently a shoulder, at about 300 mμ and then a peak at about 235 mμ with an absorbance intermediate between the first two. The uniformity of the UV data strongly indicates that the chromophores giving rise to the spectra are the same in all three cases. It has already been demonstrated that the compounds exist as the hydrazone tautomer in freshly prepared solutions (cf. p.5).

Another compound, benzaldehydemethylphenylhydrazone, also exhibits very nearly the same UV spectrum as the phenylhydrazones of benzophenone, acetophenone and benzaldehyde. The conclusion is reached that the same chromophores exist in solution in all four compounds and that the effect of the methyl substituted nitrogen in benzaldehydemethylphenylhydrazone on the chromophore is nil. This is not too surprising since UV spectra involve transitions in the energy of electrons and it is well known that alkyl groups have only a small electron releasing capability (inductive and

hyperconjugative effects).

2.) The UV Spectra of Benzophenonemethylphenylhydrazone and Acetophenonemethylphenylhydrazone.

The profound effect on the UV spectrum of benzophenone-phenylhydrazone and acetophenonephenylhydrazone when a methyl group is substituted for the hydrogen on the terminal nitrogen is apparent from the data presented (cf. Fig. III). This change consists essentially of a drastic lowering of the absorbance of the 340 and 300 mu bands (hypochromic effect) and a shift to longer wave lengths of the 340 mu band (bathochromic shift). The band near 235 mu rises in intensity (hyperchromic effect) and shifts to a position near 250 mu. The effect of this substitution on benzaldehydephenylhydrazone has already been shown to be essentially nonexistent. Therefore, this profound change in spectra cannot be caused by any postulated electron releasing property of the methyl group.

It is to be noted that an examination of the three-dimensional model for the structure of these compounds reveals that the presence of the N-methyl group completely hinders free rotation about the N-N bond. This interference to rotation is caused by the close proximity of one of the substituents on the terminal nitrogen of the hydrazone to one of the groups on the parent carbonyl compound. This is clearly illustrated for the case of acetone-methylhydrazone and acetone-dimethylhydrazone in Fig. I and II.

3.) Effect of Strong Acid on the Spectra of Phenylhydrazones of Aromatic Ketones and Aldehydes

The UV spectra of acetophenonephenylhydrazone, benzaldehydemethylphenylhydrazone and benzaldehydephenylhydrazone in acid solution have no 340 mμ band but do have the 250 mμ band noted in the methylphenylhydrazones of these compounds. All three compounds also exhibit a low intensity band around 350 mμ. The spectrum of benzophenonephenylhydrazone in acid solution also has the low intensity band near 360 mμ but does not have the 250 mμ band. The reason for the lack of the 250 mμ band is not readily apparent; however, it must be realized that in acid solution there is a positive charge on the molecule that alters the electron distribution and which in this case may have more effect. The UV spectrum of benzaldehyde has peaks at 244 and 279 mμ and log ϵ values of 4.11 and 2.98 respectively (28).

When the hydrazones are dissolved in strong acid solution the amino nitrogen is protonated, thus, effectively preventing the delocalization of the extra pair of electrons and preventing their promotion to higher energy states and accompanying absorption of ultraviolet light *.

A comparison of the spectra of the hydrazones in acid solution to the spectra of the tetra-substituted hydrazones

* The amino nitrogen is protonated rather than the imino nitrogen because it is more basic.

in ethanol reveals a striking similarity. In both cases there is no 340 mμ band and the general characteristics of the spectra are the same (cf. Table II and Fig. III-V).

4.) The UV Spectra of Alkyl Hydrazones of Aromatic Ketones and Aldehydes.

A number of mono and dialkyl hydrazones of benzophenone, acetophenone and benzaldehyde were prepared and their electronic spectra were compared to determine if corresponding changes occur as were observed in the case of the aromatic hydrazones. In the case of benzophenone-dimethylhydrazone a small absorbance at 320 mμ was observed and a much larger one at 239 mμ. This pattern is similar to that found in benzophenonemethylphenylhydrazone except there is one less band. The loss of the band is probably due to the lack of an aromatic ring on the hydrazine part of the molecule. The important point to be made here is that the band at higher wavelength has a low absorbance. The same general pattern is obtained from the spectrum of benzophenonemethyl-t-butylhydrazone salt when run in ethanol or alkaline solution. The spectrum of acetophenonedimethylhydrazone is also similar to that of other tetra-substituted hydrazones and is essentially unchanged in acid solution. The spectra of compounds containing the H-H or C-H moiety are similar to the corresponding aromatic hydrazones. The data for benzophenone-t-butylhydrazone, benzaldehydedimethyl-

hydrazone and benzaldehydemethylhydrazone are given in Table II and are in essential agreement with the above analysis. In the case of benzophenone-t-butylhydrazone and benzophenonehydrazone spectra in acid solution, it is seen that the only peak corresponds to the expected absorbance of benzophenone itself*. This may be due to extremely rapid hydrolysis. A kinetic study might be carried out to confirm this.

5.) Aromatic and Aliphatic Hydrazones of Acetone

In an attempt to determine the electronic spectra of the fundamental hydrazone chromophore in the hindered and unhindered forms, a series of acetone hydrazones were prepared. In the case of acetonephenylhydrazone a single large absorption peak at 270 mμ was observed. Both the absorption and wavelength were low in comparison to the aromatic ketones and most likely reflects the saturated nature of the ketone. In acid solution there is the usual drop in absorbance of the longer wavelength peak. The peaks at 273 and 222 mμ are most likely due to the methylaniline type chromophore with allowance for the effect of the positive charge on the molecule (See footnote on next page). The peak at 269 mμ for acetone is lost in the baseline.

* The ultraviolet spectral data for benzophenone is given on page 37

A consideration of the effect of methyl groups or hydrogen at all four of the substitution positions in the fundamental hydrazone chromophore reveals again the same pattern as encountered before. Thus, a comparison of acetone methyl and dimethyl hydrazones shows the drop in absorption (hypochromic effect) and the rise in wavelength (bathochromic shift). It should be noted that the data for acetone methylhydrazone in acid solution is very close to experimental error and is not too reliable.

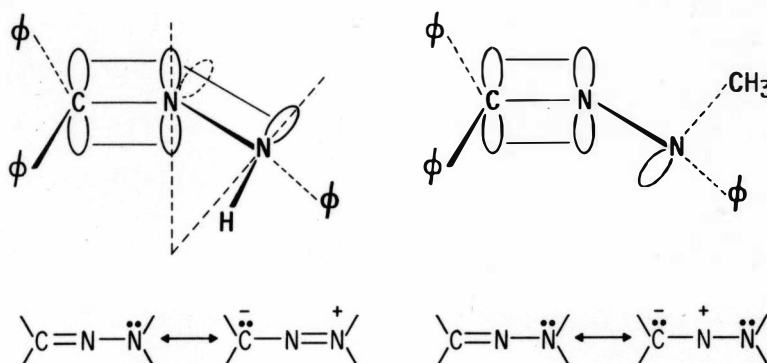
6.) Interpretation of Steric Hindrance Effect on UV Spectra

Each of the nitrogens in the fundamental hydrazone chromophore have a non-bonding pair of electrons and these undoubtedly have an effect on the UV spectra. The unshared pair of electrons on the terminal nitrogen are likely in a sp^3 hybridized atomic orbital analogous to carbon where the electron orbitals are directed in space to the apexes of

The UV spectral data for the pertinent substituted anilines and acetone are: (28)

	<u>λ_{\max}</u>	<u>$\log \epsilon$</u>
acetone	269 μ	1.20
methylaniline	240	4.0
	294	3.18
dimethylaniline	251	4.11
	298	3.28

a tetrahedron. The nonbonding electrons on the imino nitrogen are reasonably in an sp^2 orbital. Inspection of Fig. I and II reveal that when there is a hydrogen on the terminal nitrogen or on the carbon of the parent carbonyl compound then rotation (in excess of 180°) about the N-N bond is allowed and it becomes possible for the non-bonding sp^3 orbital of the terminal nitrogen to be coplanar with the p orbital of the imino nitrogen. This is illustrated by the diagram below for the case of benzophenone-phenylhydrazine and benzophenonemethylphenylhydrazine.



It is postulated that the formation of a non-linear, non-localized π bond (hereafter designated as a pseudo π bond) results from overlap of the p and sp^3 atomic orbitals and is an important factor in describing the ground state of the unhindered hydrazones. There is some evidence that the formation of a pseudo π bond between a p and sp^3 orbital can occur in other systems as well. Wepster (30) has shown that the UV spectra of 2,4,6-tri-*t*-butyl-N-methylaniline can be explained by an sp^3 hybridization

of the amino nitrogen and partial overlap of the non-bonding sp^3 orbital with the π orbital system of the phenyl ring. It should be noted, however, that in the case of the phenyl and methylphenylhydrazones full overlap of the sp^3 nonbonding orbital with the π orbital system of the phenyl ring is allowed. This is added evidence that the 250 μ band noted previously is partially due to the N-substituted aniline type chromophore. It is not likely that the 340 μ band is caused by overlap of the two non-bonding orbitals (sp^2 and sp^3) because both orbitals are filled with electrons*. Therefore, one of the orbitals would have to be emptied in some manner and the use of the sp^3 orbital would be involved in a second order effect.

In the less likely situation that the terminal nitrogen has sp^2 hybridization, the non-bonding electrons in trisubstituted hydrazones occupy a p orbital which may become parallel with the adjacent p orbital resulting in more efficient overlap. This situation is analogous to that observed in the bent, non-localized π bond system of the carboxylic acid group. The planar sp^2 nitrogen atom would enhance molecular crowding (relative to sp^3)

* According to the Pauli exclusion Principle more than two electrons per orbital is forbidden.

in the tetra-substituted system and also predict a twisted molecule. It is conceivable that the true situation is intermediate between these two extremes.

If, however, we consider the case where there are no hydrogens on either the carbonyl carbon or on the nitrogen containing the phenyl ring, then the possibility of formation of the pseudo N-N π bond is excluded from consideration for steric reasons and the formation of the chromophores giving rise to the benzophenonephenylhydrazone type UV spectrum is impossible. The overall effect of this forced twisting of the N-N bond is to effectively cut in two the extended chain of non-bonding electron - π conjugation of the fundamental hydrazone chromophore and results in formation of two new, isolated, chromophores*. Of the two newly formed chromophores, one is an N-substituted aniline type and the other is analogous to that of an aromatic ketone with the oxygen replaced by a nitrogen.

* The isolation of chromophores by steric effects has been classified by Forbes. The tetra-substituted hydrazones fit the Forbes classification type three. In this group, the original chromophore is completely divided and absorbs as two different chromophores. See reference 30, chapter 6, page 62.

The aromatic imino group is, electronically, very much like the original ketone. In both cases the carbonyl carbon is doubly bonded to an atom having filled, non-bonding orbitals. It can be seen from the data that the UV spectra of the rotationally hindered hydrazones do indeed exhibit the principal peaks that would be expected from an aromatic ketone and N-substituted aniline*. The fact that the principal band of benzophenone, acetophenone and dimethylaniline all fall about 250 mμ also explains the hyperchromic effect on the absorbance of the band around 235 mμ and its bathochromic shift to around 250 mμ which has been noted previously.

Since the 340 mμ band in the unhindered hydrazone spectra is the one that is nearly lost when steric hindrance is introduced, then this must be related to the extended conjugation across the >C=N-N< chromophore.

* The λ_{max} and $\log \epsilon$ values for the pertinent ketones and dimethylaniline are: (28)

	<u>λ_{max}</u>	<u>$\log \epsilon$</u>
benzophenone	254 mμ	4.25
	333	2.20
acetophenone	242	4.25
	279	3.03
dimethylaniline	251	4.11
	298	3.28

It is interesting to note that in the case of the disubstituted hydrazones of benzaldehyde the UV spectra require that the terminal nitrogen be anti to the phenyl ring of the parent benzaldehyde and the configuration of other aldehyde hydrazones may be predicted on the basis of an examination of the UV spectra.

A suggested means of further investigating the effects of N-N bond rotation on the UV spectra of hydrazones would be the preparation of a series of compounds in which the ends of the hydrazone chromophore are linked by carbon bridges of various lengths. It should then be possible to observe a change in the absorption of the 340 mμ band as the length of the carbon bridge is changed.

B. Nuclear Magnetic Resonance Spectra

At the beginning of this study it was thought that the differences in UV spectra might possibly be due to tautomerism. With this in mind the NMR spectra were obtained to determine the proportion of the solute sample in solution that is in each form. However, even though no tautomerism was involved it was thought worthwhile to continue the determination of the NMR spectra for purposes of checking for the purity of the prepared hydrazones; also, since the NMR spectra of many of these compounds have not been determined previously they are included in this thesis as a source of reference material.

It was considered possible that the NMR spectra might also be used to determine the syn and anti conformation about the C=N bond in the hydrazone moiety. After inspection of the data it was found that in the case of the acetone hydrazones there was evidence for the presence of two different types of methyl groups. The acetone methyls absorb separately near -110 cps. The less negative peak is most likely the one that is due to the methyl group anti to the nitrogen substituent because it is less shielded and therefore absorbs at a less negative frequency.

The NMR spectra of the acetophenone hydrazones also show the effects of the syn and anti configuration by the fact that the phenyl hydrogens are split into two distinct groups. The ortho hydrogens absorb in a group slightly downfield from the meta and para hydrogens. In this case, however, there is no easy means of determining if the splitting is caused by the amino nitrogen being syn or anti to the phenyl ring. There is the possibility, however, that substitution on the phenyl ring may further differentiate the aromatic hydrogens and allow an easier interpretation of the data.

In NMR spectra the proximity of a nonbonding pair of electrons has a decided and predictable effect on the absorption frequency of the nearby protons. The effect of the nonbonding electrons is to shield the nearby protons and to cause them to absorb at a more negative frequency. A con-

sideration of the proximity of the non-bonding electrons on the terminal nitrogen to one of the methyl groups in the acetone hydrazones reveals that this particular methyl group should absorb at a more negative frequency in the case of the di-substituted hydrazones. This is indeed the case as can be seen from Table III. Only in the acetone hydrazones is the differentiation of the above noted effects easily made. In most of the other cases, geometric isomerism makes the interpretation more difficult. Benzophenone hydrazones avoid syn-anti isomerism but the aromatic hydrogens are difficult to separate. With this supporting NMR evidence the credibility of the outlined interpretation of the UV spectra is enhanced.

SUMMARY

A large number of aromatic and alkyl hydrazones of various carbonyl compounds have been prepared and their electronic and NMR spectra obtained. The basic reason for the difference in electronic spectra of mono and di substituted hydrazones has been shown to be due to steric interference between the substituents on the extreme ends of the >C=N-N< system and electronic interpretation has been presented. The data support previous evidence showing that fresh solutions of hydrazones do not contain any detectable amounts of the azo or ene-hydrazine forms.

The NMR spectra of a large number of hydrazones have been determined for the first time and provide confirmation of the presence of a steric factor and suggest a possible means of assigning configuration to the isomeric hydrazones.

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VITA

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He completed one semester at Kalamazoo College. He was married to Shirley Standish in April 13, 1953 and has fathered six children.

Resuming his studies at Western Michigan University in September 1954, he received a Bachelor of Science degree in Chemistry in July 1958 from this institution. While attending the School of Graduate Studies at Western Michigan University, he was employed as an analytical chemist at The Upjohn Company.

APPROVAL OF EXAMINING COMMITTEE

(Chairman)

Date
