THE PHOTOCHEMISTRY OF NITRAMINES, I: PREPARATION OF NITROXIDES IN SOLUTION AND IN SITU IN SINGLE CRYSTALS

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THESIS

THE PHOTOCHEMISTRY OF NITRAMINES, I: PREPARATION OF NITROXIDES IN SOLUTION AND *IN SITU* IN SINGLE CRYSTALS

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The Photochemistry of Nitramines, I:
Preparation of Nitroxides in Solution
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ABSTRACT

Ultraviolet irradiation of cyclic nitramines, both in solution and as single crystals, reveals an EPR signal due to nitroxide radicals. Photolysis of solutions of nitramines in 1,3-propanediol cyclic carbonate in the EPR cavity allowed preparation and assignment of the spectra of pyrrolidine N-oxide, piperidine N-oxide, morpholine N-oxide, 4-methylpiperidine N-oxide, 4-t-butylpiperidine N-oxide, 4-nitropiperazine N-oxide, 3-nitro-1,3,-diazacyclohexane N-oxide, and 3,5-dinitro-1,3,5-triazacyclohexane N-oxide. Photolysis of N-nitropyrrolidine and N-nitromorpholine single crystals led to <u>in situ</u> generation of pyrrolidine N-oxide and morpholine N-oxide respectively, and hyperfine tensors for both nitrogen and hydrogen coupling were assigned.

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ACKNOWLEDGEMENT

I would like to take this opportunity to thank Dr. Charles F. Rowell, my thesis advisor, for his aid and encouragement throughout the course of this study.

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I. INTRODUCTION

Investigations into the photodecomposition of nitramines have had inconsistent results. Since the chemistry of RDX and HMX is complicated by the fact that the nitramine groups are separated by only one carbon, studies on simpler model nitramines was undertaken by Lt. Harry Whittaker [1]. During the course of his investigations he found that irradiation of N,N'-dinitropiperazine in the cavity of an EPR spectrometer gave a signal due to a radical intermediate.

Assignment of this and intermediates of the photodegradation of nitramines would be of great help in determining the mechanism of breakdown. Therefore, the aim of this investigation was to assign and to study the intermediates using EPR techniques.

II. HISTORICAL

A. THE DECOMPOSITION OF NITRAMINES

The use of the cyclic nitramines RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane as military explosives has led to interest in their stability and "shelf life." Studies of thermal and photochemical decomposition of nitramines have, therefore, centered on RDX and HMX.

Results on thermal decomposition of nitramines are still too variable to allow any definite conclusion to be drawn about the mechanism. Some results are listed below:

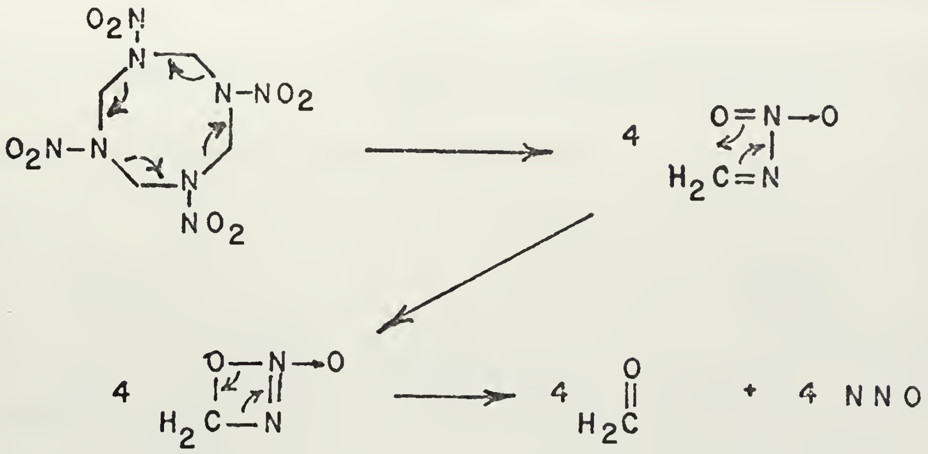
TABLE I: THERMAL DECOMPOSITION PRODUCTS OF NITRAMINES
(as percent of total product)

Investigator	Suryanarayana, *et*. *al*.	Maksinov	Robertson	Robertson
Nitramine	HMX	HMX	HMX	RDX[1]
N_2O	40.0		38.5	14.0
NO	9.9	Major[2]	16.6	17.2
N_2	9.6		18.5	34.4
HCN	4.5			
CH_2O	8.5	Major[2]	Present[2]	Present[2]
CO_2	8.5		9.4	22.4
CO	4.1		16.4	11.2
H_2				0.2
H_2O			Present[2]	Present[2]
Reference	2	3	4	4

[1] also "considerable solid residue"

[2] quantity not reported

Suryanarayna [2] proposed the following mechanism for the thermal degradation of HMX based on nitrogen-15 tracer studies:



Flourney [5] found that the thermal products of dimethylnitramine (1 mole) were dimethylnitrosamine (0.80 moles), nitromethane (0.14 moles), water (0.44 moles), and small amounts of CO_2, CO, NO_2, NO, and N_2. The reaction was first order and unaffected by addition of NO. From these data this mechanism was proposed:

$$(CH_3)_2NNO_2 \longrightarrow (CH_3)_2N\cdot + NO_2 \quad \text{(rate determining)}$$

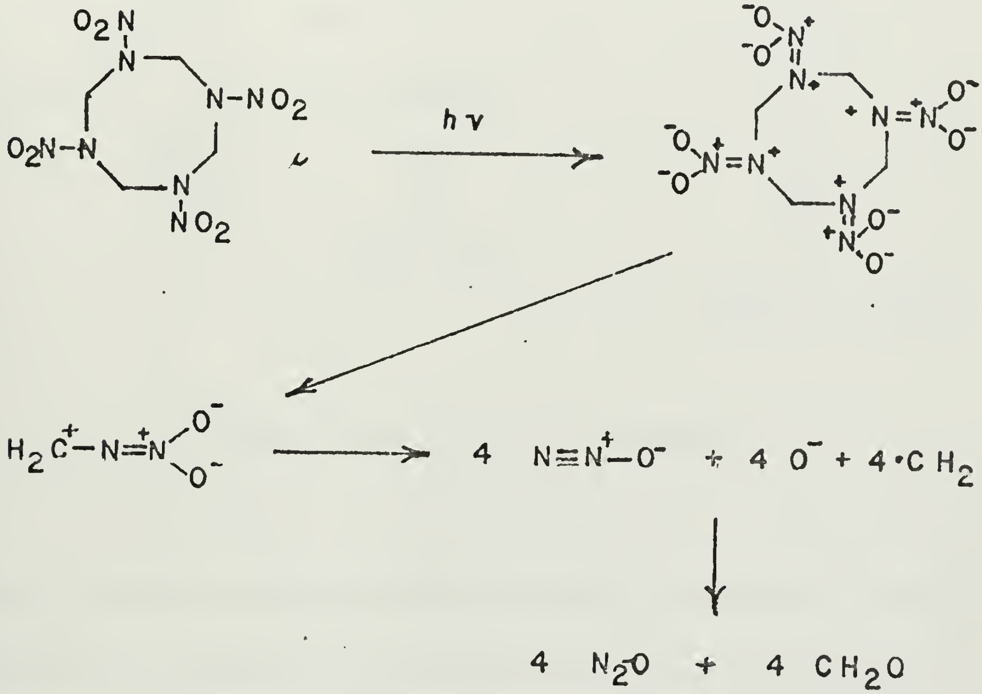
$$NO_2 + (CH_3)_2NNO_2 \longrightarrow NO + \text{oxidation products}$$

$$(CH_3)_2N\cdot + NO \longrightarrow (CH_3)_2NNO$$

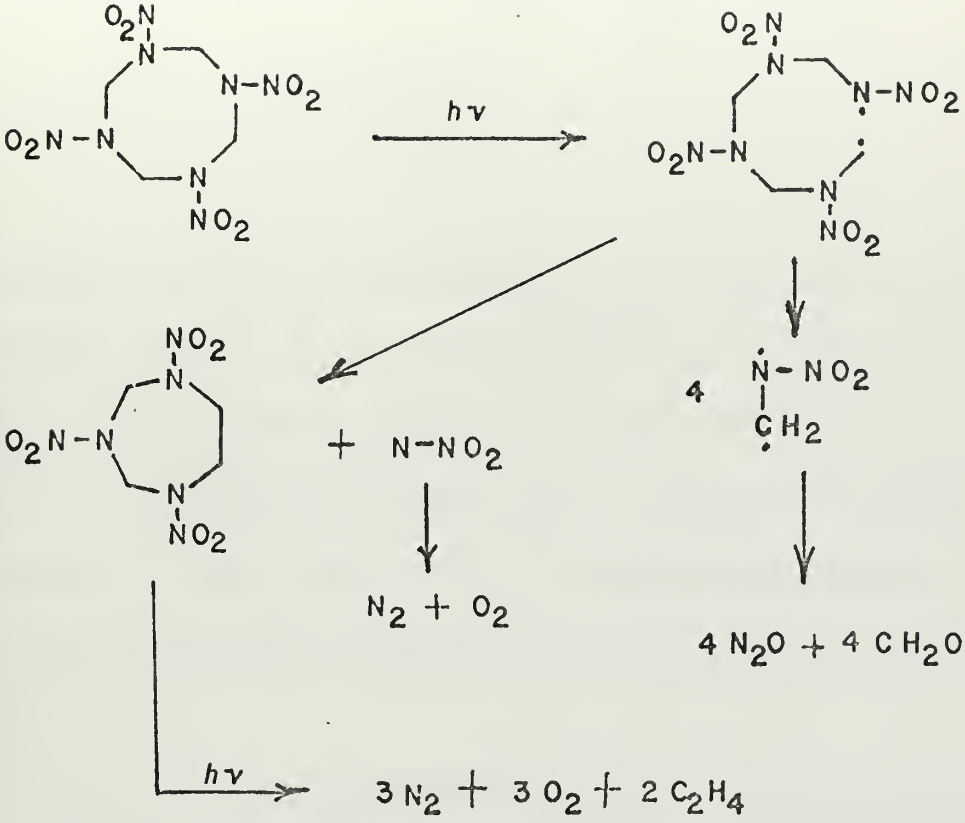
Hence, the investigations thus far have not demonstrated whether the breaking of a C-N or N-N bond is the first step in the degradation.

Similar variation has been found in the investigations into the mechanism for photochemical decomposition. The nitramine group

typically has an absorption maximum at about 230 mm with an ϵ of about 6,000 to 10,000. Ultraviolet light has been shown to lead to degradation. However, the mechanism is still in doubt. Maycock [6] reported the major products of ultraviolet irradiation as N_2O and CH_2O, and he suggested the following mechanism for their formation:



Torbitt [7] found that the photochemical products of HMX depended on the environment of irradiation. In acetone solution N_2, C_2H_2, O_2, CO_2, and N_2O were liberated; solid HMX in a vacuum gave off N_2, C_2H_4, and O_2; under a Helium atmosphere solid HMX degraded to N_2, C_2H_4, CH_2O, and N_2O. In acetone an unidentified solid product was also reported. The data were consistent with the proposed mechanism:

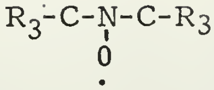


There is only one study in the literature which attempts to characterize possible intermediates in the decomposition. This study [8] reports that RDX powder or RDX in acetonitrile solution will give an EPR signal upon irradiation. No assignment of the spectrum was made.

B. NITROXIDES

Recently there has been much interest in substituted nitroxide free radicals due to their stability and ease of characterization by EPR. These properties have led to extensive use of these radicals as spin labels for organic compounds.

Organic nitroxides have the structure:

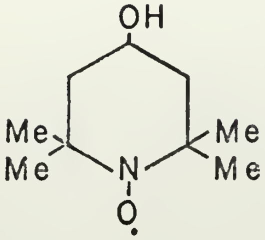


$$R_3\text{-}C\text{-}\underset{\underset{\bullet}{O}}{N}\text{-}C\text{-}R_3$$

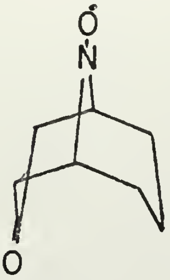
The unpaired electron is localized largely in the nitrogen and oxygen p orbitals, leading to a characteristic EPR spectrum with a N^{14} interaction (3 equally spaced and equally intense lines) of 9 to 10 gauss spacing at X-band for aromatic β-carbons and 14 to 17 gauss for aliphatic β-carbons [9]. (See Table II.) If R = H further splitting is seen, but if all R are aliphatic, the spectrum consists of only the three N^{14} lines.

Nitroxides have been prepared in many ways: by oxidation of the corresponding amines or hydroxylamines either by metal ions [10,11], peroxides [12], or peracids [9]; by alkali metal reduction of nitro compounds [13]; photolysis of nitroso compounds [14]; photolysis of amines in the presence of oxygen [15]; or photolysis of hydroxylamines [16]. When any R = H, the radicals are short-lived and only a steady state concentration of the nitroxide can be detected by EPR techniques. However, if all substituents are aliphatic, the radicals are extremely stable, i.e. 2,2,6,6-tetramethyl-4-piperidinol N-oxide (I) can be recrystallized, characterized, and stored indefinitely. It undergoes reactions quite independent of the radical [17]. The nitroxide is also stable if the nitrogen

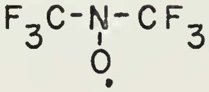
is in a bicyclic system as in norpseudopelletierine-N-oxide (II) [18].



I



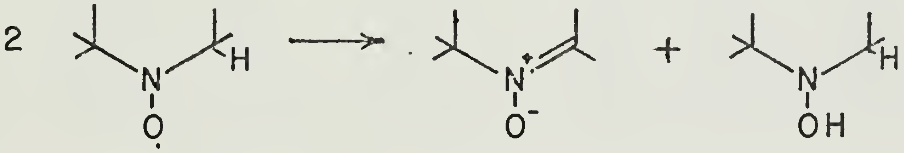
II



III

It has been shown that the decay of diethyl nitroxide is second order [19], and the cycloaddition product expected from a nitrone derived from diethyl nitroxide is formed when the nitroxide is allowed to decompose in the presence of methacrylate [20]. Bis (trifluoromethyl) nitroxide (III) has been synthesized and isolated as a stable product [21] suggesting that it is the lack of β-hydrogens rather than steric crowding that gives the β-tetraalkyl nitroxides their stability.

This data has led to the proposal of a bimolecular mechanism for decay of nitroxides to nitrones and hydroxylamines [18].



Thus, nitroxides without β-hydrogens are stable since this mechanism is impossible for them, as is the case for II since formation of the nitrone would result in a double bond at a bridgehead carbon which is forbidden by Bredt's rule.

TABLE II: CHARACTERISTIC NITROXIDE EPR SPECTRA

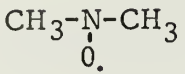
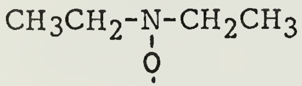
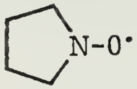
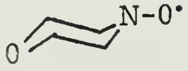
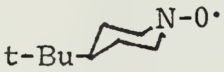
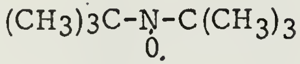
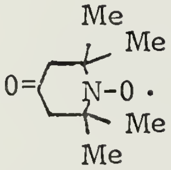
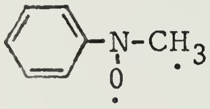
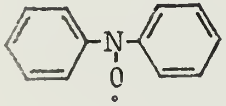
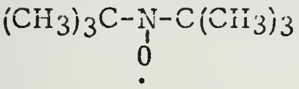
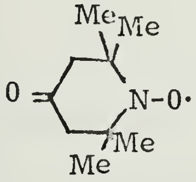
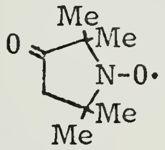
Nitroxide	Method of Formation	Solvent	Appearance of Spectrum	a_N	a_H	Ref.
 $CH_3-\underset{\overset{\vert}{O\cdot}}{N}-CH_3$	Oxidation of dimethylamine by p-nitroperoxybenzoic acid	CH_2Cl_2	3 × 7 lines; intensity = 1-6-15-20-15-6-1	16.1	13.4	9
 $CH_3CH_2-\underset{\overset{\vert}{O\cdot}}{N}-CH_2CH_3$	Oxidation of amine by p-nitroperoxybenzoic acid	CH_2Cl_2	3 × 3 lines; 1-2-1	15.0	4.4	9
	Oxidation of amine by p-nitroperoxybenzoic acid	CH_2Cl_2	3 × 5 lines; 1-4-6-4-1	14.9	19.6	9
	Oxidation of amine by p-nitroperoxybenzoic acid	CH_2Cl_2	3 × 5 lines: 1-I-4-I-1, I's are broad	16.8	$a_{ax}+a_{eq}$ $=22.6$	9
	Oxidation of amine by hydrogen peroxide	H_20	As above with each line split into 1-2-1	18.0	12.3 a $=0.75$	22
	Oxidation of amine by p-nitroperoxybenzoic acid	CH_2Cl_2	3 × 3 lines; 1-4-1	16.8	$a_{ax}+a_{eq}$ $=22.0$	9

TABLE II: CHARACTERISTIC NITROXIDE EPR SPECTRA (Continued)

Nitroxide	Method of Formation	Solvent	Appearance of Spectrum	a_N	a_H	Ref.
	Ultraviolet irradiation of 1-hydroxy-4-methylpiperidine	CH_2Cl_2	3 x 9 lines; 1-2-1-2-4-2-1-2-1 at -25°C.	16.85	$a_{ax}=19.6$ $a_{eq}=4.0$	16
	Oxidation of amine by hydrogen peroxide	H_2O	3 x 9 lines; 1-2-1-2-4-2-1-2-1	18.0	$a_{ax}=21.7$ $a_{eq}=4.1$	23
 $(CH_3)_3C-\underset{O\cdot}{N}-C(CH_3)_3$		di-t-butyl ketone	3 lines; 1-1-1	15.1		24
		di-t-butyl ketone	3 lines; 1-1-1	14.3		24
	Oxidation of amine by p-nitroperoxybenzoic acid	CH_2Cl_2	6 groups of lines	11.0	$a_o=2.9$ $a_p=2.9$ $a_m=1.0$ $a_H=10.4$	9
	Oxidation of amine by p-nitroperoxybenzoic acid	CH_2Cl_2	37 lines	10.1	$a_o=1.9$ $a_p=1.9$ $a_m=0.9$	9

Although many nitroxides have been characterized in solution, few studies of nitroxides in single crystals have been reported. Nitroxides with β-hydrogens are not stable enough to grow crystals or to be prepared and trapped in host crystals, and the customary techniques to prepare the radicals preclude in situ preparation in solids. Studies of several stable β-tetraalkyl nitroxides have been done by trapping them in host crystals [24, 25]. The results of this work is tabulated below.

TABLE III: HYPERFINE TENSORS OF NITROXIDE RADICALS

Radical	A_{xx}	A_{yy}	A_{zz}
 $(CH_3)_3C-\underset{\overset{|}{\dot{O}}}{N}-C(CH_3)_3$ *	7.59±.05g	5.95±.05g	31.78±.05g
	5.2	5.2	31
	4.7	4.7	31

* $g_{xx}+ 2.00872$, $g_{yy}= 2.00616$, $g_{zz}= 2.00270$

x: along N-0 bond
y: perpendicular to x and z
z: along 2p orbital of nitrogen

Recently, nitroxides have been used extensively by biochemists as spin labels due to the extreme stability of the β-tetraalykyl nitroxides. The fact that a functional group (i.e. the hydroxy group on 2,2,6,6-tetramethyl-4-piperdinol N-oxide (I)) can undergo reactions without destruction of the radical has allowed incorporation of nitroxides into proteins and other macromolecules. Taking advantage of the known correlation of EPR spectrum broadening with the rate of tumbling of the radical and the correlation between the magnitude of the N^{14} coupling and solvent polarity, biochemists have been able to probe the environment and reactions near the point of attachment of the nitroxide to the macromolecule. Reviews of the advances in this field to date have been written by Hamilton and McConnell [26], and Griffith and Waggoner [27].

III. EXPERIMENTAL

A. SYNTHETIC

1. N-Nitropiperidine [28]

Into a 100 ml round bottom flask fitted with a reflux condensor was placed 12 ml (0.121 moles) of piperidine, and 5.8 ml (0.154 moles) of 97% formic acid was added slowly. The mixture was refluxed 50 minutes and a fraction boiling at 98-104° C. was distilled off.

Three solutions were made up and cooled on an ice bath: 1) 28 ml, (0.67 moles) of red fuming nitric acid, 2) 20 ml (0.27 moles) of trifluoroacetic acid and 48 ml (0.84 moles) of acetic anhydride, and

3) the material remaining after the distillation above. The nitric acid was added slowly to the second solution. This mixture was cooled to 3° and the distillation residue was added with the temperature maintained below 10°. When this addition was over, the solution was stirred at room temperature for 35 minutes and quenched on ice.

The aqueous solution was extracted twice with 50 ml portions of methylene chloride, and the aqueous layer was discarded. The yellow oil remaining after evaporation of the solvent was chromatographed on an activity II acidic alumina column using chloroform.

The liquid obtained was distilled through a short path system yielding 4.61 g (23%) clear viscous liquid (b.p. 40-42° at 50-55 microns; $n_D^{23.5} = 1.4972$). Literature values for N-nitropiperidine are [29] $n_D^{20} = 1.4968$; b.p. 62-64° (0.2 mm).

2. N-Nitromorpholine [28]

Using 10.4 ml (0.12 moles) of morpholine, the title compound was prepared as above. After the extraction step a yellow oil was obtained which yielded 0.17 g (1.1%) white needles from hot hexane (m.p. 48-50°). Recrystallization from hexane by evaporation gave colorless lathes (m.p. 51-52°) which were used for further study. Emmons and Freeman [29] report a melting point of 51-53° for n-nitromorpholine.

3. N-Nitropyrrolidine [28]

Using 27 ml (0.35 moles) of pyrrolidine, 15 ml (0.39 moles) of formic acid, 40 ml of trifluoroacetic acid, 35 ml of acetic anhydride,

and 25 ml of red fuming nitric acid, N-nitropyrrolidine was prepared as above.

The extraction with 150 ml of methylene chloride left a yellow oil on removal of the solvent. This oil was chromatographed on an activity III acidic alumina column with chloroform yielding 0.19 g (0.4%) of a white solid. Recrystallization from hexane by evaporation gave white hexagonal prisms (m.p. 58°). The literature reports 55-57° [29].

4. N-Nitro-4-methylpiperidine (N-Nitro-γ-pipecoline) [28]

The nitration procedure outlined above was used with 15 ml (0.129 moles) of 4-methylpiperidine. After chromatography the resulting yellow oil was distilled (B.P. 58-68° at 30 microns). Redistillation and collection of the fraction boiling at 50-51° at 40-45 microns gave 3.74 g (20%) of product. Since this compound was previously unreported, the following data were obtained for N-nitro-4-methylpiperidine:

M.P. 8-10° ; $n_d^{22.5} = 1.4887$

UV; $\lambda_{max} =$ 245 nm. (MeOH), $\epsilon = 6300$

NMR;(in CCl_4 with TMS reference)

Broad doublet (2H) - 4.45 δ

Broad triplet (2H) - 3.05

Ill-defined multiplet (5H) - 1.95 to 1.20

Sharp doublet (3H) - 0.97

IR; (KBr pellet)

2920 (s.), 1500 (s.), 1430 (s.), 1370 (s.), 1310, 1280 (s.), 1260 (s), 1215, 1150, 1072 (w), 1054, 950, 936, 814 (w), 764, 753, 598 (w), 574

ANALYSIS; Calculated for $C_6H_{12}N_2O_2$

C- 49.99%, H- 8.39%

Found, C- 50.12%, H- 8.59%

5. N-Nitro-4-t-butylpiperidine [28,30]

Into a 500 ml flask fitted with a dry ice condensor was placed 13.5 g (0.10 moles) of 4-t-butylpyridine and 140 ml of liquid ammonia. The solution was stirred while 2.8 g (0.40 g atom) of lithium metal was added in small pieces. Another 250 ml of ammonia was added to the then deep blue solution followed by 21.4 g (0.40 moles) of ammonium chloride. The ammonia was allowed to evaporate, and the white solid residue was extracted with about 50 ml of ether. The ethereal solution was hydrogenated at 1800 psig for 75 minutes using PtO_2 as a catalyst.

The solution was filtered, the ether distilled off, and the residue distilled under vacuum. The distillate (which NMR showed to be a mixture of 4-t-butylpyridine and an aliphatic compound) was refluxed with 3.8 ml of formic acid for 35 minutes. After distillation of a fraction boiling at 78-85° under vacuum (about 100 mm), the residue was distilled at 90 microns pressure. A fraction at 30-32° proved to be 4-t-butylpyridine and was discarded. The fraction boiling at 66-70° (1.05 g, 6.6%) had NMR

and IR spectra consistent with N-formyl-4-t-butylpiperidine and was nitrated in the usual manner using 1.3 ml of trifluroacetic acid, 2.8 ml of acetic anhydride, and 1.6 ml of red fuming nitric acid. When the nitrating mixture was poured onto ice, a yellow solid precipitated. Recrystallization from petroleum ether yielded 0.34 g (34%) of yellow solid (m.p. 65-74°). White flakes were obtained from a water-acetone mixture (m.p. 85-86°). N-nitro-4-t-butylpiperidine, previously unreported, has the following physical constants:

NMR; (in D_6 acetone with TMS reference)

Broad Doublet (2H) - 4.00 δ

Very broad poorly defined
multiplet ($\sim$5H) - 2.9 to 2.2

Sharp Singlet (9H) - 0.32

UV; $\lambda_{max} = 244$ nm. (MeOH), $\epsilon = 6500$

IR; (KBr pellet)

2950 (s), 2850 (w), 1490 (s), 1445, 1410 (s), 1345, 1308, 1266 (s), 1248 (w), 1234 (w), 1100, 1034 (w), 1021, 948, 928 (w), 920 (w), 762 (w), 748 (w), 602 (w), 442

ANALYSIS; Calculated for $C_9H_{18}N_2O_2$

C - 58.04%, H - 9.74%

Found, C - 55.39%, H - 9.02%

6. 1,3-Dinitro-1,3-diazacyclohexane

a. 1,3 Diaminopropane dihydrochloride

In a beaker on an ice bath were mixed 23 ml (0.270 moles) of 1,3-diaminopropane and 44 ml of concentrated hydrochloric acid. White crystals formed which were filtered and gave 19.5 g (49%) of 1,3-Diaminopropane · 2HCl melting at 248-251° (literature [31] m.p. 243°).

b. N,N'-Biscarbomethoxy-1,3-diaminopropane [32]

A solution of 19.5 g (0.135 moles) of 1,3-diaminopropane · 2HCl in 51 ml (0.27 moles base) of 6N sodium hydroxide was stirred on a salt-ice bath during the simultaneous dropwise addition of 51 ml of 6N sodium hydroxide and 32 ml (0.27 moles) of methyl chloroformate. The solution was stirred for one hour, then extracted three times with 40 ml of chloroform. Removal of the solvent and trituration with hot hexane left 20.9 g (8.1%) of the title compound melting at 68-73° (literature [32] m.p. 74-75°).

c. N,N'-Biscarbomethoxy-N,N'-dinitrodiaminopropane [28]

Nitration of 11.8 g (0.06 moles) of N,N'-biscarbomethoxy-1,3-diaminopropane was done in the usual manner using 20 ml of trifluoroacetic acid, 43 ml of acetic anhydride, and 25 ml of red fuming nitric acid. When the nitrating mixture was poured onto ice, a solid precipitated, which upon filtration gave 15.4 g (91%) of the title compound, a yellow powder melting at 88-90° (literature [32] m.p. 89-90°).

d. N,N'-Dinitro-1,3-diaminopropane (Trimethylenedinitramine) [32]

In a beaker was warmed 4.0 g (0.014 moles) of the above product in 8 ml concentrated ammonia. After 5 minutes 5 ml of water was added, the excess ammonia was evaporated by warming under an air stream, and the solution was acidified with 6N hydrochloric acid. Extracting three times with 10 ml ethyl acetate and stripping off the solvent left 0.93 g (40%) of a product (m.p. 58-61°). Recrystallization from water and drying in a dessicator yielded 0.50 g of trimethylene dinitramine melting at 63-66°. The literature [32] reports 68-69°.

e. 1,3-Dinitro-1,3-diazacyclohexane [33]

The above product (0.0056 moles) was added slowly to a solution of 0.24 g (0.008 moles) of paraformaldehyde in 10 ml of concentrated sulphuric acid on an ice bath. After 8 minutes the solution was poured on to ice and 0.09 g (9.0%) of a solid formed. Recrystallization from ether gave 0.025 g of the title compound melting at 76-77°. The literature reports 84.5-86.5° [33].

7. Unknown Nitration Product from 4-Methylpiperidine

An attempt to synthesize N-nitro-4-methylpiperidine was made using the method of Woodcock [32]. However, the product obtained was not as expected.

To 5 ml (0.05 moles HCl) of concentrated hydrochloric acid in a beaker on an ice bath was added slowly 5 ml (0.043 moles) of 4-methylpiperidine. The water was evaporated, and the resulting white solid was

dissolved in 19 ml (0.10 moles base) of 6N sodium hydroxide in a 500 ml flask on an ice bath. Nineteen ml of 6N sodium hydroxide and 12 ml (0.10 moles) of methyl chloroformate were simultaneously added dropwise. The solution was stirred for 35 minutes and poured into a separatory funnel where a small yellow layer separated on top. The aqueous layer was discarded, and the yellow layer was dissolved in chloroform and washed twice with water. The chloroform was evaporated, and the remaining liquid was distilled on a short path system (b.p. 46-48° at 20-23 microns). This yielded 2.52 g (37%) of N-carbomethoxy-4-methylpiperidine which had the following properties:

$n_D^{22.5} = 1.4574$

IR; 3450 (w,br) 2910 (s), 2860, 1780 (s), 1430 (s), 1385,
1300, 1270, 1232 (s), 1184, 1150, 1088, 1016 (w),
971 (w), 959 (w), 764.

ANALYSIS; Calculated for $C_8H_{15}N\,0_2$

C - 61.12% , H - 9.62%

Found, C - 58.89%, H - 9.39%

The above compound was then nitrated. Into a solution of 2.5 ml of trifluoroacetic acid and 5.6 ml of acetic anhydride on an ice bath was poured slowly 3.1 ml of red fuming nitric acid. The N-carbomethoxy-4-methylpiperidine from above (2.5g) was added slowly and, the solution was stirred for 5 minutes. It was taken off the ice bath and stirred for 55 minutes more at room temperature. The solution was poured onto ice,

extracted twice with 15 ml of methylene chloride, and the solvent was evaporated. A yellow solid was obtained which was recrystallized from heptane yielding 0.67 g melting at 69-71°. Further recrystallization from petroleum ether gave pale yellow flakes (m.p. 73-73.5°) with the spectral data listed below:

IR; 3390 (v br), 2930, 2890, 1710 (s), 1620 (s), 1470 (s), 1420 (s), 1380 (s), 1350, 1285 (s), 1270 (s), 1216, 1200, 1139, 1111 (w), 1092, 1051, 996 (w), 771 (w), 761 (w), 747, 533 (w), 505 (w).

NMR; in D_6 acetone with a TMS reference

Singlet (1H) - 8.46 δ

Singlet (3H) - 3.81

Multiplet ($\sim 3H^+$) - 4.0 to 3.0

Multiplet ($\sim 3H$) - 1.9

Doublet (3H) - 1.12

UV; in ethanol

λ_{max} = 324 nm, ϵ = 53 x Molecular Weight

λ_{max} = 235 nm, ϵ = 17 x Molecular Weight

ANALYSIS; Calculated for $C_8H_{12}N_2O_4$

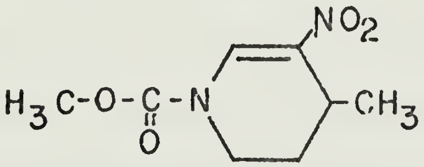
C - 47.96%, H - 6.04%

Found C - 48.16%, H - 6.14%

VAPOR PRESSURE OSMOMETER; the compound showed the very unusual characteristic of an apparent molecular weight which decreased with concentration.

Concentration (g/1)	Apparent M.W.
0.74	372
1.24	258
1.72	260
2.86	225
5.56	209

These data suggest that the product has the structure shown below or one of its isomers, but the evidence is inconsistent enough to require further work to make a definite assignment.



B. ELECTRON PARAMAGNETIC RESONANCE STUDIES OF NITRAMINE PHOTOLYSIS

1. Solution Studies

All spectra were recorded on a Varian V-4502-13 EPR spectrometer with a Fieldial V-F-2503 and a nine-inch magnet, using 100 kc modulation. Solutions were placed in a quartz flat cell with a 1.0 by 0.05 cm cross section and cooled by directing a stream of cold nitrogen (which had been passed through a heat exchanger immersed in liquid nitrogen) directly into the cavity against the cell. Temperatures were measured with a copper-Constantan thermocouple placed in the cell. A

Christie Xenolite Model UF10JKK xenon-mercury vapor lamp was used to irradiate the samples in the cavity while recording the spectrum.

The photolysis was done in the same way for N-nitropyrrolidine, N-nitropiperidine, N-nitromorpholine, N-nitro-4-methylpiperidine, N-nitro-4-t-butylpiperidine, 1,3-dinitro-1,3-diazacyclohexane, and N,N' Dinitropiperazine. The sample was dissolved in 1,3-propanediol cyclic carbonate (PDCC) in about 0.05 to 0.5 M concentration. Photolysis in the cavity gave the same room temperature spectrum for all of the above, consisting of three lines with a splitting of 13.3 to 13.8 G. This spectrum is shown in Figure 1. The nitrogen flow was then started, and at 10 to -40° the spectrum was again recorded. In all cases the appearance of the spectrum had changed. These low temperature spectra are shown in Figure 4 to Figure 10, and the splittings obtained from them are listed in Table IV in the Results.

Room temperature spectra of NO and NO_2 dissolved in PDCC were also recorded under irradiation as above. These spectra are shown in Figure 2 and Figure 3.

A saturated solution of N,N' dinitropiperazine was photolyzed, and again the room temperature spectrum showed three lines with a splitting of 13.4 G. As the temperature was decreased, these lines persisted as another spectrum grew in intensity (Figure 11). Degassing the solution by passing nitrogen through it did not affect the spectra. Recording the low temperature spectrum with a filter that passes 230 nm radiation placed over the lamp showed an increase in the relative intensity of the

three line spectrum (Figure 12). If the light was then turned off and the spectrum recorded 1 minute later, only three lines remained (Figure 13). Using a 290 nm filter caused only the second, more complex spectrum to be seen (Figure 14).

Irradiation of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) in PDCC gave a 30 line spectrum at 30° to -1°C. but the signal was very poorly resolved. In acetonitrile at room temperature a signal was obtained with better resolution (Figure 15).

Irradiation of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) in both PDCC and acetonitrile gave signals that were very weak and poorly resolved (Figure 16).

The kinetics of the decay of the radicals were followed by setting up a photo-steady-state concentration of radicals, shuttering the lamp and plotting EPR signal intensity as a function of time. This was done for N-nitropyrrolidine, N-nitropiperidine, N-nitromorpholine , N-nitro-4-methylpiperidine, and N-nitro-4-t-butylpiperidine. In all cases the plot of the reciprocal of relative signal intensity versus time was linear indicating second order kinetics. The plots for N-nitropyrrolidine are shown in Figure 17.

Figure 1. EPR spectrum N-nitropyrrolidine irradiated in PDCC at 25 to 26° C.

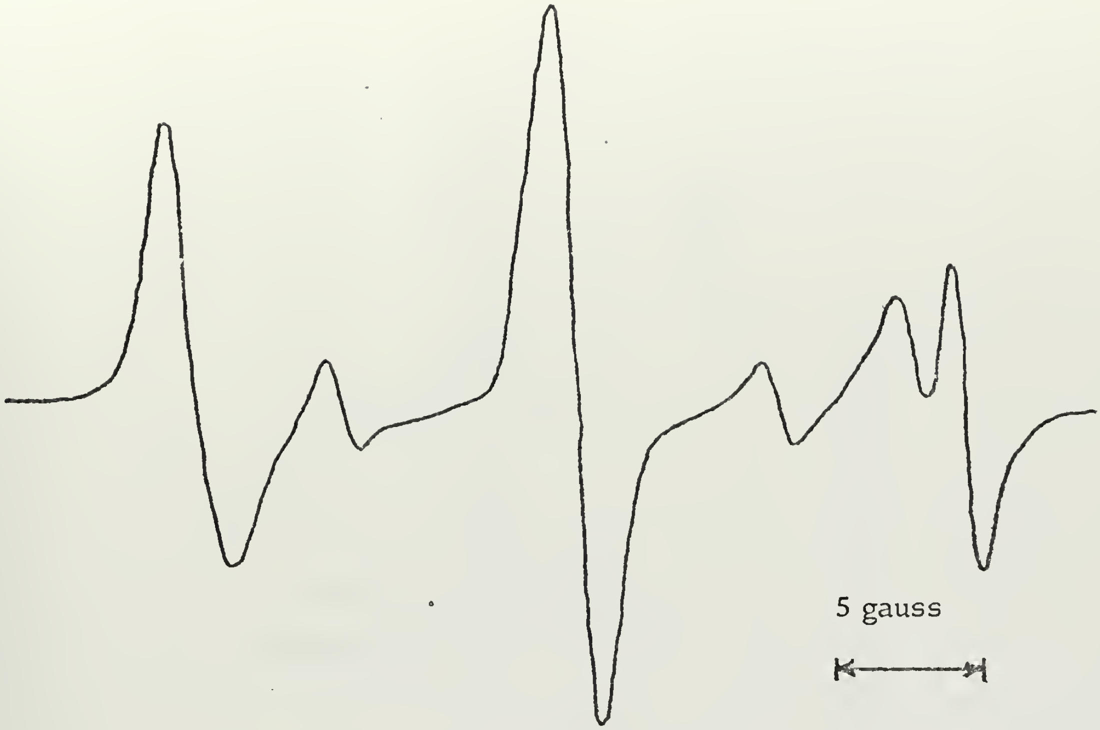


Figure 2. EPR spectrum of N0 irradiated in PDCC at room temperature.

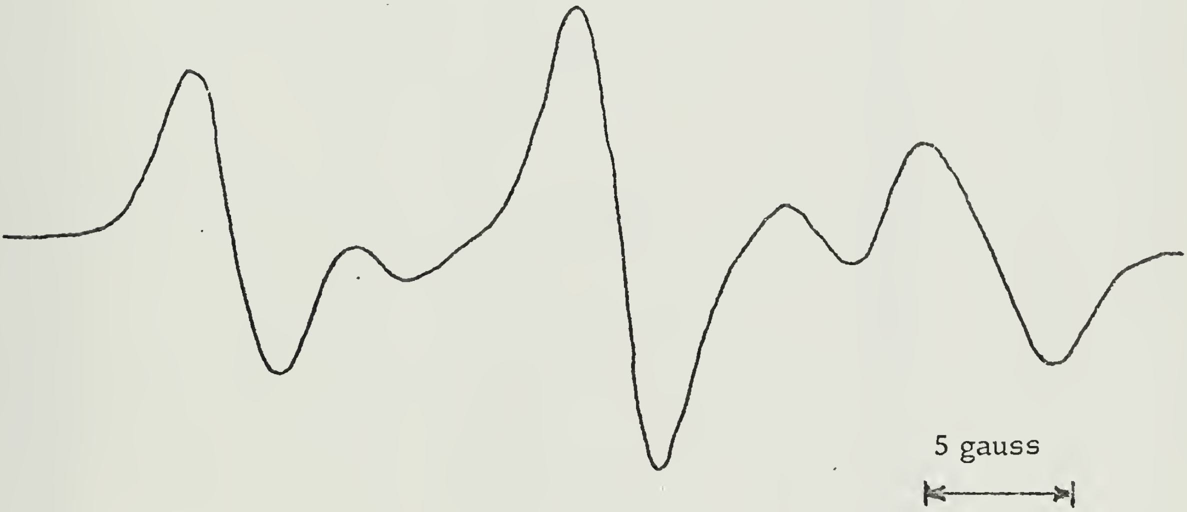


Figure 3. EPR spectrum of $N0_2$ irradiated in PDCC at room temperature.

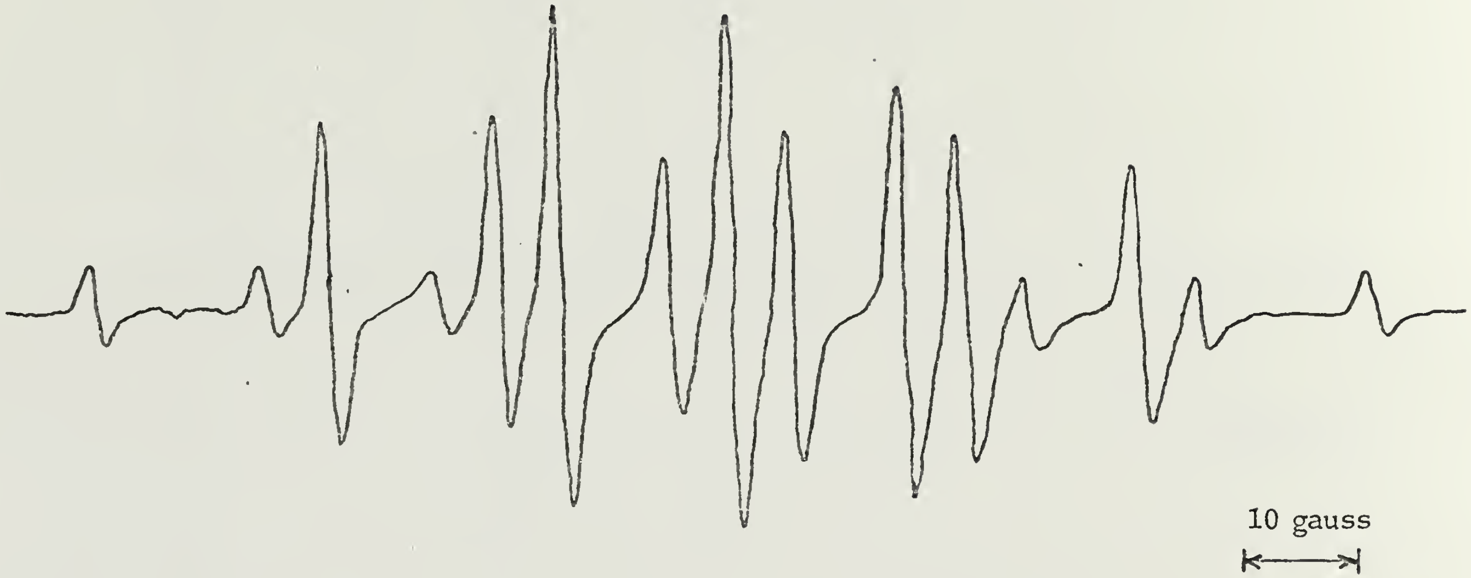


Figure 4. EPR spectrum of N-nitropyrrolidine irradiated in PDCC at -13° C.

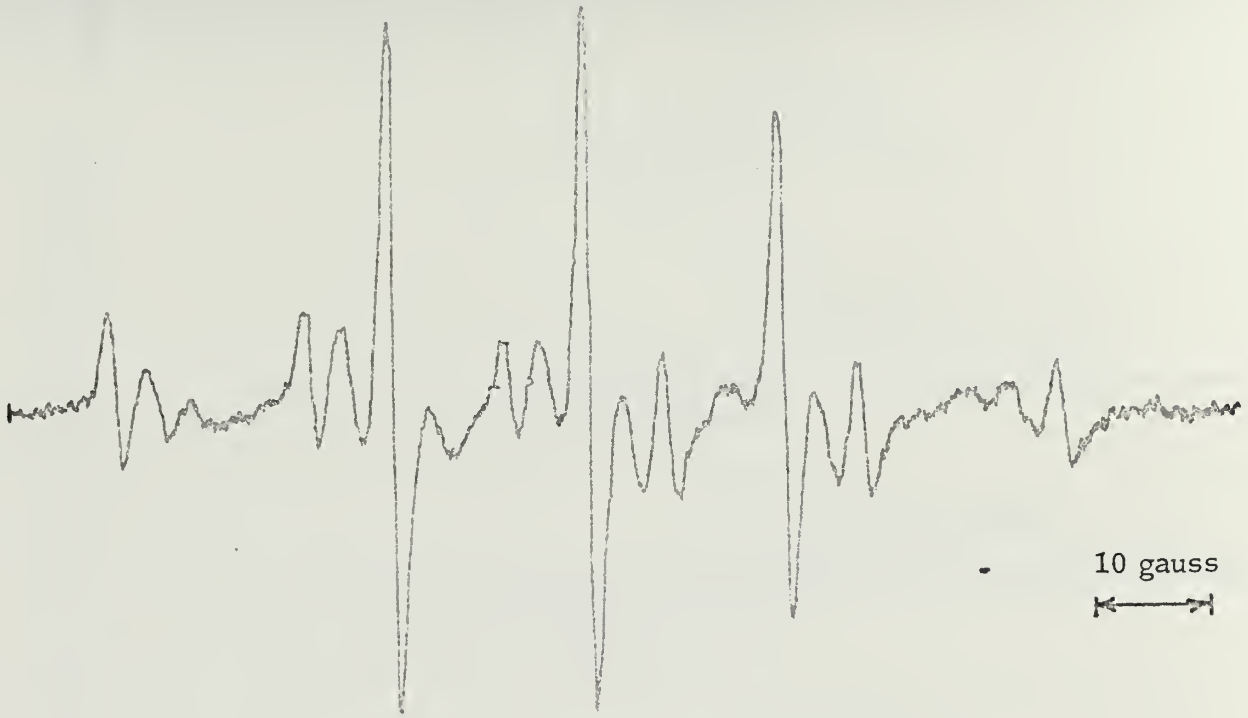


Figure 5. EPR spectrum of N-nitropiperidine irradiated in PDCC at -33° C.

Figure 6. EPR spectrum of N-nitromorpholine irradiated in PDCC at -34 to -35° C.

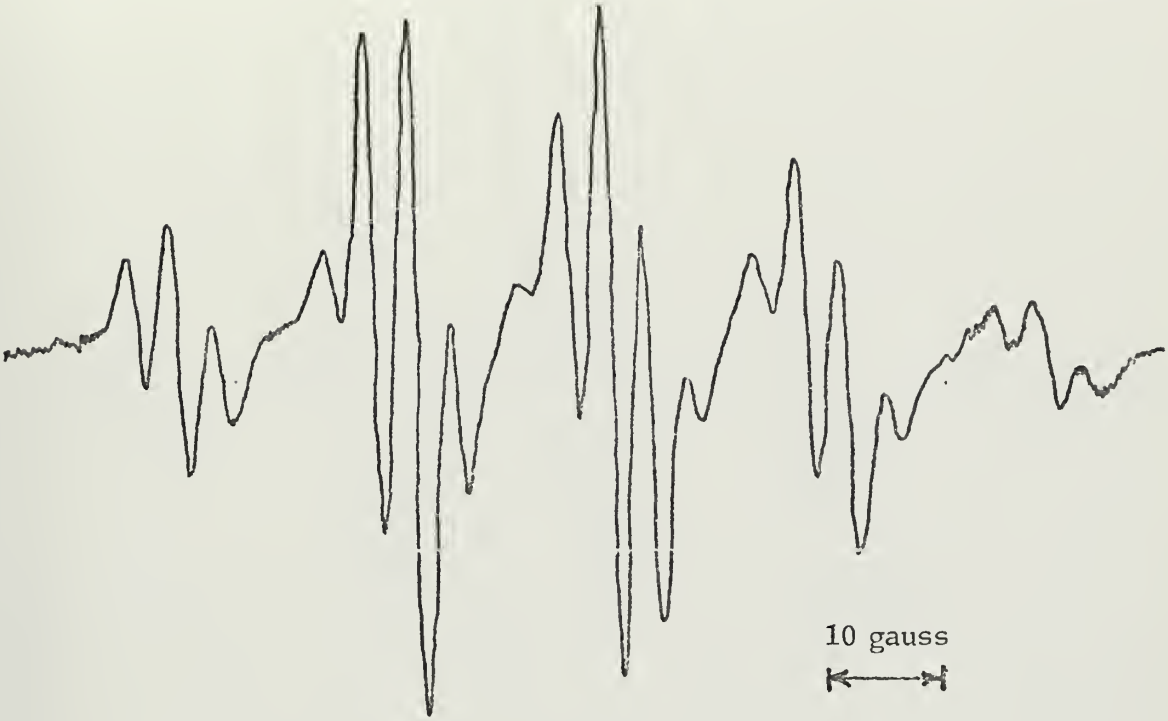


Figure 7. EPR spectrum of N-nitro-4-methylpiperidine irradiated in PDCC at -23 to -26° C.

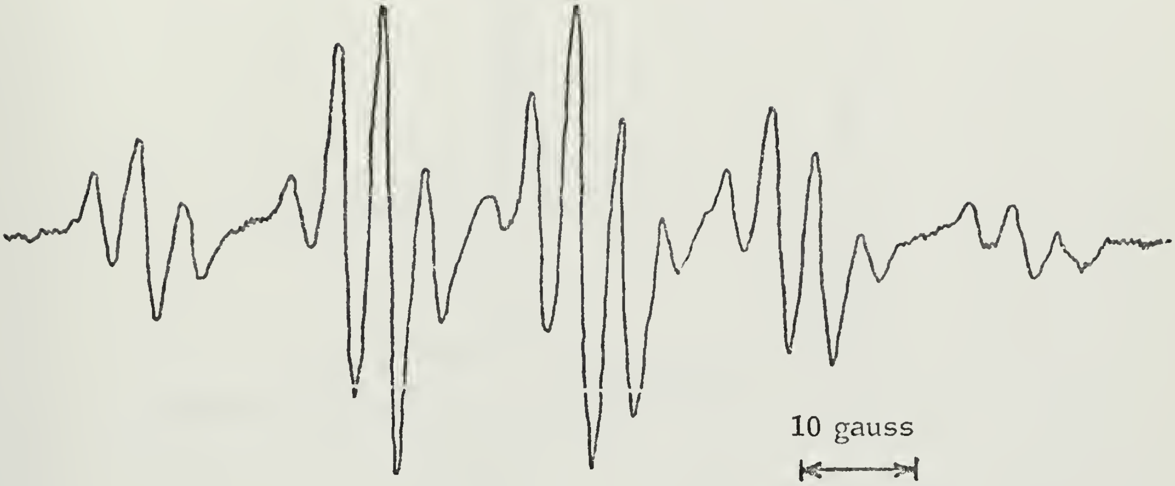


Figure 8. EPR spectrum of N-nitro-4-t-butylpiperidine irradiated in PDCC at -25 to -27° C.

Figure 9. EPR spectrum of N,N'-dinitropiperazine irradiated in PDCC at 1°.

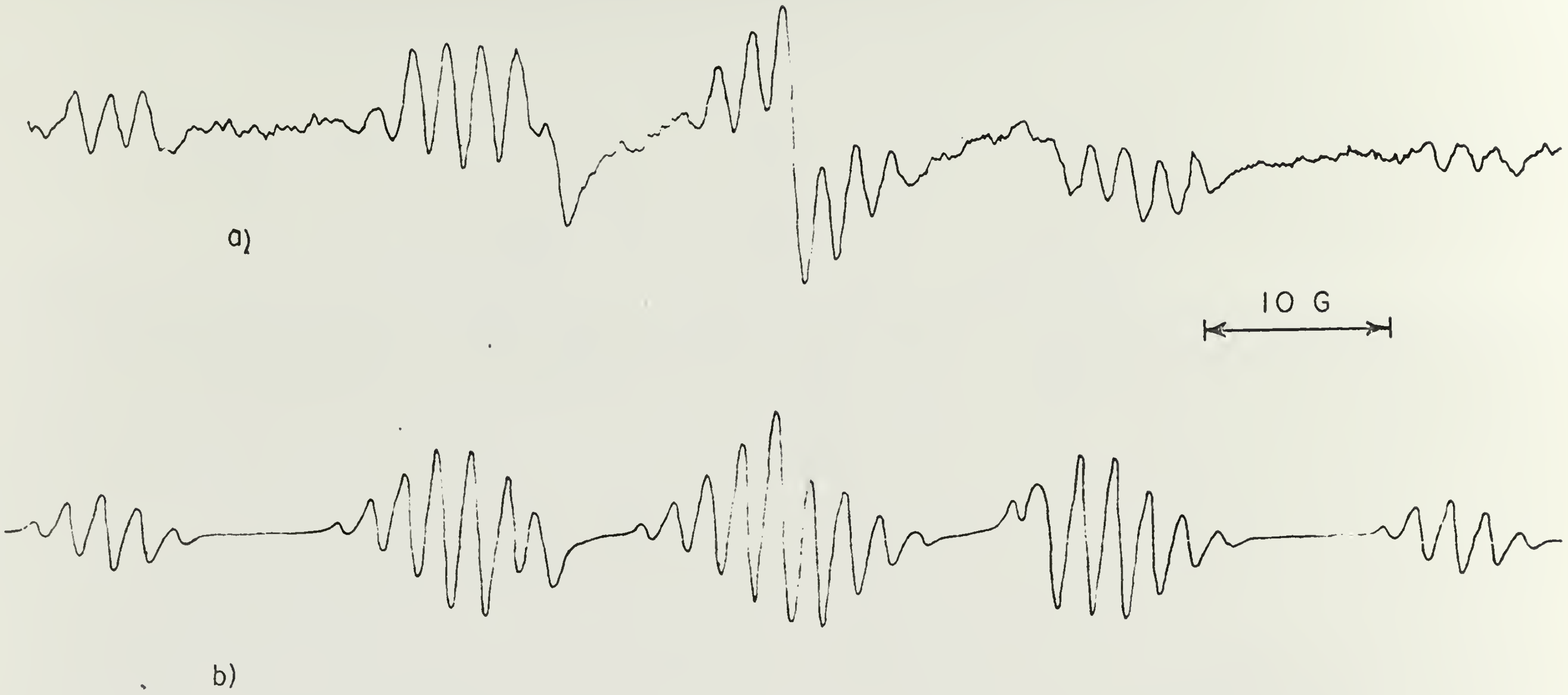


Fig. 10. EPR spectrum of 1,3-dinitro-1,3-diazacyclohexane.
a) irradiated in PDCC at -37° C.
b) computer simulation. (See Results).

Fig. 11. EPR spectrum of a saturated solution of N,N'-dinitropiperazine irradiated in PDCC at 10° C.

Fig. 12. EPR spectrum of a saturated solution of N,N'-dinitropiperazine irradiated in PDCC with 230 nm wavelength light at -16° to -18° C.

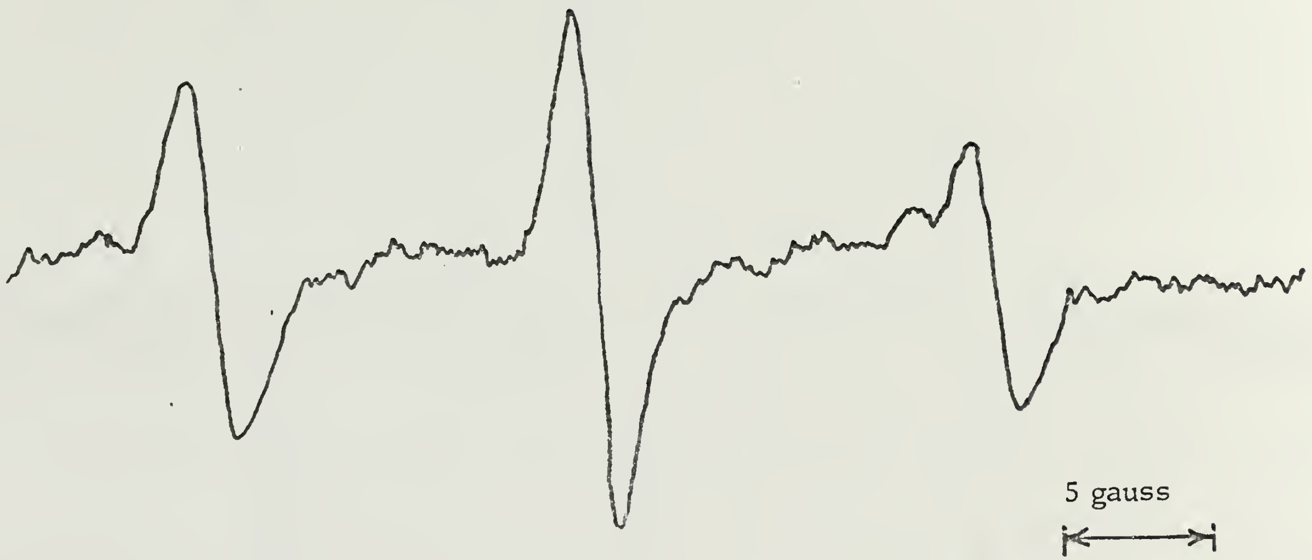
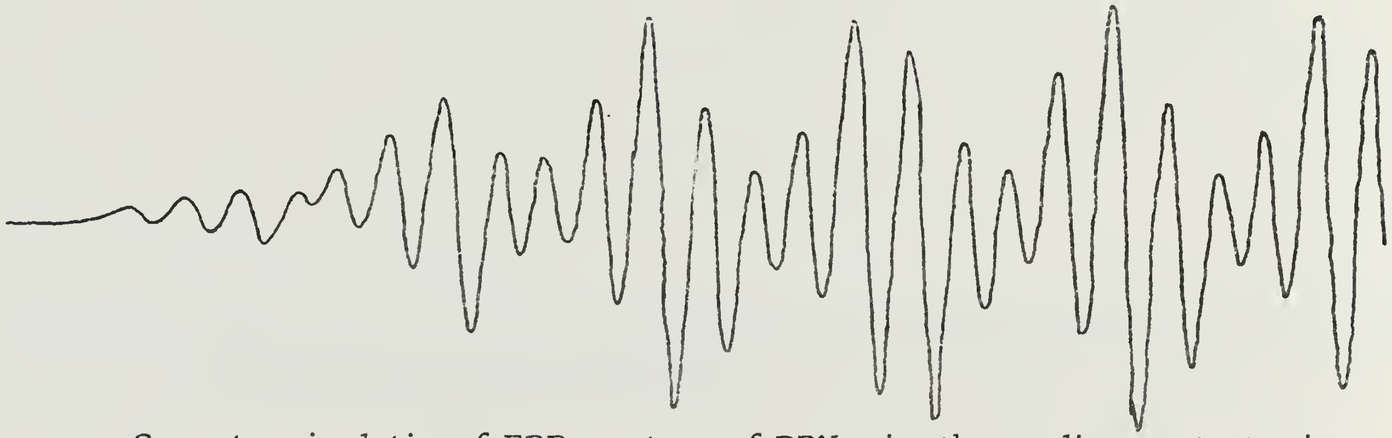


Figure 13. EPR spectrum of N,N'-dinitropiperazine in PDCC. This spectrum was recorded 1 minute after the 230 nm radiation source was turned off at -21° C.

Fig. 14. EPR spectrum of a saturated solution of N,N'-dinitropiperazine irradiated in PDCC with 290 nm wavelength light at -21° C.

Figure 15. EPR spectrum of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) irradiated in CH_3CN at room temperature. The arrow indicates the center of the spectrum.



Computer simulation of EPR spectrum of RDX using the coupling constants given in Table IV. (See Results section).

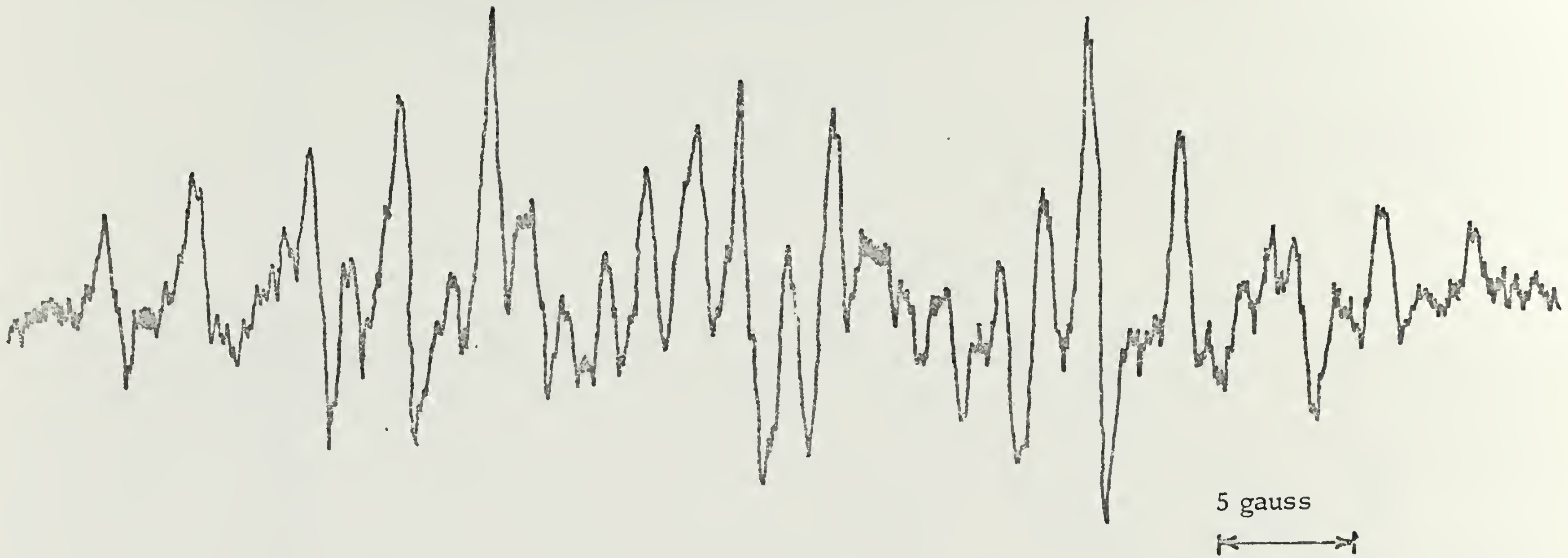


Figure 16. EPR spectrum of 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX) irradiated in acetonitrile at room temperature.

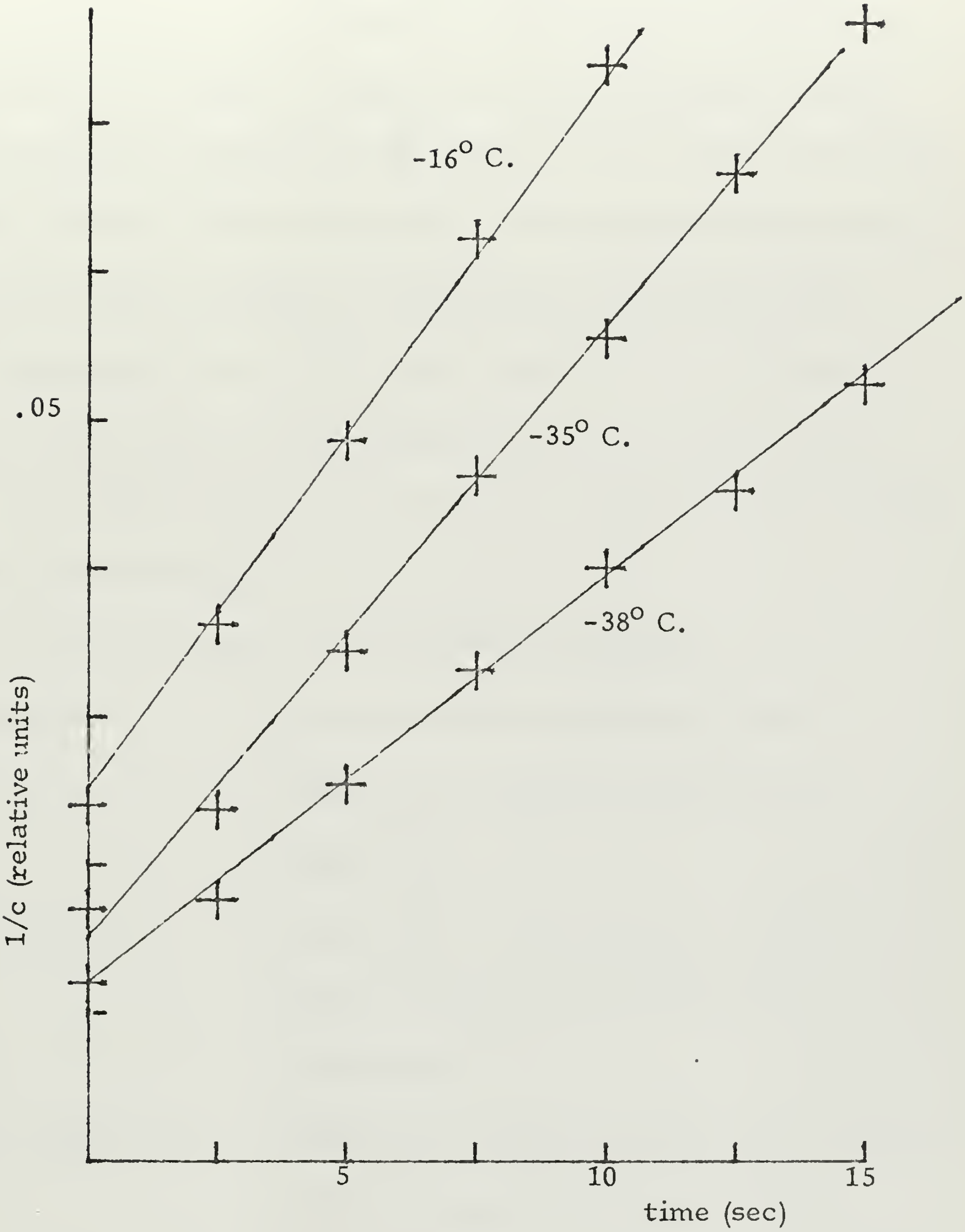


Figure 17. The rate of decay of pyrrolidine N-oxide in PDCC solution. 1/c is in terms of relative concentration of radical.

2. Single Crystal Studies

Crystal spectra were recorded by irradiating the crystal for 5 to 15 minutes, mounting it on a quartz rod, and recording the spectra for magnetic field orientations of $\phi = -45^\circ, 0^\circ, 45^\circ$, and 90° at intervals of $\theta = 0^\circ, 30^\circ, 60^\circ, 90^\circ, 120^\circ$, and 150°. The rod had two flats ground parallel to each other on either end. The crystal was mounted with a film of stopcock grease on one flat using a Baush and Lomb microscope and goniometer to measure the angle (ϕ) between the rod axis and the crystal y axis. The rod was then attached to an angle indicator to measure θ positioned over the spectrometer cavity.

The data was taken for the nitramines as follows:

N-nitropyrrolidine -	spectra with excellent signal to noise ratios; one magnetically distinct site; results below.
N-nitromorpholine -	spectra with excellent signal to noise ratios; one magnetically distinct site; results below.
N,N'-dinitropiperazine -	spectra with adequate signal to noise ratios; at least 2 magnetically distinct sites as evidenced by broadening at most orientations; no further interpretation.
N-nitro-4-t-butylpiperidine -	spectra with adequate signal to noise ratios; at least 2 magnetically distinct sites as evidenced by broadening at most orientations; no further interpretation.

RDX - no signal detectable after 30 minutes irradiation.

HMX - no signal detectable after 30 minutes irradiation.

N-nitropiperidine - liquid at room temperature; no crystal studies attempted.

N-nitro-4-methylpiperidine - liquid at room temperature; no crystal studies attempted.

a. N-Nitropyrrolidine

Single crystals of N-nitropyrrolidine were grown by evaporation from petroleum ether. Hexagonal prisms were obtained as shown in Figure 18 with the axes chosen for data plotting superimposed. The crystal was irradiated for 10 minutes, and the spectra were taken as mentioned above. The pattern seen was 3 x (1-4-6-4-1) as shown in Figure 20 and 21 which correspond to the maximum and minimum nitrogen splitting. The data from the other orientations are listed in the Appendix. The signal obtained was still detectable 24 hours after irradiation.

Laue patterns were taken of a N-nitropyrrolidine crystal (Figure 24) which showed two perpendicular two-fold axes or reflection planes when the x-ray beam was in the direction of the x axis and two perpendicular two-fold axes or reflection planes along the z axis. When the x-rays were along the direction $\phi = 45^\circ$ and $\theta = 45^\circ$ no symmetry was seen.

b. N-Nitromorpholine

Single crystals were grown from petroleum ether by evaporation. The flat lathes obtained are shown in Figure 19 with the axes used to plot the data superimposed.

A crystal was irradiated for 5 minutes and the spectra obtained as before. The splitting pattern of 3 x (1-4-1) is evident in the representative spectra (Figure 22 and 23). The data are again listed in the Appendix. When the crystal was cooled to -40° C. the lines broadened in most orientations, indicating the presence of at least two magnetically distinct sites.

Laue patterns taken perpendicular to the arbitrary y axis all showed a plane of reflection. For one orientation (Figure 25) a stereographic projection showed low order planes in the x-z plane and in a plane defined by the y axis and a line in the x-z plane 33° from the z axis.

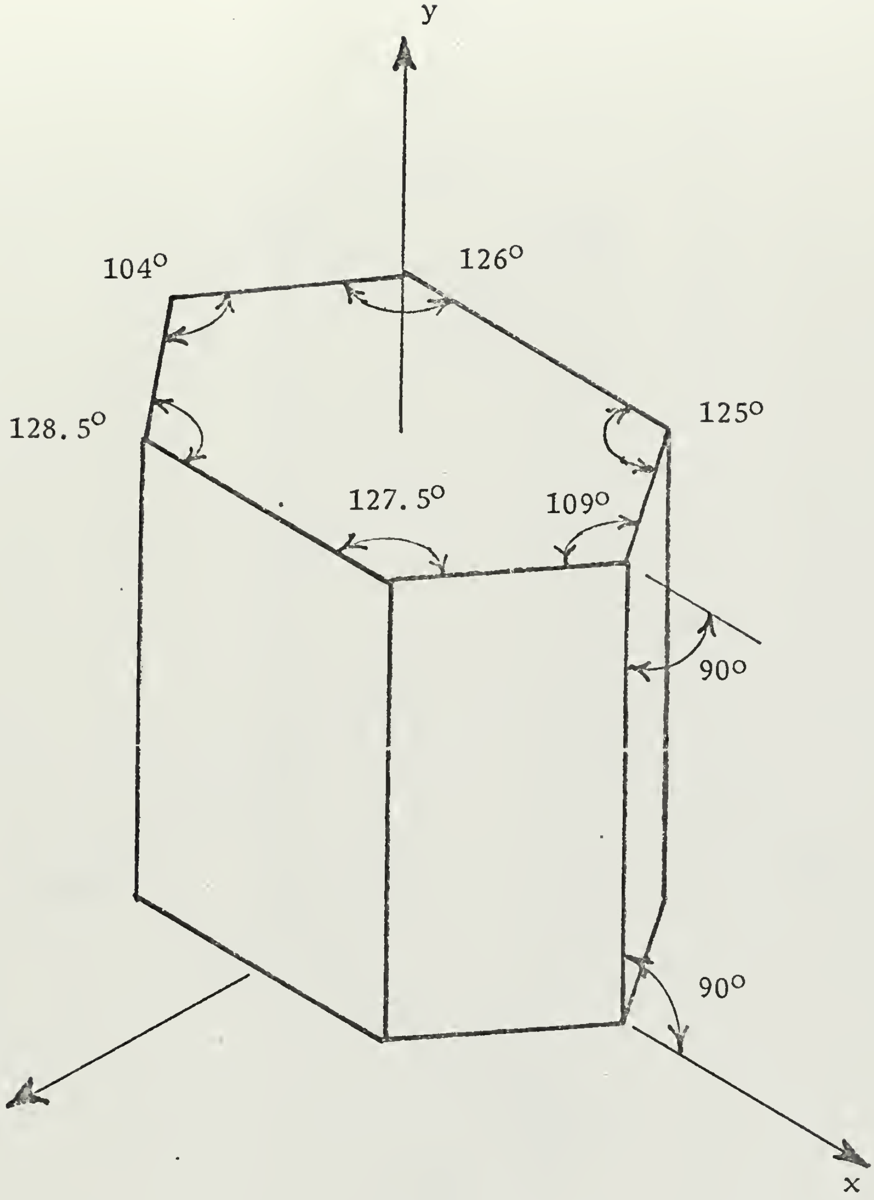


Figure 18. Crystal form and axis system chosen for N-nitropyrrolidine.

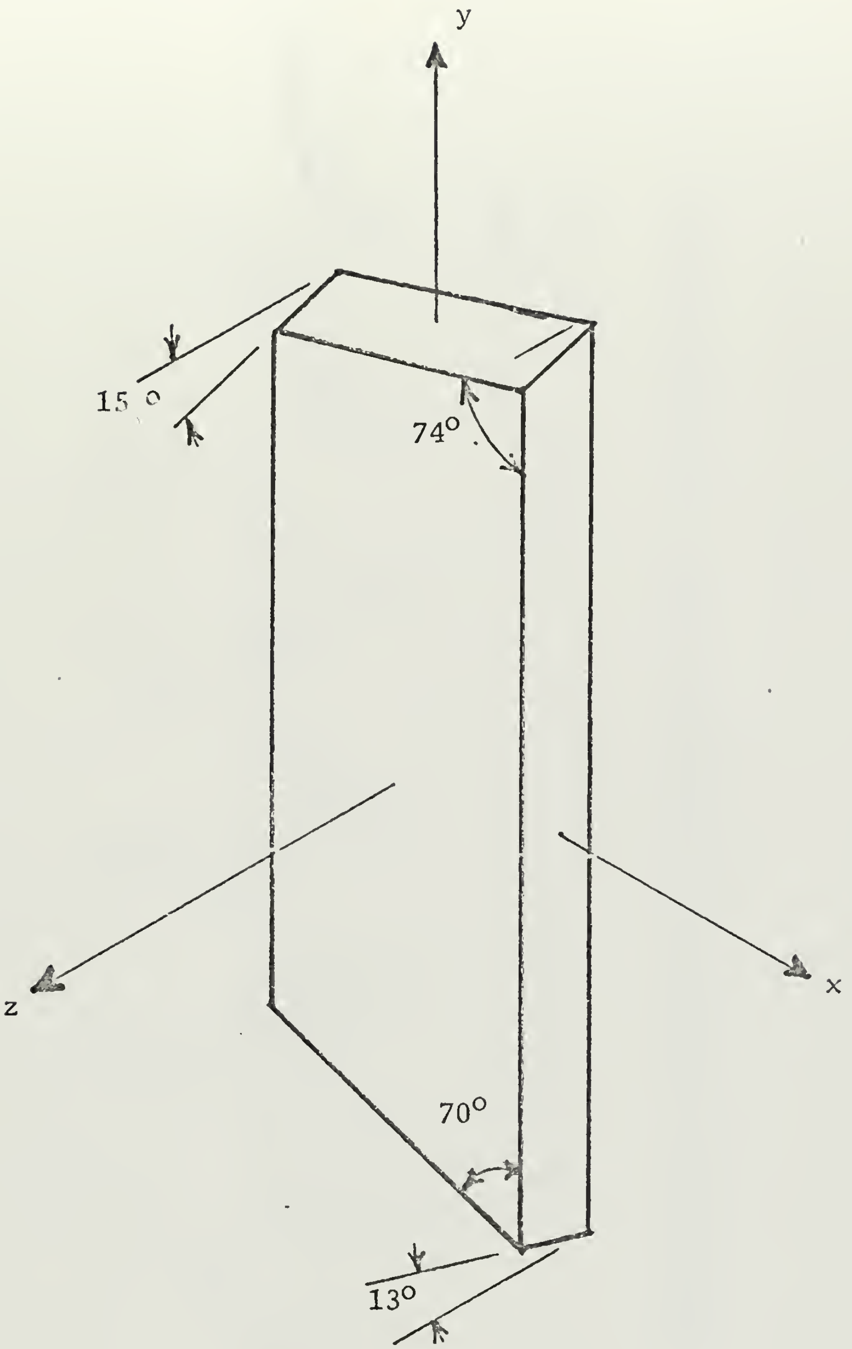


Figure 19. Crystal form and axis system chosen for N-nitromorpholine.

Figure 20. EPR spectrum of irradiated N-nitropyrrolidine crystal. The magnetic field is along the y axis (i.e. $\phi = 90^\circ$, $\theta = 90^\circ$).

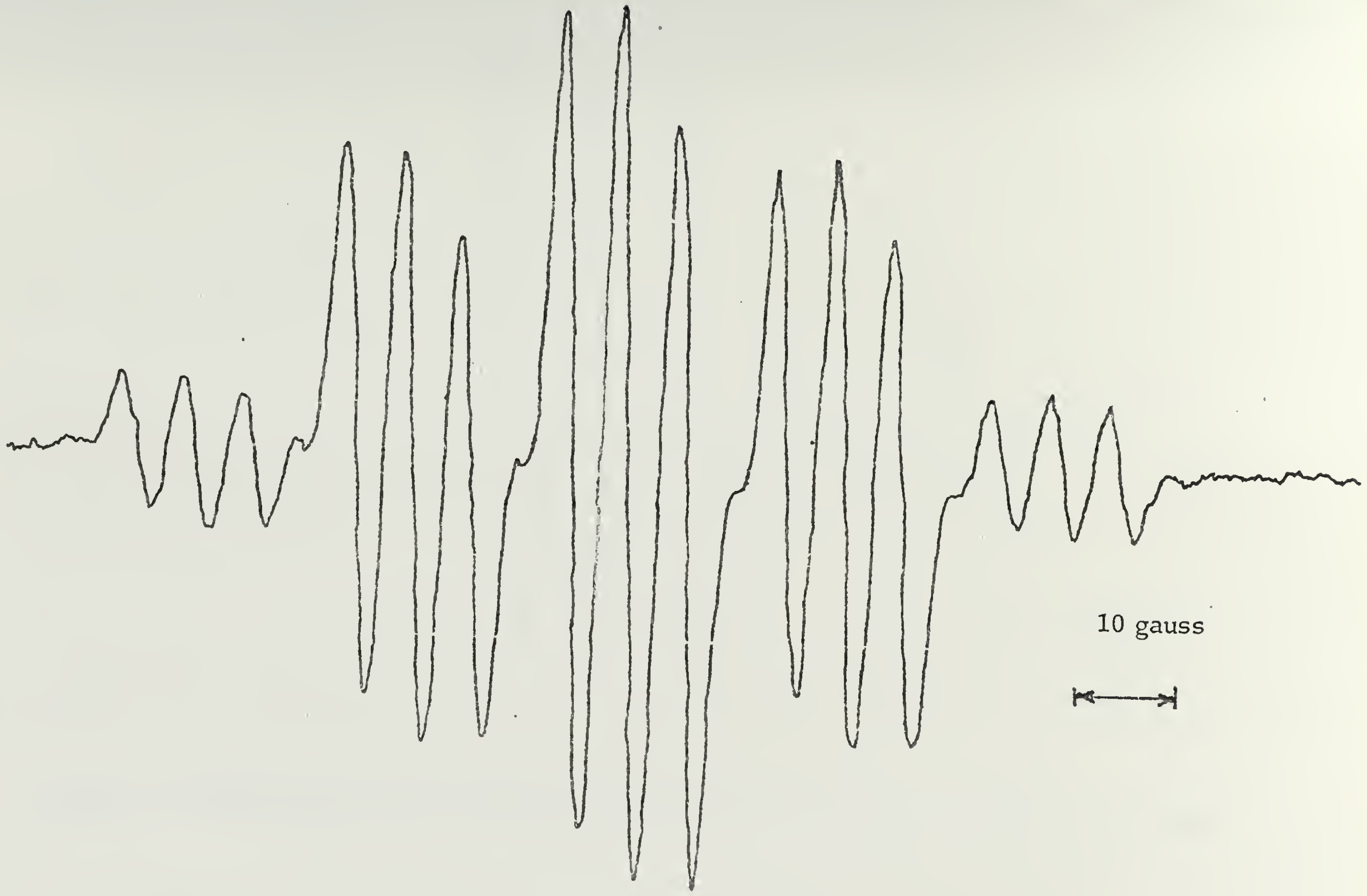


Figure 21. EPR spectrum of irradiated N-nitropyrrolidine crystal. The magnetic field is along the z axis (i.e. $\phi = 0^\circ$, $\theta = 0^\circ$).

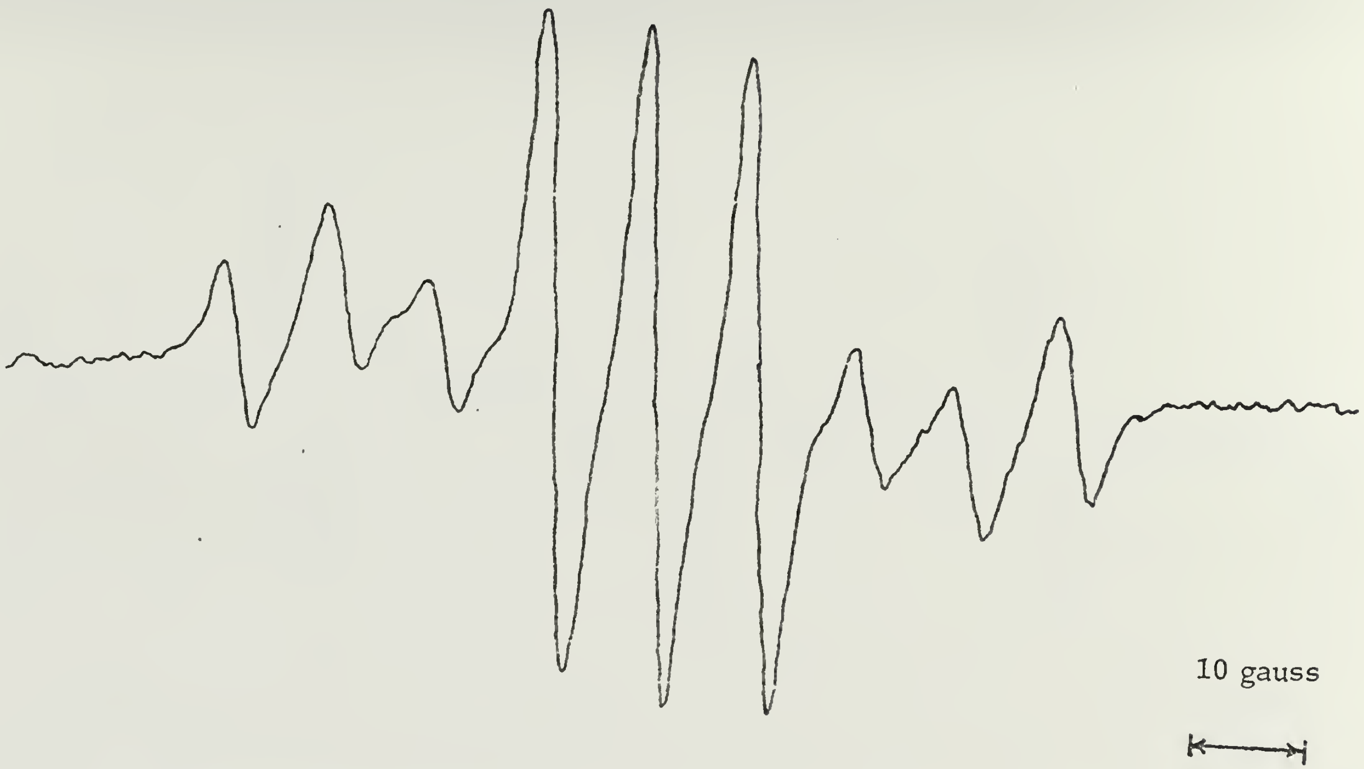


Figure 22. EPR spectrum of irradiated N-nitromorpholine crystal. $\phi = 0°$, $\theta = 120°$.

Figure 23. EPR spectrum of irradiated N-nitromorpholine crystal. $\phi = 0°$, $\theta = 30°$.

X-ray beam along x axis

X-ray beam along z axis

Figure 24. Laue patterns for N-nitropyrrolidine crystal.

Figure 25. Laue pattern for N-nitromorpholine crystal. The x-ray beam is in the x-z plane rotated 17° from the x axis.

IV. RESULTS

A. SOLUTION STUDIES

At room temperature spectra obtained from the photolysis of PDCC solutions of N-nitropyrrolidine, N-nitropiperidine, N-nitromorpholine, N-nitro-4-methylpiperidine, N-nitro-4-t-butylpiperidine, 1,3-dinitro-1,3-diazacyclohexane, and N,N'-dinitropiperazine all showed three lines with a splitting of 13.3 to 13.8 G. Solutions of NO and NO_2 had a similar spectrum under the same conditions.

When the temperature was lowered, this spectrum grew weaker and was gradually replaced by another more complicated spectrum in each case. Each one of these spectra was interpreted as a nitroxide, as shown in Table IV. In the case of the six membered ring structures the interchange between the axial and equatorial protons causes the lines to broaden as shown in Figure 26. Thus for the nitroxides from N-nitropiperidine, and N,N'-dinitropiperazine the spectra reported were the 1-4-1 patterns caused by slow inversion while those from N-nitromorpholine, N-nitro-4-methylpiperidine, N-nitro-4-t-butylpiperidine, and 1,3-dinitro-1,3-diazacyclohexane gave the 1-2-1-2-4-2-1-2-1 pattern of the chair form which is not interconverting. Since the spectrum of 3-nitro-1,3-diazacyclohexane N-oxide has not been previously reported, a computer simulation of the couplings reported superimposed upon the

TABLE IV: NITROXIDES FORMED BY IRRADIATION OF NITRAMINES

Nitramine	Nitroxide	Solvent (conc.)	Temp.	Appearance of Spectrum	a_N	a_H	Ref.
N-nitropyrrolidine	Pyrrolidine N-oxide	PDCC	-13°C.	3 x (1-4-6-4-1)	14.7G	19.7G	9
N-nitropiperidine	Piperidine N-oxide	PDCC (0.22 M)	-33°	3 x (1-4-1)	16.8	23.4	9
N-nitromorpholine	Morpholine N-oxide	PDCC	-31 to -32°	3 x (1-2-1) x (1-2-1).	16.7	19.5; 3.7	9
N-nitro-4-methyl-piperidine	4-methylpiperidine N-oxide	PDCC (0.58 M)	-23 to -26°	3 x (1-2-1) x (1-2-1)	16.7	20.1; 3.7	16
N-nitro-4-t-butyl-piperidine	4-t-butylpiperidine N-oxide	PDCC (0.04 M)	-25 to -27°	3 x (1-2-1) x (1-2-1)	16.7	20.3; 3.8	23
N,N'-dinitropiperazine	4-nitropiperazine N-oxide	PDCC (0.02 M)	+1°	3 x (1-4-1)	16.7	21.4	-
1,3-dinitro-1,3-diazacyclohexane	3-nitro-1,3-diazacyclohexane N-oxide	PDCC (0.04 M)	-37°	3 x 3 x (1-2-1) x (1-2-1)	16.2; 1.9	19.8; 1.9	-
1,3,5-trinitro-1,3,5-triazacyclohexane	3,5-dinitro-1,3,5-triazacyclohexane N-oxide	CH_3CN (sat.)	25 to 26°	3 x (1-2-3-2-1) x (1-4-6-4-1)	15.8; 1.9	7.0	-

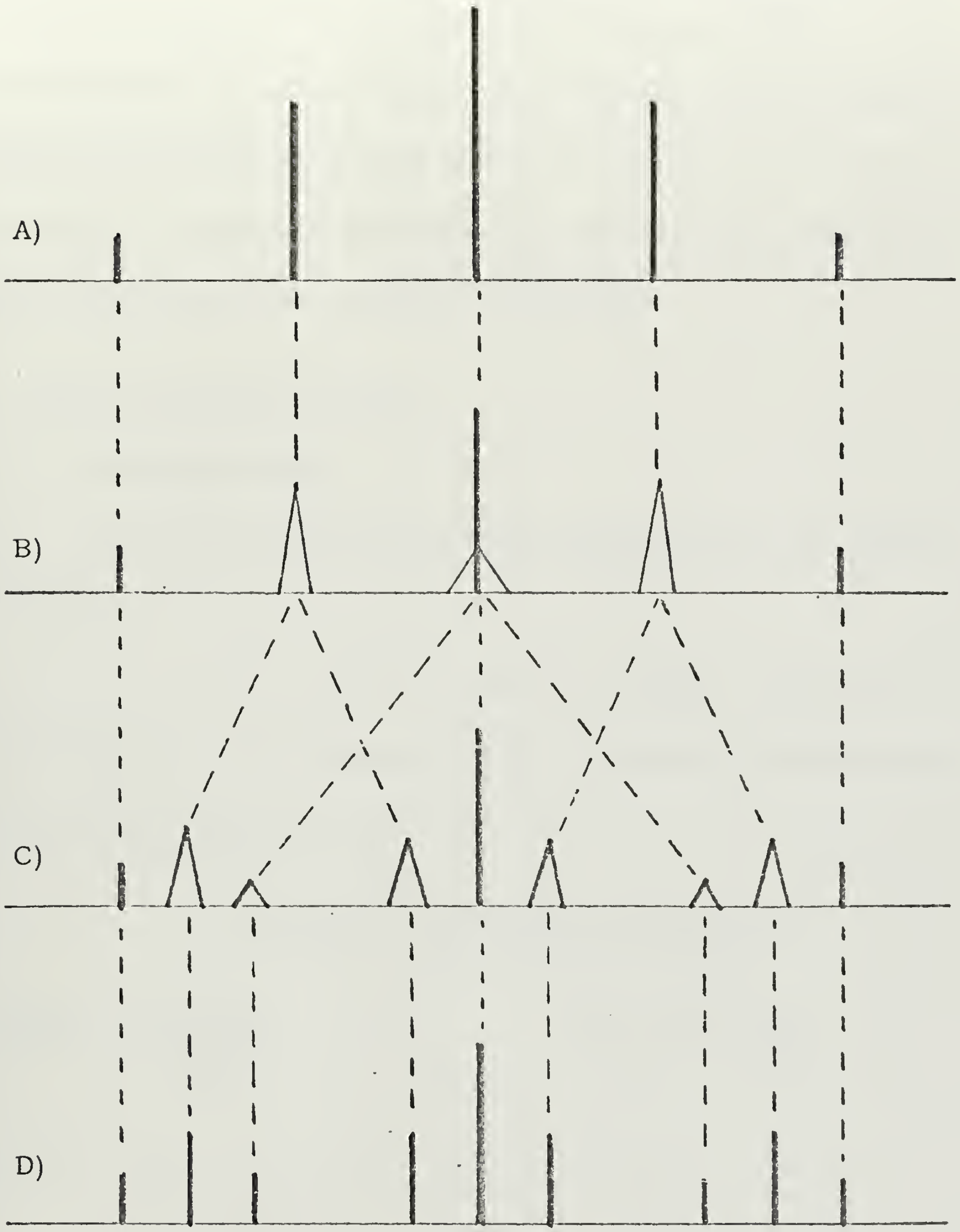


Figure 26. Correlation diagram showing line broadening due to interchange of axial and equatorial protons [35].

A) Fast interchange; all protons are equivalent.

B)&C) Slow interchange; lines shown as triangles are broadened and lost.

D) A blocked chair or boat form; axial and equatorial protons are distinguishable.

3 line spectrum with a = 13.3 is shown in Figure 10 for comparison to the experimental data. The room temperature spectrum of RDX in CH_3CN was interpreted as a nitroxide which is undergoing rapid interconversion (with axial and equatorial protons then being equivalent). This assignment was computer simulated [34] as shown in Figure 15 and the close match to the experimental curve verified the assignment.

B. SINGLE CRYSTAL STUDIES

1. N-Nitropyrrolidine

A least squares fit [34] of the experimental data was made to the relationship [25]:

$$A = (A_{xx}^2 \sin^2\theta \cos^2\phi + A_{yy}^2 \sin^2\theta \sin^2\phi + A_{zz}^2 \cos^2\theta)^{1/2}$$

This resulted in the following tensors for the coupling to the nitrogen and 4 equivalent β-protons.

TABLE V: HYPERFINE TENSORS FOR PYRROLIDINE N-OXIDE

Nucleus	Principle Value	Direction Cosines x	y	z
N^{14}	$A_{xx} = 5.1 \pm 0.5$ G.	0.87	-0.02	0.50
	$A_{yy} = 32.2 \pm 0.4$	0.00	1.00	0.03
	$A_{zz} = 5.3 \pm 0.3$	0.50	0.03	-0.87
4H	$A_{xx} = 19.0 \pm 0.1$	1.00	-0.04	-0.03
	$A_{yy} = 18.4 \pm 0.1$	0.05	1.00	0.00
	$A_{zz} = 21.08 \pm 0.05$	0.04	-0.01	1.00

The fit of these tensor values to the experimental data is plotted in Figure 27. The average and dipolar contributions were extracted using the method in Carrington and McLaughlin [36] to resolve the sign ambiguity as shown in Figure 28:

N^{14}; $a = +14.2$ G   4H; $a = +19.5$ G

$t'_1 = -9.1$ $t'_1 = -0.5$

$t'_2 = +18.0$ $t'_2 = -1.1$

$t'_3 = -8.9$ $t'_3 = +1.6$

The average values correspond well to the values in solution of a_N=14.7 G and a_H=19.7 G, and the principle values are characteristic of a nitroxide [24,25].

Laue patterns of a N-nitropyrrolidine crystal showed three mutually perpendicular reflection planes of two-fold axes parallel to the x,y, and z laboratory axes and no three-fold axis at $\phi = 45^\circ$ and $\theta = 45^\circ$. Therefore the crystal showed orthorhombic symmetry with the crystal axes parallel to the laboratory axes.

To orient the radicals in the crystal it was noted that the maximum principle value of the nitrogen tensor laid along the nitrogen p-orbital and the maximum value of the hydrogen tensor was along a line through the two β-carbons. Thus the nitroxide is trapped in the N-nitropyrrolidine crystal as shown in Figure 29.

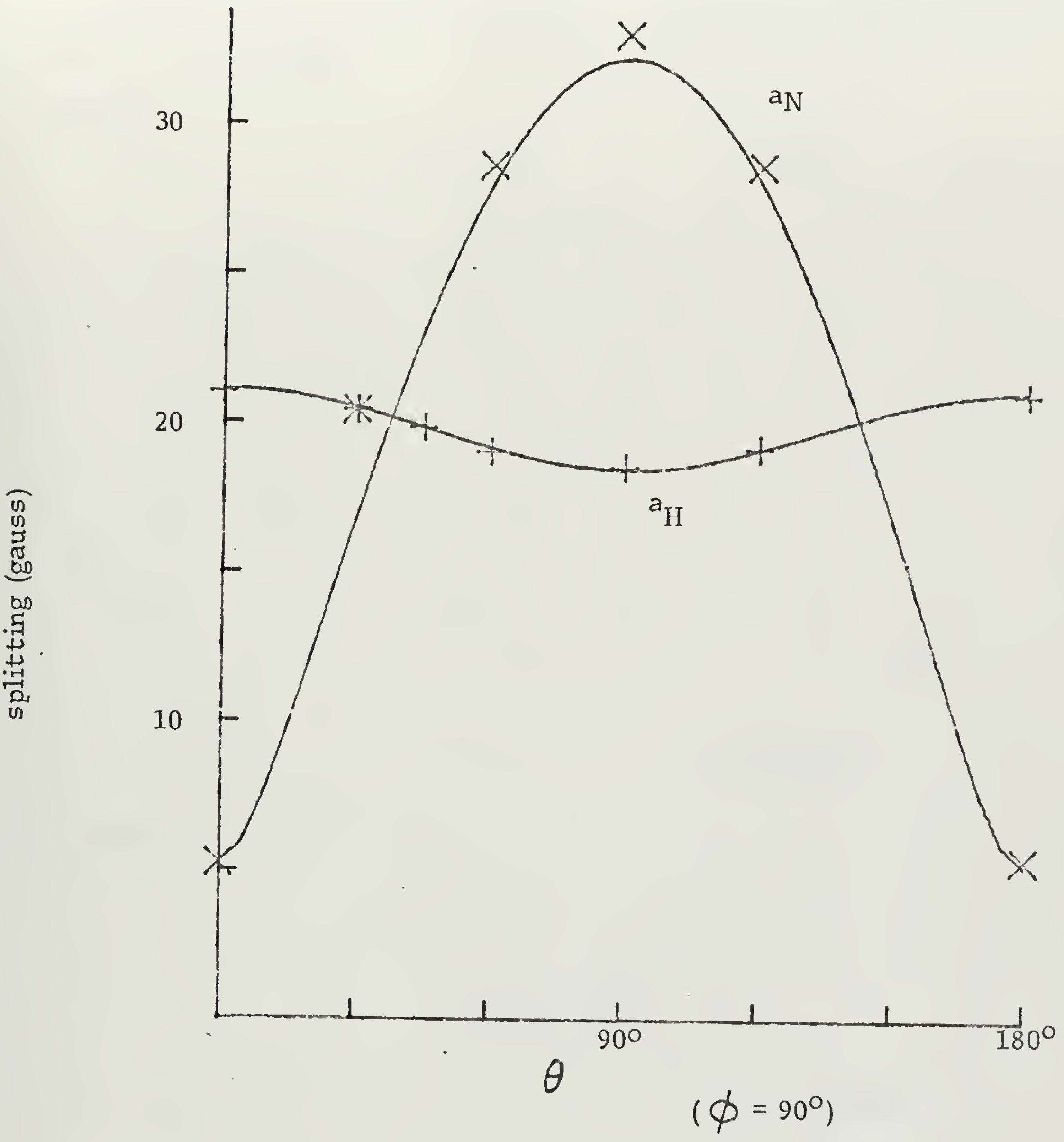
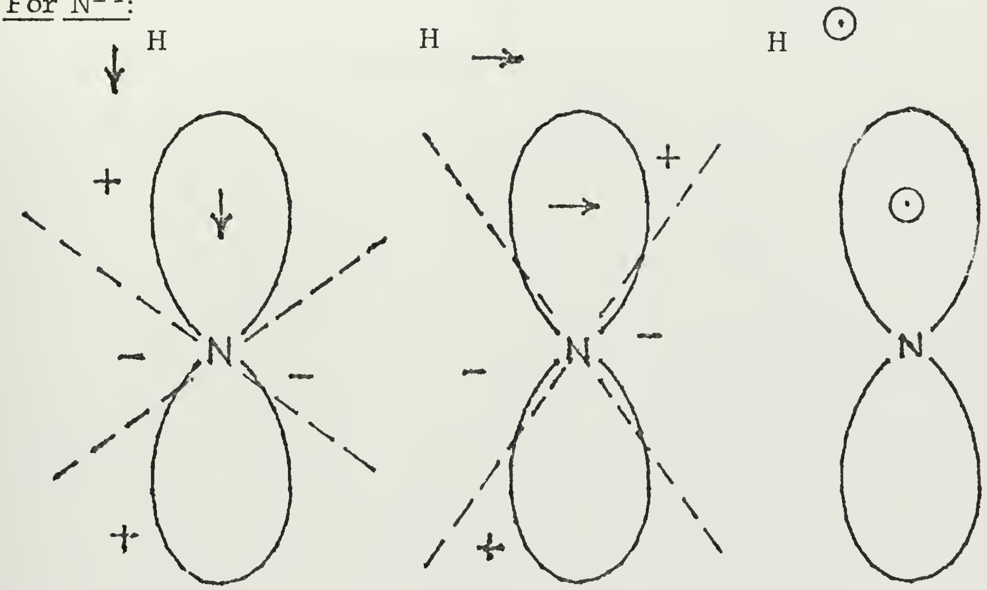


Figure 27. Variation in the average splitting with direction of the magnetic field for pyrrolidine N-oxide in a crystal of N-nitropyrrolidine. The solid line is the theoretical result, and the crosses are experimental points. This orientation is the worst fit of experimental to theoretical.

Figure 28. Determination of signs of tensor elements for N-nitropyrrolidine.

t' is a function of $\langle 3\cos^2\theta - 1\rangle$. Therefore the dipolar coupling is positive in a cone around the magnetic field where $0 < \theta < 54^\circ 44'$ or $125^\circ 16' < \theta < 180^\circ$ [35]

For N^{14}:



t' - positive

t' - negative and equal

For 4 H :

t' - positive

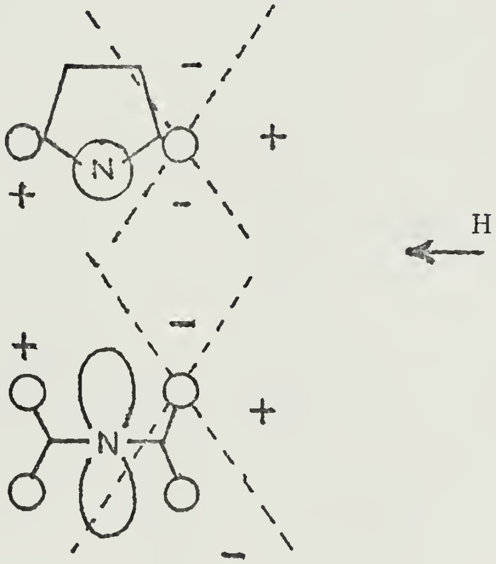
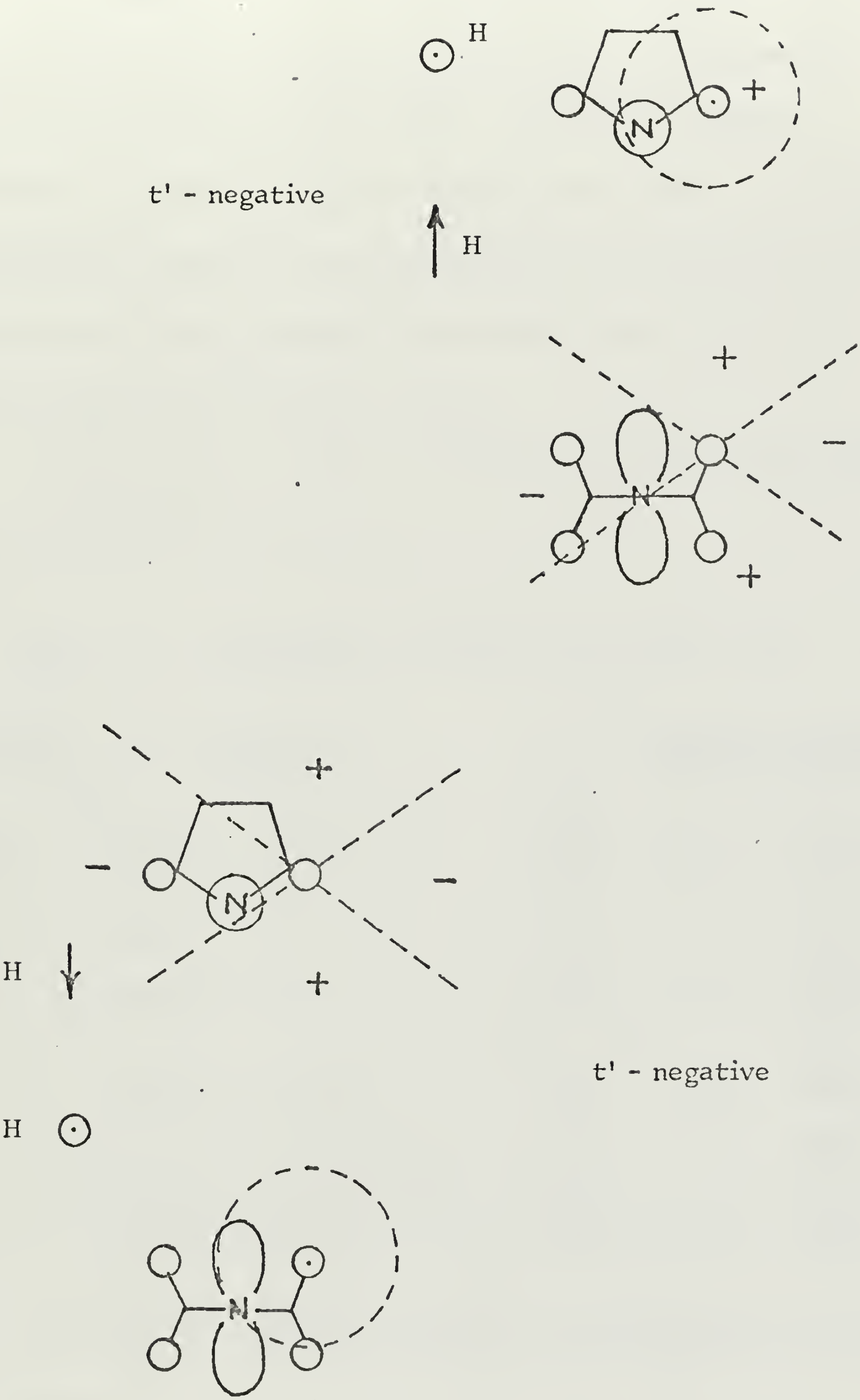


Figure 28 (Continued)



2. N-Nitromorpholine

The nitroxide formed in N-nitromorpholine showed at room temperature the 1-4-1 pattern of lines caused by slow interchange between the axial and equatorial protons. The radical, therefore, was still free enough in the crystal to change from chair to boat form, and the hydrogen hyperfine tensor measured at room temperature was the sum of the axial and equatorial proton interactions, and accordingly the coupling was referred to as a_{2H}.

A least squares fit [34] to the relationship used for pyrrolidine N-oxide yielded the following tensors:

TABLE VI: HYPERFINE TENSORS FOR MORPHOLINE N-OXIDE

Nucleus	Principle Value	Direction Cosine		
		x	y	z
N^{14}	$A_{xx} = 8.6 \pm 0.3$ G	0.83	0.23	-0.52
	$A_{yy} = 9.4 \pm 0.3$	-0.17	0.97	0.15
	$A_{zz} = 31.3 \pm 0.1$	0.54	-0.03	0.84
4H	$A_{xx} = 27.1 \pm 0.1$ G	0.84	0.01	-0.54
	$A_{yy} = 22.7 \pm 0.1$	0.42	0.62	0.66
	$A_{zz} = 22.8 \pm 0.1$	0.34	-0.78	0.52

A plot of the fit of the calculated tensors to the experimental data is shown in Figure 30.

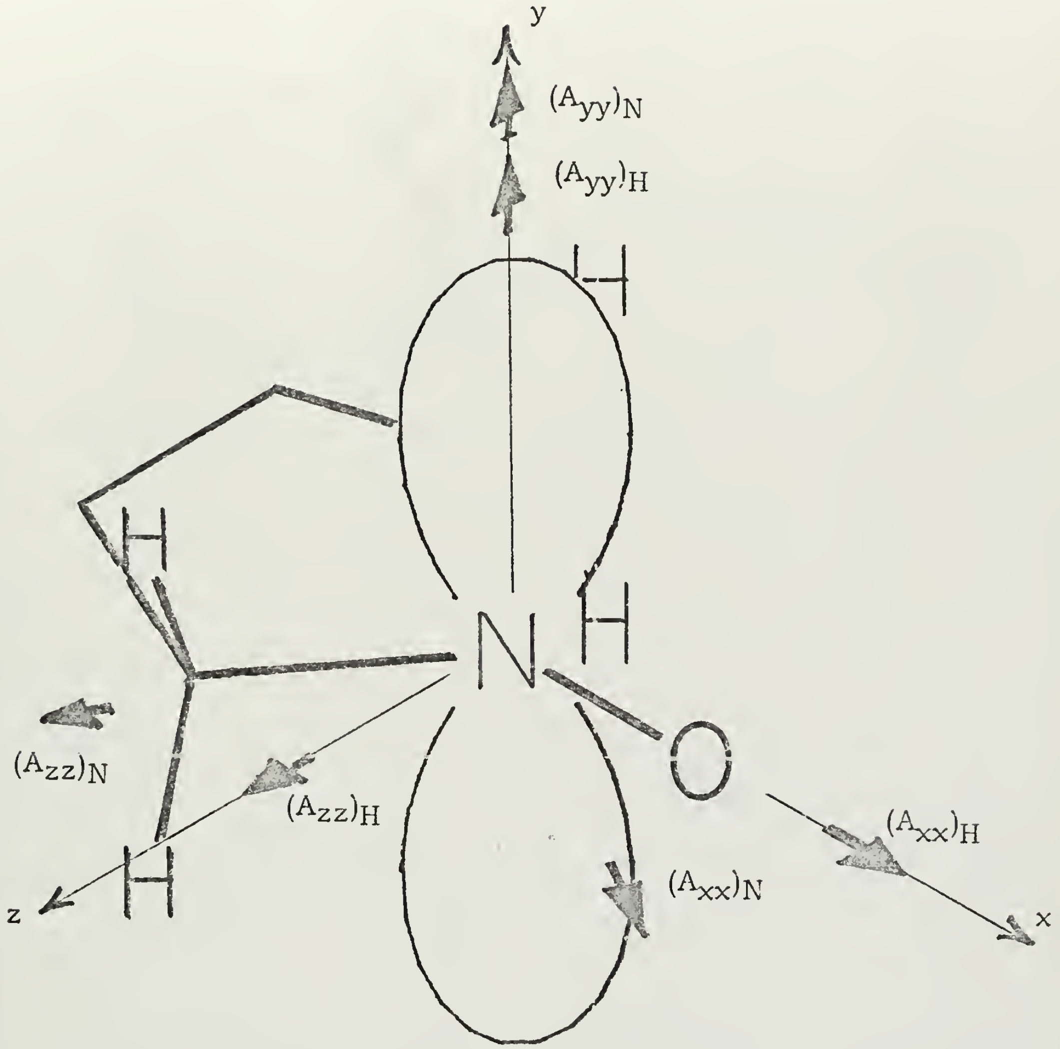


Figure 29. The orientation of pyrrolidine N-oxide prepared in situ in a crystal of N-nitropyrrolidine. The x,y, and z axes are both the crystallographic axes and the laboratory axes defined in Figure 18.

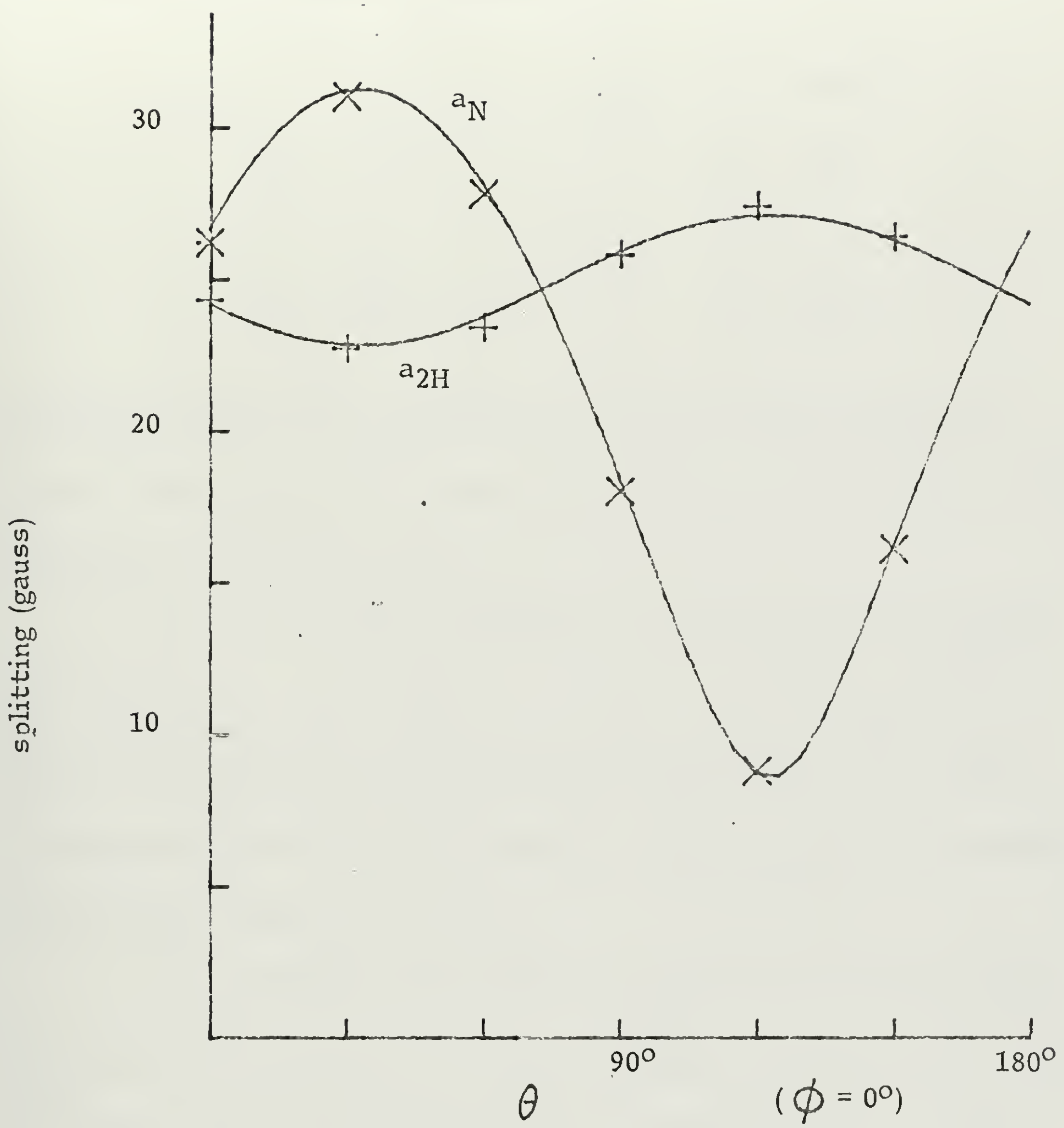


Figure 30. Variation in the splitting with the direction of the magnetic field for the EPR spectrum of morpholine N-oxide in a crystal of N-nitromorpholine. The solid line is the theoretical result, and the crosses are experimental points.

Using the same reasoning as for pyrrolidine N-oxide (Figure 28) the tensors were assigned as follows:

$\underline{a}_N$:	a	$=+16.4$ G	$\underline{a}_{2H}$;	a	$=+24.2$ G
	t_1'	$= -7.8$		t_1'	$= +2.9$
	t_2'	$= -7.0$		t_2'	$= -1.5$
	t_3'	$=+14.9$		t_3'	$=-1.4$

Again the average values correspond to the same radical being seen in solution where $a_N = 16.7$ G and $a_{ax} + a_{eq} = 23.2$ G, and the nitrogen tensor is characteristic of a nitroxide.

Laue patterns showed monoclinic symmetry for N-nitromorpholine with the unique axis along the y axis and low order planes in the y-z plane and rotated from the y-z plane about the y axis by 33°. Strong intensities suggested that these were the a and c axes, but Laue patterns cannot confirm this.

The orientation of morpholine N-oxide in the N-nitromorpholine crystal is shown in Figure 31. Since the hydrogen coupling tensor is axially symmetric within experimental error A_{xx} was plotted as $A_{\parallel}$ and the plane containing A_{yy} and A_{zz} became $A_{\perp}$.

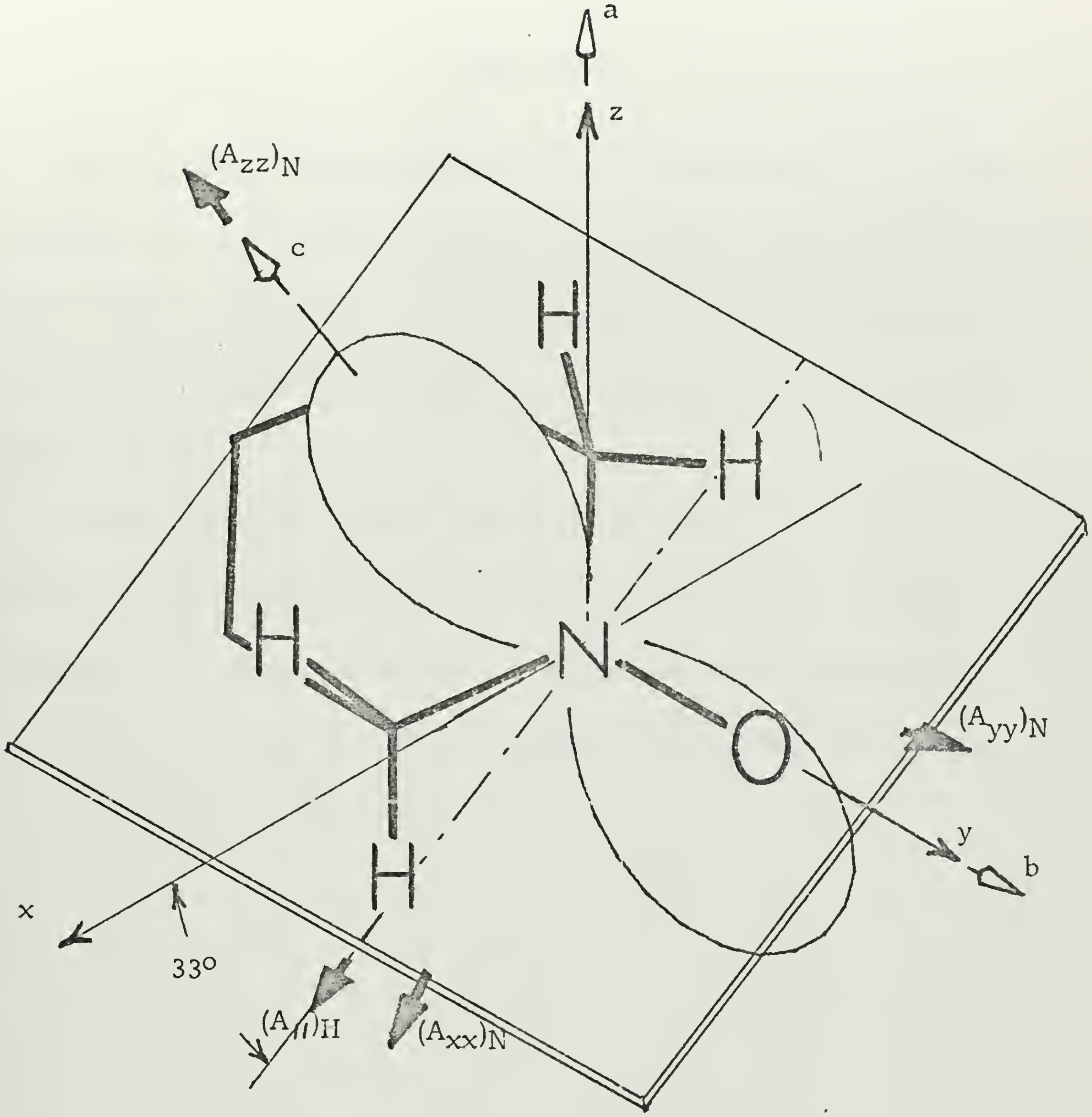
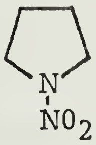


Figure 31. Orientation of morpholine N-oxide prepared in situ in a crystal of N-nitromorpholine. The plane shown is defined by the C-N-C bond. The a, b, and c axes are the crystallographic axes, and the x, y, and z axes are the laboratory axes defined in Figure 19. The plane containing $(A_{\perp})_H$ is defined by the b and c axes.

V. DISCUSSION

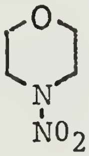
The EPR study of thephotolysis of cyclic nitramines has shown that nitroxides are intermediates in their decomposition. While this has furthered the understanding of the mechanism involved, it also has led to a method of preparing and studying nitroxides both in solution and in single crystals.

The nitramines used in the study were N-nitropyrrolidine (I), N-nitropiperidine (II), N-nitromorpholine (III), N-nitro-4-methylpiperidine (IV), N-nitro-4-t-butylpiperidine (V), N,N'-dinitropiperazine (VI), 1,3-dinitro-1,3-diazacyclohexane (VII), and 1,3,5-trinitre-1,3,5-triazacyclohexane (RDX, VIII).



(I)

(II)



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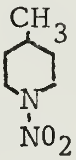

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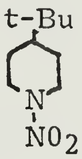
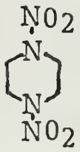
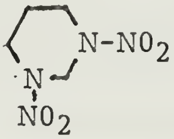


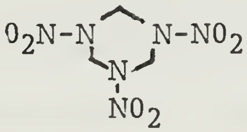
(V)



(VI)



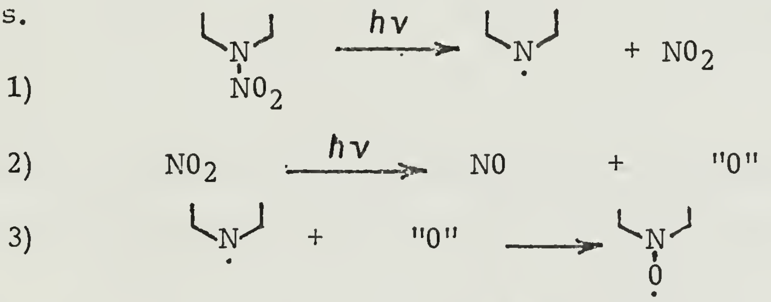
(VII)



(VIII)

The nitramines I through V and VII were synthesized using standard techniques without difficulty except that the reduction of 4-t-butylpiperidine in the synthesis of V required lithium and liquid ammonia. Compounds IV and V are new, and their physical constants and spectral data have been reported in the Experimental section.

Upon irradiation with ultraviolet light in 1,3-propanediol cyclic carbonate solution compounds I through VII showed the same EPR spectrum as NO or NO_2 dissolved in PDCC under the same conditions. At lower temperatures a spectrum was seen in each case corresponding to the nitroxide formed by replacing one nitro group by an oxygen molecule. A similar nitroxide was seen for RDX (VIII) irradiated in CH_3CN at room temperature. It has been reported that NO_2 dissolved in dimethylsulfoxide when irradiated forms a nitroxide by insertion into the solvent [37], and NO_2 dissolved in olefinic solvents has an EPR spectrum consisting of three lines with a splitting of 11 to 14 G [38]. Also, it is known that NO_2 decomposes photochemically into NO and molecular oxygen [39]. These data suggest a mechanism for the photodecomposition of nitramines.

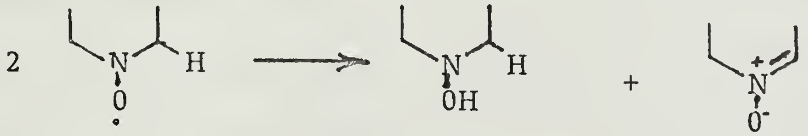


4) NO and/or NO_2 + PDCC → Insertion radicals

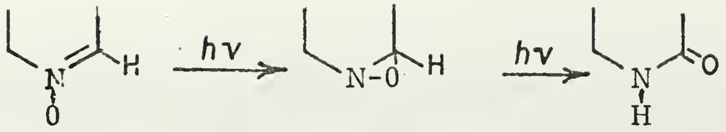
5) Combination of radicals to diamagnetic products

The behavior of the nitramines is easily explained in this way, assuming that the rate of step 4) is more strongly temperature dependent than the others. At room temperature the rate of solvent interaction with NO (or NO_2) is sufficiently fast for an EPR spectrum to be seen while the nitroxide radicals decay too quickly to be detected. However, at lower temperatures the solvent interaction is slowed so that insertion radicals are not seen, and the concentration of nitroxides increases because their rate of decay is slowed and also slower diffusion forces the NO_2 to remain near the site of its formation and consequently there is a greater probability of a reaction to form the nitroxide in the original solvent cage. Contrary to the previous proposed mechanisms it is the N-N bond rather than a C-N bond that breaks upon absorption of radiation; all the nitroxides studied had the ring structure of the original nitramine still intact.

There is evidence [18, 19, 20] that nitroxides undergo a bimolecular reaction to form a hydroxylamine and a nitrone.



The decay of the EPR signal was second order for compounds I to V indicating that the oxidizing conditions in the reaction mixture do not affect this step. These two products have a photochemistry of their own: the hydroxylamine forms more nitroxide [16] and the nitrone rearranges to an oxaziridine then to an amide [40].



Therefore, the hydroxylamine and amide (or their photochemical products or oxidation products with NO) should be found as final products of the photolysis.

The spectra detected in crystalline N-nitropyrrolidine and N-nitromorpholine were strong and well resolved allowing the hyperfine tensors to be measured for both the nitrogen and β-hydrogens. The nitrogen hyperfine tensors of stable nitroxides have been measured [24,25], and the tensors of the radicals generated in the crystalline nitramines have values consistent with those reported. This supports the proposed mechanism with the crystal lattice rather than a solvent cage keeping the NO_2 at the point of formation until the nitroxide can be formed.

Difficulties arise in attempting to study nitroxides in solids, since oxidation is required, and a reaction in solution is normally the only feasible way to accomplish this. Preparing the nitroxide and trapping it in a host crystal has been done [24, 25], but nitroxides with β -protons are too unstable to use that technique. By irradiating nitramine crystals, the oxidizing agent is generated <u>in situ</u>, allowing even the unstable nitroxides to be trapped and studied. The EPR signal from pyrrolidine N-oxide was detectable over 24 hours after irradiation

in a crystal while it lasted only seconds in solution after the lamp was turned off.

The hyperfine tensors measured for the protons of the trapped unstable nitroxides, while new, are not unusual. The β-protons in the $CH_3\dot{C}HCOOH$ radical [41] have an isotropic splitting of +25.1 G and dipolar terms of -1.2, -1.0, and +2.2 G. Since both the carboxylic acid radical and a nitroxide have the unpaired electron localized largely in the p-orbital of the carbon and nitrogen respectively, similar properties for both are expected. An average value with a positive sign is also expected for coupling by hyperconjugation. Therefore, the experimental values of a = +19.5, t' = -0.5, -1.1, +1.6 for pyrrolidine N-oxide and a = +24.2, t' =-1.4, -1.5, +2.9 for morpholine N-oxide are consistent with theory.

Interpretation of the nitrogen tensors varies somewhat depending on the model system chosen. Following the method of Hamilton and McConnell [26] it is found that comparison of the isotropic splitting of a nitroxide to the splitting of NH_3^+ leads to the conclusion that the unpaired electron of pyrrolidine N-oxide has a spin density of 0.75 in the $2p\pi$ orbital of the nitrogen while the value for morpholine N-oxide is about 0.85. However, the general method of Carrington and McLaughlin [36] uses the isotropic value to compare to the calculated s orbital splitting of N^{14} [41] giving the s orbital spin density of about 0.02 for both radicals. Then comparison of the maximum dipolar interaction with the calculated dipolar interaction of a pure Slater $2p\pi$ orbital [26],

gives a $2p\pi$ spin density of 0.60 for pyrrolidine N-oxide and 0.52 for morpholine N-oxide. In either calculation the electron is localized mainly in the $2p\pi$ orbital, but the comparison of values merely shows how crude such calculations really are. Also, localization in this orbital would result in an axially symmetric tensor. This is true for pyrrolidine N-oxide, but for morpholine N-oxide the tensor can be written:

$$A = \begin{vmatrix} -7.8 & & \\ & +14.9 & \\ & & -7.0 \end{vmatrix} = \begin{vmatrix} -7.6 & & \\ & +15.1 & \\ & & -7.6 \end{vmatrix} + \begin{vmatrix} -0.3 & & \\ & -0.3 & \\ & & +0.6 \end{vmatrix}$$

Thus the $2p\pi$ orbital is mainly occupied, but there is some electron density in a 2p s orbital, the one along the N-0 bond. This orbital is in a node of the $2p\pi$ orbital of the planar pyrrolidine N-oxide, but morpholine N-oxide is not planar which allows some unpaired spin character to this orbital.

As a result of this investigation the somewhat unusual situation has arisen of having the intermediates characterized while the products of the reaction are not known with certainty. Since the reactions of nitroxides are known, this suggests that future investigations into the photodecomposition of nitramines should be concerned with looking for the breakdown products of nitroxides as the final products. Of special interest in determination of the mechanism would be the isolation of the "solid residue" mentioned [47] in the studies on HMX and RDX.

More work in the characterization of nitroxides is also suggested by this study. The existence of two inequivalent sites in irradiated N,N'-dinitropiperazine, N-nitro-4-t-butylpiperidine, and in N-nitromorpholine at low temperatures might be useful in determining the conformations of the cyclic nitroxides and measuring their barriers to internal rotation. A new method for preparation of unstable nitroxides has been presented which should allow a wide range of the radicals to be studied, and which quite possibly could have application in spin labeling.

APPENDIX: DATA FOR HYPERFINE TENSORS OF PYRROLIDINE N-OXIDE AND MORPHOLINE N-OXIDE

		Pyrrolidine N-oxide		Morpholine N-oxide	
ϕ	θ	a_N	a_H	a_N	$a_{ax}+a_{eq}$
-45°	0°	5.5	21.1g	27.4 g	24.0 g
-45	30	11.0	20.8	29.2	22.7
-45	60	19.2	19.2	24.2	23.5
-45	90	22.6	18.7	16.2	24.3
-45	120	19.5	19.5	9.15	25.4
-45	150	13.2	20.3	18.2	25.3
0	0	5.6	21.2	26.2	24.3
0	30	5.2	20.4	31.0	22.7
0	60	5.5	19.7	27.8	23.4
0	90	5.35	19.0	18.0	25.8
0	120	5.3	19.4	8.8	27.4
0	150	5.3	20.5	16.1	26.4
45	0	5.25	21.2	27.0	24.1
45	30	12.2	20.7	29.1	22.8
45	60	19.2	19.2	23.6	23.6
45	90	19.7	18.8		24.1
45	120	19.2	19.2	9.6	25.4
45	150	11.2	20.4	18.5	25.5
90	0	5.4	21.0	27.3	23.5
90	30	19.8	20.4	23.5	23.8
90	60	28.6	19.0	15.0	23.1
90	90	33.0	18.5	9.3	22.6
90	120	28.6	19.15	16.1	23.0
90	150			24.0	24.2
-45	130				25.4
-45	140				25.7

LIST OF REFERENCES

1. Whittaker, The Photochemistry of Nitramines, M.S. Thesis, U.S. Naval Postgraduate School, June 1971.

2. Suryanarayana, B., Autera, J.R., and Graybush, R.J., "Thermal Degradation of Secondary Nitramines: A Nitrogen-15 Tracer Study of HMX (1,3,5,7-Tetranitro-1,3,5,7-Tetraazacyclooctane," Chemistry and Industry, v. 52, p. 2177-2178, 30 December 1969.

3. Maksinov, Yu. Ya., "Thermal Decomposition of Hexogen and Octogen," Transcripts of the Moscow Chemical and Technological Institute, v. 53, p. 73-84, 1967.

4. Robertson, A.J.B., "Thermal Decomposition of Explosives II," Transactions of the Faraday Society, v. 45, p. 85-93, January 1949.

5. Flournoy, J.M., "Thermal Decomposition of Gaseous Dimethylnitramine," Journal of Chemical Physics, v. 36, p. 1106-7, 15 February 1962.

6. Maycock, J.N., Vernecker, V. R. Pai, and Lochte, W., "Physico-Chemical Properties of 1,3,5,7-Tetranitro-1,3,5,7-Tetraazacyclooctane (HMX). II," Physica Status Solidi, v. 35, no. 2, p. 849-860, October 1969.

7. Torbitt, J.B., The Photochemical Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane (HMX), M.S. Thesis, U.S. Naval Postgraduate School, April 1970.

8. Darnez, C., Paviot, J., and Cherville, J. "Étude par R.P.E. de la Radiolyse de la Cyclotrimethylene Trinitramine," Journal de chimie physique et de physio-chimie biologique, v. 66, p. 2016-7, 1969.

9. Chapelet-Letourneux, G., Lemaire, H., and Rassat, A., "Nitroxydes XVI: mise en evidence de radicaux libres dans les oxydations par les peracides," Bulletin de la Société chimique de France, p. 3283-3290, November 1965.

10. Brière, R., Lemaire, H., and Rassat, A., "Nitroxydes XV: Synthèse et étude de radicaux libres stables pipéridiniques et pyrrolidinique," Bulletin de la Société chimique de France, p. 3273-3282, November 1965.

11. Neiman, M.B., Rozantzev, E.G., Mamedova, Yu. G., "Free Radical Reactions involving no Unpaired Electrons," Nature, v. 196, p. 472-4, 3 November 1962.

12. Coppinger, G.M., Swalen, J.D., "Electron Paramagnetic Resonance Studies of Unstable Free Radicals in the Reaction of t-Butyl Hydroperoxides and Alkylamines," Journal of the American Chemical Society, v. 83, p. 4900-4902, 20 December 1961.

13. Hoffman, A.K., and Henderson, A.T., "A New Stable Free Radical: Di-t-Butylnitroxide," Journal of the American Chemical Society, v. 83, p. 4671-2, 20 November 1961.

14. Strom, E.T. and Bluhm, A.L., "Photochemical Formation of Dialkyl Nitroxides from Nitrosoalkanes," Chemical Communications, No. 4, p. 115-6, 1966.

15. Adams, J.Q., Nicksic, S.W., and Thomas, J.R., "Paramagnetic Resonance of Alkyl Nitroxides," Journal of Chemical Physics, v. 45 (2), p. 654-661, 15 July 1966.

16. Windle, J.J., Kuhnle, J.A., and Beck, B.H., "ESR Study of Interconversion of Piperidine Iminoxyls," Journal of Chemical Physics, v. 50 (6), p. 2630-2641, 15 March 1969.

17. Buchachenko, A.L., Stable Radicals, p. 135-141, Consultants Bureau, 1965.

18. Dupeyre, R-M., and Rassat, A., "Nitroxides XIX. Norpseudopelletierine N-oxyl, A New, Stable, Unhindered Free Radical," Journal of the American Chemical Society, v. 88 (13), p. 3180-1, 5 July 1966.

19. Adamic, K., Bowman, D.F., and Ingold, K.U., "Self-Reaction of Diethylnitroxide Radicals," Journal of the American Chemical Society, v. 92 (4), p. 1093-4, 25 February 1970.

20. Adamic, K., Bowman, D.F., Gillan, T., and Ingold, K.U., "Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. I," Journal of the American Chemical Society, v. 93 (4), p. 902-8, 1971.

21. Blackley, W.D., and Reinhard, R.R., "A New Stable Radical, Bis (trifluoromethyl) Nitroxide," Journal of the American Chemical Society, v. 87 (4), p. 802-5, 20 February 1965.

22. Hudson, A., and Hussain, H.A., "Electron Spin Resonance of Aliphatic Nitroxides. Part II. The Cyclic Radicals from Pyrrolidine, Piperidine, Morpholine and Hexamethyleneimine." Journal of the Chemical Society (B), p. 251-3, 1968.

23. Hudson, A., Hussain, H.A., "Electron Spin Resonance Studies of Aliphatic Nitroxides. III. A conformational Study of radicals from 4-alkylpiperidines and piperazine." Journal of the Chemical Society (B), No. 9, p. 953-5, 1968.

24. Griffith, O.H., Cornell, D.W., and McConnell, H.M., "Nitrogen Hyperfine Tensor and G Tensor of Nitroxide Radicals." Journal of Chemical Physics, v. 43, p. 2909-2910, 1965.

25. Libertini, L.J., Griffith, O.H., "Orientation Dependence of the Electron Spin Resonance Spectrum of Di-t-butyl Nitroxide," Journal of Chemical Physics, v. 53 (4), p. 1359-1367, 15 August 1970.

26. Hamilton, C.L., and McConnell, H.M., "Spin Labels," p. 115-149, in Structural Chemistry and Molecular Biology, Rich, A., and Davidson, N., ed., W.H. Freeman and Co., 1968.

27. Griffith, O.H., and Waggoner, A.S., "Nitroxide Free Radicals: Spin Labels for Probing Biomolecular Structure," Accounts of Chemical Research, v. 2 (1), p. 17-24, January 1969.

28. Coburn, M.D., and Ungnade, H.E., "Synthesis and Structure of the N-nitropyrrolidinones," Journal of Heterocyclic Chemistry, v. 2 (3), p. 308-9, 1965. (Chemical Abstracts, v. 63, p. 16290e, 1965)

29. Emmons, W.D., Freeman, J.P., "Alkaline Nitration. I. The Nitration of Cyanohydrin Nitrates," Journal of the American Chemical Society, v. 77, p. 4387-4390, 20 August 1955.

30. Organic Synthesis, coll. v. 4, p. 887-9, John Wiley and Sons, Inc., 1963.

31. Dictionary of Organic Compounds, 4th ed., v.2, p. 877, Oxford University Press, 1965.

32. Woodcock, D., "Studies on Nitroamines. Part III. The Reactions of Nitroamines with Formaldehyde," Journal of the Chemical Society, p. 1635-7, 1949.

33. Bell, J.A., and Dunstan, I., "Chemistry of Nitramines Derived from Trimethylenedinitramine," Journal of the Chemical Society (c), p. 870-2, 1966.

34. Tolles, W.H., Computer Program.

35. Espie, J-C., Lemaire, H., and Rassat, A., "Nitroxydes. XXIX.- Analyse conformationnelle par résonance paramagnetic de radicaux nitroxydes dérivant de la pipéridine," Bulletin de la Société chimique de France, p. 399-406, February 1969.

36. Carrington, A., and McLaughlin, A.D., Introduction to Magnetic Resonance, p. 99-113, p.132-145, Harper and Row, 1967.

37. Lagercrantz, C., "Electron Spin Resonance Studies of Nitroxide Radicals Formed in the Reaction between Nitrogen Dioxide and Dimethyl Sulfoxide," Acta Chemica Scandinavica, v. 23 (9), p. 3259-3261, 1969.

38. Bielski, B.H.J., and Gebicki, J.M., "Electron Spin Resonance Studies of Interaction between Nitrogen Dioxide and Olefinic Solvents," Journal of Physical Chemistry, v. 73 (5), p. 1402-6, May 1969.

39. Ford, H.W., and Jaffe, S., "Photolysis of Nitrogen Dioxide at 3660 and 4047 Å at 25° C," Journal of Chemical Physics, v. 38 (12), p. 2935-2942, 15 June 1963.

40. Delpierre, G.R., and Lamchen, M., "Nitrones," Quarterly Reviews, v. 19 (4), p. 329-348, 1965.

41. Miyagawa, I., and Itoh, K., "Electron Spin Resonance of Irradiated Single Crystals of Alanines: Hindered Rotation of the Methyl Group in a Free Radical," Journal of Chemical Physics, v. 36 (8), p. 2157-2163, 1962.
(Ayscough, P. B., Electron Spin Resonance in Chemistry, p. 228, Methuen and Co. Ltd., 1967).

42. Ayscough, p. 439.

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13. ABSTRACT

Ultraviolet irradiation of cyclic nitramines, both in solution and as single crystals, reveals an EPR signal due to nitroxide radicals. Photolysis of solutions of nitramines in 1,3-propanediol cyclic carbonate in the EPR cavity allowed preparation and assignment of the spectra of pyrrolidine N-oxide, piperidine N-oxide, morpholine N-oxide, 4-methyl-piperidine N-oxide, 4-t-butylpiperidine N-oxide, 4-nitro-piperazine N-oxide, 3-nitro-1,3,-diazacyclohexane N-oxide, and 3,5-dinitro-1,3,5-triazacyclohexane N-oxide. Photolysis of N-nitropyrrolidine and N-nitromorpholine single crystals led to *in situ* generation of pyrrolidine N-oxide and morpholine N-oxide respectively, and hyperfine tensors for both nitrogen and hydrogen coupling were assigned.

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Nitramine						
Nitroxide						
Photochemistry						

Bodnar
The photochemistry of nitramines, I: preparation of nitroxides in solution and in situ in single crystals.

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