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AD NUMBER
AD347414
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TO: unclassified
FROM: confidential
LIMITATION CHANGES
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31 Jan 1976, Group 4, DoDD 5200.10; ONR ltr dtd 16 Feb 1979

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AD 347414

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REPORT NO. 0235-01-18 (QUARTERLY)
PERIOD COVERED: 1 OCTOBER – 31 DECEMBER 1963

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

A REPORT TO

OFFICE OF NAVAL RESEARCH

AND

ADVANCED RESEARCH PROJECTS AGENCY

CONTRACT NOnr-2655(00), ARPA ORDER NO. 170
PROJECT CODE 4910

JANUARY 1964

COPY NO. CP-61-1

CHEMICAL PRODUCTS DIVISION
AEROJET-GENERAL CORPORATION
AZUSA, CALIFORNIA

(0235)

United States Patent Office Secrecy Order

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January 1964

Report No. 0235-01-18

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

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A Report To

OFFICE OF NAVAL RESEARCH
and
ADVANCED RESEARCH PROJECTS AGENCY

Contract NOnr-2655(00), ARPA Order No. 170
Project Code 4910

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AEROJET-GENERAL CORPORATION

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This is the eighteenth quarterly report prepared under Contract Nonr-2655(00). The ARPA Order No. is 170; the Project Code is 4910. It covers the period 1 October through 31 December 1963.

AEROJET-GENERAL CORPORATION

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ABSTRACT

The reaction of 1,1-dichloro-1-nitrobutane with difluoramine in fuming sulfuric acid gave 1,1-dichloro-1-(difluoramino)butane. cis 3-Chlorocrotonic acid was converted to 3-chloro-3-(difluoramino)butyric acid. Attempts to hydrate or brominate 3,3-bis(difluoramino)-1,1-dichloro-1-butene were unsuccessful. The reaction of N-[2,2-dichloro-1,2-bis(difluoramino)ethyl] acetamide with aqueous base gave the anion of N-[2,2-dichloro-1-fluoramino-2-(difluoramino)ethyl]-acetamide. The reaction of methyl vinyl ketone with difluoramine in fuming sulfuric acid gave 1,3,3-tris(difluoramino)butane and 2-methyl-2-difluoramino-5-[1,1-bis(difluoramino)ethyl] tetrahydropyran. 5-Nitro-2-pentanone was converted to 5-nitro-2,2-bis(difluoramino)pentane.

The aqueous fluorination of tetrahydro-2-pyrimidone yielded 1,3-bis-(difluoramino)propane, 3-difluoraminopropylcarbamyl fluoride, 3-difluoraminopropyl isocyanate, and 3-difluoraminopropionitrile. The carbamyl fluoride and isocyanate were treated with alcohols to form carbamates, which could be fluorinated further. Methanetriscarbamates, prepared from ethyl orthoformate and carbamates, underwent degradation during their fluorination.

The reaction of isopropyl N-fluorocarbamate with 70% perchloric acid yielded a white solid after most of the acid was removed under vacuum. The addition of dioxane gave a recrystallizable solid, identified as a 1:1 complex of N-fluorammonium perchlorate and dioxane. Most of the dioxane was removed from the complex under high vacuum.

2,2-Dinitro-2-fluoroethanol reacted with 100% nitric acid to give the corresponding nitrate. This alcohol also reacted with sodium hypochlorite to form chlorofluorodinitromethane and with primary or secondary amines to give the Mannich reaction products. The product from ammonia was unstable, but it was reacted with ethyl chloroformate to give ethyl dinitrofluoroethylcarbamate and ethyl dinitrofluoroethylcarbonate.

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I. INTRODUCTION

The objective of this program is to develop new methods of preparing high-energy materials for military applications.

II. TECHNICAL DISCUSSION

A. REACTIONS OF DIFLUORAMINE (K. Baum, F. J. Gerhart)

1. Discussion

Efforts to prepare a 1,1,1-trisdifluoraminoalkane were continued. It was found previously that the reaction of vinylidene chloride with difluoramine in fuming sulfuric acid gave 1,1-dichloro-1-difluoraminoethane, 1-chloro-1,1-bis(difluoramino)ethane, and a small amount of another material, the proton NMR spectrum of which was consistent with the 1,1,1-tris(difluoramino)-ethane structure.* Two attempts to reproduce this experiment for the purpose of characterizing the latter compound resulted only in the isolation of the former compounds.

Because of experimental difficulties resulting from the high volatility of these products, an effort was made to apply this reaction to a higher homologue. Since it had previously been shown that nitro groups can be removed in the presence of difluoramine and sulfuric acid,** the reaction of 1,1-dichloro-1-nitrobutane with difluoramine was attempted with the objective of preparing 1,1-dichloro-1-(difluoramino)butane. This compound was synthesized in 61% yield after 2 hours when the reaction was conducted at ambient temperature using fuming sulfuric acid. Its infrared spectrum is shown in Figure 1 and its proton and fluorine NMR spectra are shown in Figure 2 and Figure 3.

$$CH_3CH_2CH_2CCl_2NO_2 \xrightarrow{HNF_2} CH_3CH_2CH_2CCl_2NF_2$$

An unsuccessful attempt was made to replace the chlorine atoms by extending the reaction time to 24 hours; only 1,1-dichloro-1-(difluoramino)butane was isolated.

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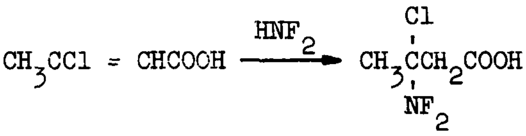
*Aerojet-General Report 2730, October 1963, p. 4 (Confidential).
**Aerojet-General Report 0235-01-11, 14 July 1961, p. 3 (Confidential).

The reaction of cis 3-chlorocrotonic acid with difluoramine was studied with the objective of synthesizing 3,3-bis(difluoramino)butyric acid. This model reaction would give a route to a new, potentially useful class of compounds; acetoacetic esters did not undergo the expected difluoramine reaction. When cis-3-chlorocrotonic acid was treated with refluxing difluoramine in fuming sulfuric acid, 3-chloro-3-(difluoramino)butyric acid was isolated, and was identified by elemental analysis, and by infrared (Figure 4), proton (Figure 5), and fluorine (Figure 6) NMR spectra. When this reaction was repeated at ambient temperature in a pressure reactor, the same product was formed. The inductive effect of the carboxyl, possibly protonated, could be responsible for inhibiting displacement of the chlorine.



$$CH_3CCl = CHCOOH \xrightarrow{HNF_2} CH_3\overset{Cl}{\underset{NF_2}{C}}CH_2COOH$$

The reaction of 1,1-dichloro-1-buten-3-one with difluoramine was previously shown to give either 3,3-bis(difluoramino)-1,1-dichloro-1-butene of N-[2,2-dichloro-1,2-bix(difluoramino)ethyl] acetamide, depending on the experimental conditions.[*] Some further work was done to determine the chemical properties of these materials. Thus, the hydration of 3,3-bis(difluoramino)-1,1-dichloro-1-butene would be expected to give a β,β-bis(difluoramino)carboxylic acid. No reaction took place when this olefin was heated with dilute sulfuric acid or with constant boiling hydrochloric acid. When the olefin was heated with concentrated sulfuric acid, it decomposed, and no product could be isolated. The olefin was also found to be unreactive toward bromine in carbon tetrachloride or water. The reaction of the olefin with alcoholic sodium hydroxide gave a material with acetylenic absorption in the infrared spectrum. Characterization of the product is incomplete.

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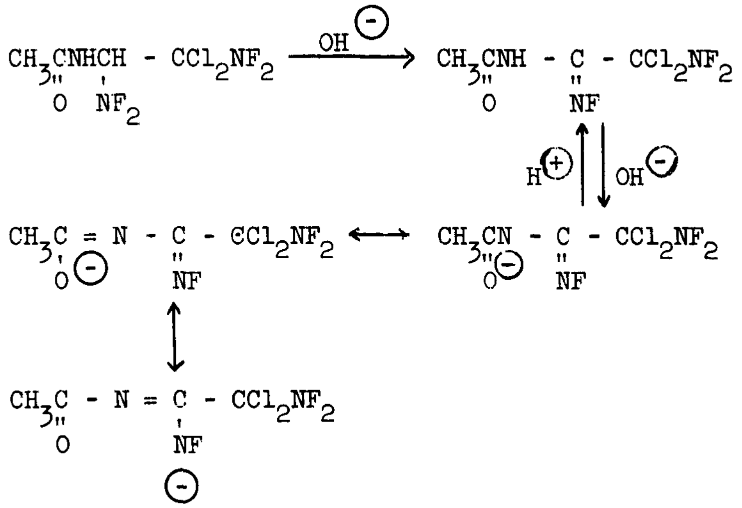
[*] Aerojet-General Report 2730, October 1963, p. 5 (Confidential).

When N-[2,2-dichloro-1,2-bis(difluoramino)ethyl] acetamide was treated with aqueous sodium hydroxide, a homogeneous solution was formed. When this solution was acidified, a new compound precipitated, which was identified by elemental analysis and by infrared (Figure 7), proton (Figure 8), and fluorine (Figure 9) NMR spectra as N-[2,2-dichloro-1-fluoramino-2-(difluoramino)ethyl]-acetamide. This material was found to be soluble in aqueous base and insoluble in acid. Its acidic properties are attributed to the amide hydrogen, the removal of which gives an anion stabilized by the carbonyl and fluorimino groups.



Although the reaction of methyl vinyl ketone with difluoramine in concentrated sulfuric acid is known to give 1,3,3-tris(difluoramino)butane,[*] this reaction was re-examined using fuming sulfuric acid as the solvent because of the unexpected results that were obtained with the chlorinated analog under these conditions. The product was found to contain, in addition to 1,3,3-tris-(difluoramino)butane, 2-methyl-2-difluoramino-5-[1,1-bis(difluoramino)ethyl]-tetrahydropyran. The infrared spectrum and proton and fluorine NMR spectra of this compound are shown in Figures 10, 11, and 12, respectively. This material might be formed either by the reaction of the intermediate, 3,3-bis(difluoramino)-1-butene, with methyl vinyl ketone or by the acid-catalyzed self-condensation of the latter, followed by reaction with difluoramine.

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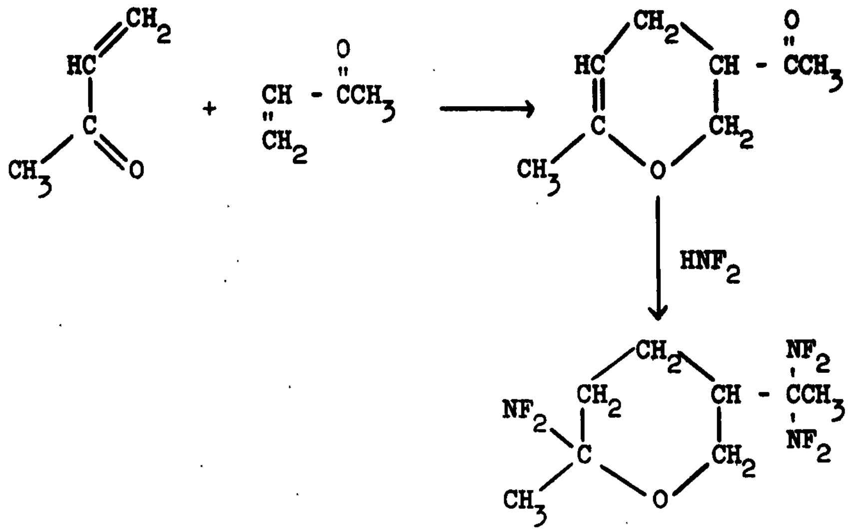
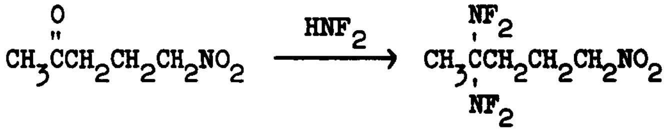
[*] Aerojet-General Report 0235-01-11, July 1961, p. 2 (Confidential).



5-Nitro-2-pentanone was also treated with difluoramine in fuming sulfuric acid. The product, 5-nitro-2,2-bis(difluoramino)pentane was characterized by elemental analysis, and by infrared (Figure 13), and proton (Figure 14), and fluorine (Figure 15) NMR spectra. Reactions of this compound will be studied.



$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2NO_2 \xrightarrow{HNF_2} CH_3\underset{NF_2}{\overset{NF_2}{C}}CH_2CH_2CH_2NO_2$$

2. Experimental

a. 1,1-Dichloro-1-(difluoramino)butane

1,1-Dichloro-1-nitrobutane* (4 g, 0.0232 mole) was added to a refluxing mixture of approximately 27 g of difluoramine and 11 ml of 20% fuming sulfuric acid in a 500-cc glass reactor fitted with Fischer-Porter glass needle valves. After 1 hour the color of the mixture was light purple. The valves were closed and the reaction was continued at room temperature for 2 hours. The reactor was then vented and the contents were drained into a beaker containing

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*J. B. Tindall, U.S. Patent 2,397,384 (1944).

50 g of ice. The aqueous mixture was extracted with three 30-ml portions of methylene chloride which were combined and dried over sodium sulfate. The methylene chloride solution was distilled through a 25-cm platinum spiral column to give 2.8 g (0.0143 moles, 61% yield) of 1,1-dichloro-1-(difluoramino)butane, b.p. 45°C/40 mm.

Anal. Calc'd for $C_4H_7NF_2Cl_2$: C, 27.0; H, 3.96; N, 7.86; F, 21.4

Found: C, 27.1; H, 4.03; N, 7.65; F, 20.7

The proton NMR spectrum (Figure 2) consists of an irregular triplet at 1.03 ppm and complicated multiplets with maximum intensities at 109 and 133 cps. The irregular triplet at 1.03 ppm is assigned to the terminal methyl group, $-CH_2C\underline{H}_3$. The 109 cps multiplet is assigned to the $-CH_2C\underline{H}_2CH_3$ methylene group and the 133 cps multiplet to the $-C\underline{H}_2CH_2CH_3$ methylene group. On a first order basis the latter two signals would be expected to be a sextet and a triplet, respectively. Obviously there is a large amount of second order splitting. The fluorine spectrum (Figure 3) consists of a single, somewhat broadened signal at -41.92 ppm.

b. 3-Chloro-3-(difluoramino)butyric Acid

cis-3-Chlorocrotonic acid (2.4 g, 0.02 moles) was added to a refluxing mixture of approximately 27 g of difluoramine and 10 ml of 20% fuming sulfuric acid. The mixture was allowed to reflux for 4-1/2 hours, and then the excess difluoramine was removed. The remaining liquid was drained into 50 g of ice and the mixture was extracted with three 20-ml portions of methylene chloride. The extracts were combined and dried over sodium sulfate. The solvent was distilled through a 25-cm platinum spiral column and the remainder was distilled to give 2.05 g (0.0119 moles, 59% yield) of 3-chloro-3-difluoraminobutyric acid, b.p. 68°C/0.2 mm. The product solidified in the receiver, giving a white solid, m.p. 29-30°C.

Anal. Calc'd for $C_4H_6NF_2ClO_2$: C, 27.7; H, 3.49; N, 8.09; F, 21.9

Found: C, 27.5; H, 3.24; N, 8.02; F, 20.1

The 60-mc proton NMR spectrum (Figure 5), obtained using a CCl_4 solution with TMS (tetramethylsilane) as an internal standard, consists of a triplet at 2.07 ppm ($C\underline{H}_3C(NF_2)Cl-$), a singlet at 3.16 ppm ($-C(NF_2)ClC\underline{H}_2CO-$), and a singlet at 11.74 ppm ($-COO\underline{H}$). The fluorine NMR spectrum (Figure 6) consists of a non-equivalence quartet, chemical shifts -32.63 and -36.16 ppm, coupling constant 563 cps.

c. N-[2,2-Dichloro-1-fluorimino-2-(difluoramino)ethyl]-acetamide

N-[2,2-Dichloro-1,2-bis(difluoramino)ethyl]acetamide* (3 g, 0.0116 moles) was dissolved in 15 ml of a 5% aqueous solution of sodium hydroxide. The solution was stirred at room temperature for 15 min and was then extracted with three 10-ml portions of methylene chloride. The aqueous phase was acidified with sulfuric acid, and was then extracted with three 10-ml portions of methylene chloride. The acid extracts were combined and dried over sodium sulfate. The solvent was distilled off and a pale yellow oil remained. The oil was dissolved in hot cyclohexane. White crystals formed upon cooling to room temperature. The solid was recrystallized and dried in vacuum to give 1.7 g (0.0071 moles, 61% yield) of N-[2,2-dichloro-1-fluorimino-2-(difluoramino)-ethyl]acetamide.

<u>Anal</u>. Calc'd for $C_4H_4N_3F_3Cl_2O$: C, 20.2; H, 1.68; N, 17.7; F, 24.0

Found: C, 21.0; H, 1.62; N, 17.4; F, 24.4

The 60-mc proton NMR spectrum (Figure 8) was obtained using a $CDCl_3$ solution with TMS added as an internal reference. The intense signal at 2.25 ppm is assigned to the methyl group, $-COC\underline{H}_3$. The signal shows some evidence of splitting on the order of 1 cps or less, which may result from long-range coupling or possibly from the presence of <u>cis</u> and <u>trans</u> forms of the amide. The broad, weak signal at 7.83 ppm is assigned to the amide proton, $-N\underline{H}CO-$. The F^{19} spectrum, Figure 9 (56.4 mc, $CFCl_3$ internal reference) contains

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*Aerojet-General Report 2730, October 1963, p. 17 (Confidential).

a signal at -43.47 ppm, assigned to the $Cl_2C(NF_2)$difluoramino group. The signal at -25.25 ppm (roughly half the intensity of the former) is assigned to the fluorimino fluorine, $-C(=N\underline{F})-$.

d. Reaction of Methyl Vinyl Ketone with Difluoramine

Methyl vinyl ketone (3 g, 0.043 moles) was added dropwise to a refluxing mixture of 27 g of difluoramine and 10 ml of 20% fuming sulfuric acid. After the solution was allowed to reflux for 3 hours, 50 ml of pentane was added and the unreacted difluoramine was vented off. The acid layer was drained into a beaker containing 50 g of ice. The aqueous mixture was extracted with three 30-ml portions of methylene chloride, which were combined and dried over sodium sulfate. The pentane solution was distilled through a 25-cm platinum spiral column to give 3.4 g (0.0161 moles, 37.5% yield) of 1,3,3-tris-(difluoramino)butane, b.p. 50°C/23 mm. The methylene chloride solution was distilled to give 0.70 g (0.0025 moles, 5.8% yield) of 2-methyl-2-difluoramino-5-[1,1-bis(difluoramino)ethyl]tetrahydropyran.

<u>Anal</u>. Calc'd for $C_8H_{13}N_3F_6O$: C, 34.2; H, 4.66; N, 14.95; F, 40.5

Found: C, 34.2; H, 4.48; N, 15.2; F, 41.1

The 60-mc proton NMR spectrum (Figure 11) was obtained using a CCl_4 solution with TMS added as an internal reference. The triplet at 1.44 ppm is assigned to the $>C(NF_2)C\underline{H}_3$ methyl group. The quintet at 1.63 ppm is assigned to the $C\underline{H}_3C(NF_2)_2$-methyl group. The broadened doublet at 4.61 ppm is assigned to the $>CHC\underline{H}_2O$-methylene group. The broad complicated multiplet partially overlapped by the triplet and quintet (maximum intensity at 108 cps) is assigned to the remaining ring protons.

The 56.4-mc F^{19} NMR spectrum (Figure 12) was obtained using the same solution with $CFCl_3$ as an internal reference.

The relatively intense signal at -27.80 ppm is assigned to the geminal difluoramino groups $CH_3(N\underline{F}_2)_2$-. The "nonequivalence quartet" (chemical shifts -11.35 and -17.39 ppm, coupling constant 593 cps) is assigned to the $>C(N\underline{F}_2)CH_3$ difluoramino groups.

e. 5-Nitro-2,2-bis(difluoramino)pentane

5-Nitro-2-pentanone (5 g, 0.038 moles) was added to a refluxing mixture of 27 g of difluoramine and 17 ml of 20% fuming sulfuric acid. The solution was allowed to reflux for 2-1/2 hours, and then 50 ml of methylene chloride was added and the unreacted difluoramine was removed. The mixture was drained into a beaker containing 50 g of ice and was extracted with three 20-ml portions of methylene chloride. The extracts were combined and dried over sodium sulfate. The methylene chloride solution was distilled through a 25-cm platinum spiral column to give 4.8 g (0.0219 moles, 57.7% yield) of 5-nitro-2,2-bis-(difluoramino)pentane, b.p. 65°C/0.25 mm.

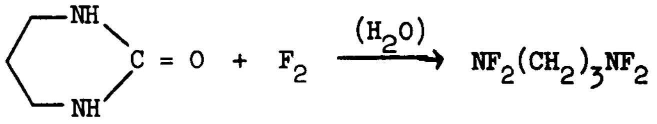
Anal. Calc'd for $C_6H_9N_3F_4O_2$: C, 27.4; H, 4.11; N, 19.18; F, 34.7
Found: C, 27.7; H, 4.30; N, 18.6; F, 34.9

The 60-mc proton and 56.4-mc F^{19} NMR spectra of the adduct were obtained using a CCl_4 solution with TMS and $CFCl_3$ added as internal references. The quintet (Figure 14) at 1.63 ppm (splitting a few cps) is assigned to the $-C(NF_2)_2\underline{CH_3}$ methyl group. The broadened, poorly resolved signal with maximum intensity at 131 cps is assigned to the overlapping signals of the two $NO_2CH_2\underline{CH_2}\underline{CH_2}$-methylene groups. The irregular triplet at 4.37 ppm is assigned to the $NO_2\underline{CH_2}CH_2$-methylene group. The fluorine spectra (Figure 15) consists of a single slightly broadened signal at -26.94 ppm.

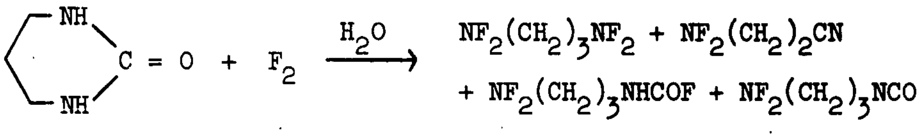
B. AQUEOUS FLUORINATION (V. Grakauskas)

1. Discussion

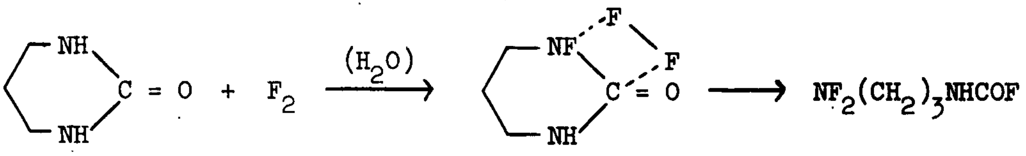
The aqueous fluorination of tetrahydro-2-pyrimidone was studied with the objective of obtaining an improved method for the preparation of 1,3-bis(difluoramino)propane, which is required for stability studies.



However, only a 5 to 7% yield of this product was isolated from the reaction mixture. The main reaction product was identified as 3-difluoraminopropylcarbamyl fluoride, $NF_2(CH_2)_3NHCOF$. This identification was made on the basis of the product's elemental analysis, its infrared spectrum (Figure 16), and its proton (Figure 17) and fluorine (Figure 18) NMR spectra. Other products of this reaction were the previously identified 3-difluoraminopropyl isocyanate, $NF_2(CH_2)_3NCO$, and 3-difluoraminopropionitrile, $NF_2(CH_2)_2CN$, identified on the basis of infrared spectrum (Figure 19), elemental analysis, and proton (Figure 20) and fluorine (Figure 21) NMR spectra. The latter apparently results from the dehydrofluorination of 1,3-bis(difluoramino)propane.



The carbamyl fluoride might be formed in a four-center reaction between the intermediate, N-fluoro-tetrahydro-2-pyrimidone, and fluorine:



The isocyanate might be produced either by dehydrofluorination of the carbamyl fluoride,

$$NF_2(CH_2)_3NHCOF \xrightarrow{-HF} NF_2(CH_2)_3NCO$$

or by a route similar to that described previously for substituted cycloalkyl ureas.*

3-Difluoraminopropylcarbamyl fluoride and 3-difluoraminopropyl isocyanate apparently did not react with water during the fluorination because

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*Aerojet-General Report 2730 (Summary), October 1963 (Confidential).

of their insolubility. The isocyanate, however, reacted readily with alcohols to give the corresponding carbamates. The carbamyl fluoride reacted with alcohols very slowly, the reaction proceeding only to 50% completion at room temperature in 5 days. However, when an ethanolic solution of 3-difluoraminopropylcarbamyl fluoride was refluxed for 5 hours, ethyl 3-difluoraminopropylcarbamate was obtained in high yield:

$$NF_2(CH_2)_3NHCOF + C_2H_5OH \xrightarrow[\Delta]{} NF_2(CH_2)_3NHCO_2C_2H_5 + HF$$

The fluorination of this carbamate gave a low yield of 1,3-bis(difluoramino)-propane, apparently because of the insolubility of the starting material. To avoid this problem, 2-hydroxyethyl 3-difluoraminopropylcarbamate, very soluble in water, was synthesized by reacting the carbamyl fluoride with a large excess of ethylene glycol:

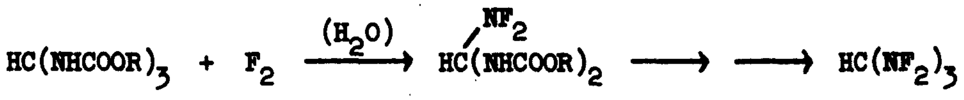
$$NF_2(CH_2)_3NHCOF + HOCH_2CH_2OH \longrightarrow NF_2(CH_2)_3NHCO_2CH_2CH_2OH$$

The compound was characterized on the basis of its elemental analysis, its infrared spectrum and its proton and fluorine NMR spectra. The compound boiled too high for distillation, so an aqueous solution of the crude material was fluorinated. However, only a 10% yield of 1,3-bis(difluoramino)propane resulted.

Methanetriscarbamates, $HC(NHCOOR)_3$, which have not been reported previously, were synthesized in 45 to 50% yields by reacting ethyl orthoformate with carbamates at 110 to 150°C in the presence of a catalytic amount of aniline sulfate:

$$HC(OC_2H_5)_3 + 3\ NH_2COOR \xrightarrow[\Delta]{\text{Aniline Sulfate}} HC(NHCOOR)_3 + 3\ C_2H_5OH$$

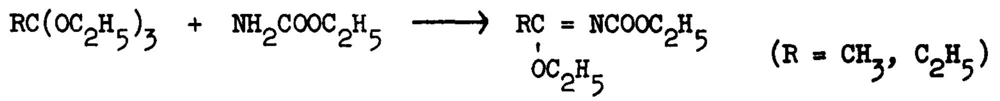
These compounds ($R = CH_3$ or C_2H_5) were characterized on the basis of their elemental analyses, their infrared spectra, and their proton NMR spectra. These compounds were synthesized with the objective of using them as starting materials for the preparation of tris(difluoramino)methane or partially fluorinated intermediates.



$$\mathrm{HC(NHCOOR)_3} + \mathrm{F_2} \xrightarrow{(\mathrm{H_2O})} \overset{\mathrm{NF_2}}{\mathrm{HC}}\mathrm{(NHCOOR)_2} \longrightarrow \longrightarrow \mathrm{HC(NF_2)_3}$$

The fluorination of either trimethyl or triethyl methanetricarbamates, however, did not give the desired products. Instead, a mixture of the corresponding alkyl carbamates and N-fluorocarbamates was isolated, indicating the hydrolysis of either the starting materials or their N-fluoro derivatives. A similar reaction also took place when an attempt was made to nitrate $HC(NHCOOEt)_3$ with nitric acid; only ethyl nitrocarbamates were obtained.

Attempts were also made to synthesize 1,1,1-ethane- and 1,1,1-propane-triscarbamates from the corresponding orthoesters. However, in both cases the reaction products were identified (elemental analysis, infrared spectra, and proton NMR spectra) as the corresponding N-carboalkoxyiminoethers:



$$\mathrm{RC(OC_2H_5)_3} + \mathrm{NH_2COOC_2H_5} \longrightarrow \underset{\mathrm{OC_2H_5}}{\mathrm{RC}} = \mathrm{NCOOC_2H_5} \qquad (\mathrm{R} = \mathrm{CH_3}, \mathrm{C_2H_5})$$

One attempt was made to fluorinate $C_2H_5C(OC_2H_5) = NCOOC_2H_5$ with the objective of replacing the carbethoxyl group by fluorine. This reaction, however, gave ethyl propionyl carbamate.

$$\mathrm{C_2H_5C(OC_2H_5) = NCOOC_2H_5} + \mathrm{F_2} \xrightarrow{(\mathrm{H_2O})} \mathrm{C_2H_5CONHCOOC_2H_5}$$

2. Experimental

a. 3-Difluoraminopropylcarbamyl Fluoride

A solution of 70 g (0.7 mole) of tetrahydro-2-pyrimidone in 650 ml water was fluorinated at 0 to 5°C until 46 liters (3.0 mole) of fluorine was consumed. The reaction mixture containing 20 to 30 ml of water-insoluble liquid was extracted with four 35-ml portions of methylene chloride. The combined extracts were dried, treated with solid sodium bicarbonate, and filtered, and the filtrate was worked up. After the solvent was removed the residual liquid was separated by distillation into three fractions: (1) b.p. 25-35°C/25 mm, (2) b.p.

25-45°C/0.2 mm, and (3) b.p. 65-80°C/0.1 mm. The material of fraction (3), 25 g, was redistilled to give a clear liquid, b.p. 65-66°C/0.1 mm, n_D^{23} 1.3980, which was identified as 3-difluoraminopropylcarbamyl fluoride.

Anal. Calc'd for $C_4H_7N_2F_3O$: C, 30.77; H, 4.52; N, 17.95; F, 36.51
Found: C, 31.0; H, 4.6; N, 17.5; F, 36.0

Infrared spectrum of the compound is shown in Figure 16.

The 60-mc proton NMR spectrum (Figure 17) was obtained using a $CDCl_3$ solution with TMS added as an internal reference. The spectrum consists of a quintet at 1.98 ppm, a complex multiplet (12 lines), and a broad signal at 5.68 ppm. The quintet is assigned to the $-CH_2CH_2CH_2-$ protons. The broad signal at 5.68 ppm is assigned to the -NH- proton. The remaining multiplets may be resolved into a triplet of triplets due to the $NF_2\underline{CH_2}CH_2-$ protons centered at 3.58 ppm (splitting 29.3 cps) in which the central triplet is overlapped by a quartet due to the $-CH_2CH_2NH-$ protons at 3.34 ppm.

The 56.4-mc fluorine NMR spectrum (Figure 18) was obtained using a chloroform solution with $CFCl_3$ as the internal reference. The spectrum consists of a triplet (splitting 28.5 cps) at -55.30 ppm and two doublets of unequal intensity at +14.59 (splitting 7.3 cps) and +21.11 (splitting 21.4 cps) ppm. The intensity of the doublet at +14.59 ppm is about ten times that of the doublet at +21.11 ppm. The triplet may be assigned to the NF_2CH_2- fluorines. The two signals at high field may be interpreted as arising from two separate configurations of the $-CH_2NHCOF$ group resulting in different magnetic shielding environments for the acid fluorine, or by assuming that the less intense signal is due to CF impurity. The splitting of the signals into doublets can be attributed to coupling to the -$\underline{NH}$- proton.

b. 3-Difluoraminopropionitrile

The material of the main fraction (2) – see paragraph II,B,2,a – 18 g, was redistilled into two fractions: (1) b.p. 38-50°C/25 mm, n_D^{23} 1.3655; 5.5 g, and (2) b.p. 58-60°C/25 mm, n_D^{23} 1.3920; 11.5 g. The lower boiling compound was identified by gas chromatography and infrared spectrum as 80% pure 1,3-bis(difluoramino)propane, contaminated with both 3-difluoraminopropionitrile and 3-difluoraminopropyl isocyanate. The higher-boiling fraction was found to be a mixture of the isocyanate and 3-difluoraminopropionitrile, containing about 40% of the latter. An analytical sample of pure 3-difluoraminopropionitrile was isolated from this fraction by gas chromatography.

Anal. Calc'd for $C_3H_4N_2F_2$: C, 33.96; H, 3.80; N, 26.41; F, 35.84

Found: C, 33.7; H, 3.9; N, 26.3; F, 37.0

In a separate experiment some of the isocyanate-nitrile mixture was treated with methanol to convert the isocyanate to the corresponding carbamate. When excess of methanol was removed 95% pure (as determined by gas chromatography), 3-difluoraminopropionitrile distilled over. Infrared spectrum of 3-difluoraminopropionitrile is shown in Figure 19.

The 60-mc proton (Figure 20) and 56.4 mc fluorine (Figure 21) NMR spectra were obtained using about 1:1 $CDCl_3/CCl_4$ solution with TMS and $CFCl_3$ as internal references. The proton spectrum is composed of a triplet at 2.80 ppm and a triplet of triplets centered at 3.81 ppm. The high-field triplet is assigned to the $-CH_2\underline{CH_2}CN$ protons. The low-field triplets have a HF splitting equal to 26.9 cps, and are assigned to the $NF_2\underline{CH_2}CH_2-$ protons.

The fluorine NMR spectrum consists of a single signal at -51.66 ppm. This signal has the appearance of a broadened triplet and is assigned to the $N\underline{F_2}CH_2$-fluorines.

c. 1,3-Bis(difluoramino)propane

Material of the lowest boiling main fraction (see paragraph II,B,2,a), 3.5 g, was identified by gas chromatography and by infrared spectrum as 75% pure 1,3-bis(difluoramino)propane. The total amount of the compound in main fractions (1) and (2) of 3-difluoraminopropylcarbamyl fluoride was crudely estimated at 7 to 9 g.

d. Ethyl 3-Difluoraminopropylcarbamate

A solution of 6.0 g of 3-difluoraminopropylcarbamyl fluoride in 15 ml absolute ethanol was heated up to 70 to 75°C and maintained at this temperature for 6 hours. The reaction mixture was worked up to give 6.0 g of the carbamate, b.p. 66-67°C/0.1 mm, which was identified by comparing its physical properties and its infrared spectrum with those of an authentic sample.*

e. 2-Hydroxyethyl 3-Difluoraminopropylcarbamate

To 30 g of ethylene glycol was added 4.0 g of 3-difluoraminopropyl isocyanate, and the reaction mixture allowed to stand with stirring at room temperature for 2.5 hours. The originally insoluble isocyanate gradually went into solution and the reaction mixture warmed to 29 to 32°C. The solution was concentrated at 70°C bath temperature at 0.1 mm to remove the excess of ethylene glycol to leave 4.3 g of pale-yellow viscous liquid. A sample of the crude material was purified in a molecular still at 130°C bath temperature at 0.1 mm pressure to give a colorless liquid, n_D^{23} 1.4475.

<u>Anal</u>. Calc'd for $C_6H_{12}N_2F_2O_3$: C, 36.36; H, 6.10; N, 14.14; F, 19.18
Found: C, 36.7; H, 6.3; N, 14.2; F, 19.8

In another experiment, 3-difluoraminopropylcarbamyl fluoride was reacted with excess of ethylene glycol by allowing the solution to stand at room temperature for a period of 10 days. Crude 2-hydroxyethyl 3-difluoraminopropylcarbamate was obtained practically quantitatively when the excess of ethylene glycol was removed at reduced pressure.

f. Triethyl Methanetriscarbamate

A mixture containing 40 g (0.27 mole) of ethyl orthoformate, 74 g (0.81 mole) of ethyl carbamate, and 0.7 g of aniline sulfate was heated in a distillation apparatus to 115 to 125°C and maintained at this

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*Aerojet-General Report 2381 (Annual Summary), October 1962, p. 46 (Confidential).

temperature until the distillation of ethanol ceased. During a period of 2.5 hours, 32 ml of ethanol distilled over. At the end of this period, the reaction temperature was gradually increased to 155°C, and an additional 13 ml of ethanol was removed from the reaction mixture over a period of 1.5 hours. The liquid reaction mixture on cooling to room temperature solidified. The crude material was purified by crystallization in methylene chloride to give a white crystalline solid, m.p. 210-211°C.

Anal. Calc'd for $C_{10}H_{19}N_3O_6$: C, 43.31; H, 6.91; N, 15.16
Found: C, 43.1; H, 6.8; N, 15.0

g. Trimethyl Methanetriscarbamate

Trimethyl methanetriscarbamate was synthesized from ethyl orthoformate and methyl carbamate in a reaction identical to that described in paragraph II,B,2,f. The crude material was purified by crystallization from methanol to give a white, crystalline solid, m.p. 176-178°C in 43% yield.

Anal. Calc'd for $C_7H_{13}N_3O_6$: C, 35.74; H, 5.57; N, 17.87
Found: C, 36.0; H, 5.6; N, 17.8

In a separate experiment a mixture of ethyl orthoformate and methyl carbamate in the absence of aniline sulfate was heated up to 145°C. No ethanol distilled over and after heating the mixture for a few hours, only the starting materials were recovered.

h. Ethyl N-Carbethoxyiminoacetate

A mixture containing 32.5 g (0.2 mole) of ethyl orthoacetate, 60 g (0.4 mole) of ethyl carbamate, and 0.7 g of aniline sulfate was heated in a distillation apparatus to 110 to 120°C and maintained at this temperature for a period of 1.5 hours. During this time, 20 ml of ethanol distilled over. The reaction mixture was cooled to 5 to 10°C and ethyl carbamate that crystallized out from the solution was removed by filtration. The filtrate was dissolved in 150 ml carbon tetrachloride and the solution was washed with two 100-ml portions of water to remove unreacted ethyl carbamate. The carbon tetrachloride solution was dried and worked up to give 27 g of a colorless liquid, b.p. 89-90°C/25 mm, n_D^{23} 1.4300. The material was found to be contaminated with 20 to 25% of ethyl carbamate, and an analytical sample was obtained by gas chromatography.

Anal. Calc'd for $C_7H_{13}NO_3$: C, 52.82; H, 8.23; N, 8.80
Found: C, 52.5; H, 8.26; N, 8.98

i. Ethyl N-Carbethoxyiminopropionate

Ethyl N-carbethoxyiminopropionate, b.p. 38-39°C/0.1 mm, n_D^{23} 1.4310, was prepared from ethyl orthopropionate and ethyl carbamate in the manner described in paragraph II,B,2,h. In this case, excess of ethyl carbamate present in the crude material was removed by thorough washing with water, and a pure product was obtained on distillation.

Anal. Calc'd for $C_8H_{15}NO_3$: C, 55.5; H, 8.7; N, 8.0
Found: C, 55.3; H, 8.65; N, 8.25

j. Fluorination of Ethyl N-Carbethoxyiminopropionate

A suspension of 13.7 g (0.08 mole) of ethyl N-carbethoxyiminopropionate in 500 ml water was fluorinated at 0 to 5°C until 2.5 liter (~ 0.1 mole) of fluorine gas was consumed. The reaction mixture was extracted with four 30-ml portions of methylene chloride. The combined extracts were dried and distilled to leave 5.0 g of a white solid residue. The material was recrystallized from a benzene-hexane mixture to give a white solid, m.p. 81-82°C which was identified as ethyl N-propionyl carbamate (N, calc'd 9.65%; found 9.6%).

C. FLUORAMMONIUM SALTS (A. Remanick)

1. Discussion

The investigation of the solvolysis of N-fluorocarbamates has been continued with the intent of isolating fluorammonium perchlorate, a potential high energy oxidizer for solid propellants. It was previously found that isopropyl N-fluorocarbamate reacted with excess 70% perchloric acid to give 90% of the theoretical amount of carbon dioxide. The F^{19} NMR spectrum of the perchloric acid solution indicated the presence of the fluorammonium cation. However, no solid material was isolated after most of the perchloric acid was removed under vacuum and the residue was diluted with diglyme or ether.

The reaction of isopropyl N-fluorocarbamate with excess 70% perchloric acid was repeated, and the perchloric acid was removed in a molecular still at 10 μ to give a white solid. Elemental analysis suggested the material was fluorammonium perchlorate contaminated with 70% perchloric acid. The material was very hygroscopic but could be manipulated in a dry atmosphere.

Because of the extended periods (40 hours) necessary to evaporate the solution to dryness, further attempts were made to isolate fluorammonium perchlorate from the slurry obtained by partial evaporation of the solution. The slurry was found to be soluble in diglyme, tetrahydrofuran, and ethyl acetate. Addition of ether, carbon tetrachloride or chloroform to the diglyme solution yielded oily products. However, washing of the slurry with dioxane left a crystalline material whose analysis indicated a 1:1 complex of fluorammonium perchlorate and dioxane. This complex could also be isolated, in analytical purity, from a tetrahydrofuran solution of the slurry by precipitation with dioxane. Confirmation of the structure was obtained by F^{19} and proton NMR spectra.

The fluorammonium perchlorate-dioxane complex was stable for several days in a dry atmosphere at room temperature. However, at 100°C, it decomposed rapidly.

Attempts to remove the dioxane from the complex have been partially successful. Thus, after 5 hours in a sublimation apparatus at 20°C/5 μ, the solid showed 46% dioxane (by carbon analysis). Additional treatment under these conditions left a solid which contained 28% dioxane. This work is being continued.

The reaction of ethyl N-fluoro- N-methyl carbamate with excess methanesulfonic acid was attempted in order to prepare a substituted fluorammonium salt. However, no solid material could be isolated from this reaction.

2. Experimental

a. Reaction of Isopropyl N-Fluorocarbamate with 70% Perchloric Acid

Isopropyl N-fluorocarbamate was reacted with excess 70% perchloric acid in the manner previously described.* Most of the solvent was removed under vacuum (20°C/10 μ) in 20 hours. A small portion of this material was placed in a sublimation pistil and the residual solvent was removed under vacuum (20°C/10 μ) in 10 hours. The solid which remained, rapidly hydrated on exposure to the atmosphere. Repetition of this procedure and subsequent manipulation in an inert atmosphere gave a white solid.

Anal. Calc'd for FNH_3ClO_4: N, 10.4; F, 14.0; ClO_4^-, 73.5

Found: N, 8.37; F, 10.0; ClO_4^-, 71.1

b. Preparation of a Fluorammonium Perchlorate-Dioxane Complex

Ethyl N-fluorocarbamate was reacted with excess perchloric acid as previously described. Solvent was removed under vacuum (20°C/10 μ) until a heavy slurry remained. The slurry was transferred to a funnel and washed with small portions of dioxane. A white amorphous solid remained.

Anal. Calc'd for $FNH_3ClO_4 \cdot C_4H_8O$: C, 21.5; H, 4.90; N, 6.6; F, 8.55

Found: C, 21.1; H, 4.98; N, 7.0; F, 8.8

By dissolving the slurry in a minimal quantity of tetrahydrofuran and adding dioxane, a white crystalline solid was obtained, m.p. 100-103°C (dec.).

Anal. C, 21.5; H, 5.06; N, 6.2; F, 8.2

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*Aerojet-General Report 2730, October 1963 (Confidential).

The F^{19} NMR spectrum of the complex in concentrated sulfuric acid was identical to that of the previously reported fluorammonium salt.* The proton NMR spectrum showed a singlet at +6.72, relative to sulfuric acid (dioxane), and a singlet at +44 cps. This signal may be regarded as the upfield member of a doublet at +0.37 ppm assignable to the FNH_3^+ ion, the low-field member of which is obscured by the intense sulfuric acid signal. This assignment is suggested by the close correspondence of displacement of the signal (+44 cps) from the sulfuric acid signal and the splitting (45 cps) observed in the F^{19} spectrum.

c. Attempted Removal of Dioxane from the Fluorammonium Perchlorate-Dioxane Complex

A small amount of the complex was placed in a sublimation pistil and subjected to high vacuum (20°C/5 µ) for 5 hours. Elemental analysis revealed 9.93% carbon. Treatment under the same conditions for an additional 6 hours left a solid which contained 5.93% carbon. Further work is in progress.

d. Reaction of Ethyl N-Fluoro-N-Methylcarbamate with Methanesulfonic Acid

To 1.0 g (0.0082 mole) ethyl N-fluoro-N-methylcarbamate in a round bottom flask was added 4.3 ml of methanesulfonic acid. The flask was connected to a gas burette and placed in a preheated (83°C) bath. Heating was continued (85 to 90°C) for 1-1/4 hours. At this time, about 60% of the theoretical amount of gas (based on carbon dioxide) had evolved. Infrared analysis of the gas showed primarily carbon dioxide with a lesser amount of ethylene and a trace of silicon tetrafluoride. After this heating period, the reaction mixture was allowed to cool to room temperature. Ether was added dropwise, with stirring, until the reaction mixture was cloudy. An oily product separated which could not be induced to solidity. No further purification was attempted.

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*Aerojet-General Report 2381, October 1962, p. 32 (Confidential).

D. REACTIONS OF 2,2-DINITRO-2-FLUOROETHANOL (V. Grakauskas)

1. Discussion

The oxidation of 2,2-dinitro-2-fluoroethanol was investigated with the objective of preparing 2,2-dinitro-2-fluoroacetaldehyde. This compound might be reacted with difluoramine to give energetic intermediates, and with nitroalcohols to give stable, lower-energy nitroplasticizers. The starting material was prepared by the flourination of salts of 2,2-dinitroethanol.*

Dinitrofluoroethanol reacted slowly with 100% nitric acid at room temperature to give the corresponding nitrate:

$$FC(NO_2)_2CH_2OH + HNO_3 \longrightarrow FC(NO_2)_2CH_2ONO_2$$

The somewhat impure compound was identified on the basis of its elemental analysis, and its infrared and NMR spectra. The alcohol also reacted slowly with 70% nitric acid, but the products have not yet been identified.

Dinitrofluoroethanol also reacted with primary or secondary amines to give the Mannich reaction products:

$$FC(NO_2)_2CH_2OH + RNH_2 \xrightarrow{(H_2O)} FC(NO_2)_2CH_2NHR + R_2NH \xrightarrow{(H_2O)} FC(NO_2)_2CH_2NR_2$$

(Dinitrofluoroethyl)methylamine ($R = CH_3$) was characterized on the basis of its elemental analysis, its infrared spectrum (Figure 24) and its proton (Figure 25) and fluorine (Figure 26) NMR spectra. Similarly, (dinitrofluoroethyl)dimethylamine was fully characterized (its infrared spectrum is shown in Figure 27). The hydrochloride salts of both amines were also prepared and characterized.

The reaction of dinitrofluoroethanol with an excess of concentrated ammonium hydroxide resulted in decomposition. On the other hand, a dilute aqueous solution containing an equimolar ratio of these reagents, deposited a yellow water-insoluble liquid which exploded after it was isolated and was allowed to

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*Aerojet-General Report 0235-01-6, April 1960, p. 3 (Confidential).

stand at room temperature overnight. In another experiment, the reaction product, in the original aqueous solution, was treated with an equimolar quantity of ethyl chloroformate:

$$FC(NO_2)_2CH_2OH + NH_4OH \longrightarrow FC(NO_2)_2CH_2NH_2 \xrightarrow{ClCOOC_2H_5} FC(NO_2)_2CH_2NHCOOC_2H_5$$

Ethyl dinitrofluoroethylcarbamate was obtained in 10 to 15% yields and was characterized on the basis of its elemental analysis, its infrared spectrum (Figure 28) and its proton (Figure 29) and fluorine (Figure 30) NMR spectra. The main product of this reaction was dinitrofluoroethyl ethyl carbonate, $C_2H_5OCOOCH_2C(NO_2)_2F$. It is not clear why, if the reaction between the alcohol and ammonia was incomplete, chloroformate did not preferably react with ammonia. Methyl dinitrofluoroethylcarbamate was similarly synthesized from the crude amine and methyl chloroformate.

The possibility that dinitrofluoroethylcarbamates in the above reactions may be produced in a Mannich reaction between dinitrofluoroethanol and carbamate (produced from chloroformates and ammonia) was eliminated when it was shown in a separate experiment that an equimolar mixture of these reagents did not react, even at elevated temperatures.

2. Experimental

a. 2,2-Dinitro-2-fluoroethylnitrate

Four grams of dinitrofluoroethanol was added at 0 to 5°C (with stirring) to 20 ml of 100% nitric acid; the resulting solution was allowed to warm up to 25°C and allowed to stand at room temperature for a period of 2 hours. The reaction mixture was poured onto 100 g of crushed ice and water-insoluble liquid was extracted with 20 ml of carbon tetrachloride. The extract was worked up to give 0.8 g of a colorless liquid, b.p. 27-28°C/0.1 mm. Infrared and NMR spectra of the product agreed well with the nitrate structure, but NMR spectra indicated the presence of a contaminant – probably the alcohol. Attempts to purify the material by gas chromatography were unsuccessful, resulting in decomposition of the nitrate.

Anal. Calc'd for $C_2H_2N_3FO_7$: C, 12.07; H, 1.01; N, 21.11; F, 9.54

Found: C, 12.6; H, 1.4; N, 19.5; F, 9.8

The aqueous phase was extracted with methylene chloride and 2.5 g of dinitrofluoroethanol was recovered.

b. Chlorofluorodinitromethane

Ten grams of dinitrofluoroethanol was added (with stirring and cooling at 5 to 10°C over a period of 10 min) to 100 ml of 5.3% aqueous sodium hypochlorite. The reaction mixture containing about 5 ml of water-insoluble liquid was extracted with 75 ml of methylene chloride, and the extract worked up to give 6.0 g of a colorless liquid, b.p. (estimated) 80-85°C. The compound was somewhat contaminated with the solvent and an analytical sample obtained by gas chromatography.

Anal. Calc'd for $CFClN_2O_4$: C, 7.58; H, 0.0; N, 17.68; F, 11.98

Found: C, 7.50; H, 0.5, N, 17.5; F, 12.0

Infrared (Figure 22) and fluorine NMR spectra (Figure 23) of the product were in agreement with the structure.

The fluorine NMR spectrum (in CCl_4 solution with $CFCl_3$ as an internal reference) consists of a single signal, a quintet at +68.45 ppm with a splitting of 11.1 cps. The quintet form of the signal suggests coupling to four equivalent protons. However, no signals were observed in the proton spectrum and the hydrogen content by elemental analysis is only 0.5%. In addition, a quintet resulting from coupling to four nuclei with a spin of 1/2 should have an intensity distribution 1:4:6:4:1, which does not correspond to the signal observed. The only remaining possibility is that the splitting results from coupling to the two equivalent nitrogens. The two nitrogen nuclei would produce an intensity distribution 1:2:3:2:1, since the spin of nitrogen is 1. This corresponds much more closely to the observed distribution.

Such couplings of nitrogen are rarely observed since the interaction of the nitrogen quadrupole with the electrical environment usually shortens its relaxation time sufficiently to remove any splitting. Apparently, in $FC(NO_2)_2Cl$ the nitrogens are fortuitously in an environment of high electrical symmetry. Consequently, the relaxation time is lengthened, permitting observation of the splitting.

c. 2,2-Dinitro-2-fluoroethylmethylamine

A solution of 4.0 g (0.1 mole) of sodium hydroxide in 15 ml of water was added (at room temperature with stirring over a 5-min period) to a solution of 6.75 g (0.1 mole) of methylamine hydrochloride and 15.4 g (0.1 mole) of dinitrofluoroethanol in 100 ml water. The reaction mixture was stirred for additional 5 min and the yellow water-insoluble liquid was extracted with two 30-ml portions of carbon tetrachloride. The combined extracts were worked up to give 12.0 g (72% yield) of a yellow liquid, b.p. 32°C/0.1 mm, n_D^{23} 1.4275.

<u>Anal</u>. Calc'd for $C_3H_6N_3FO_4$: C, 21.56; H, 3.62; N, 25.15; F, 11.37

Found: C, 21.9; H, 3.7; N, 24.8; F, 11.6

The infrared spectrum of the compound is shown in Figure 24.

The 60-mc proton (Figure 25) and 56.4 mc fluorine (Figure 26) NMR spectra were obtained using carbon tetrachloride as the solvent and TMS and $CFCl_3$ as internal references. The proton spectrum consists of a broadened peak at 1.29 ppm, and a doublet at 3.83 ppm (splitting 18.7 cps). The signal at 1.29 ppm is assigned to the -N<u>H</u>- proton. The signal at 2.55 ppm is assigned to the $-C\underline{H}_3$ proton. The splitting on the doublet is consistent with the expected HF coupling and this signal is assigned to the $FC(NO_2)_2C\underline{H}_2$- proton.

The fluorine NMR spectrum consists of a signal-broadened peak at +109.8 ppm.

d. 2,2-Dinitro-2-fluoroethylmethylamine Hydrochloride

Three grams of concentrated hydrochloric acid was added (with stirring at room temperature) to a solution of 5.0 g (0.03 mole) of 2,2-dinitro-2-fluoroethylmethylamine in 80 ml of absolute ethanol. The clear solution was stirred for 10 min and then was treated with 200 ml of anhydrous diethyl ether, resulting in deposition of a white solid. The solid was collected, washed with diethyl ether, and vacuum dried; m.p. 120-122°C, weight 2.5 g.

Anal. Calc'd for $C_3H_7FClN_3O_4$: C, 17.70; H, 3.46; N, 20.64; F, 9.33

Found: C, 17.6; H, 3.5; N, 20.4; F, 9.4

e. 2,2-Dinitro-2-fluoroethyldimethylamine

2,2-Dinitro-2-fluoroethyldimethylamine was synthesized in 78% yield following the procedure described under paragraph II,D,2,c. The compound is a yellow liquid, b.p. 23-24°C/0.1 mm, n_D^{23} 1.4200.

Anal. Calc'd for $C_4H_8N_3FO_4$: C, 26.52; H, 4.45; N, 23.20; F, 10.49

Found: C, 26.5; H, 4.7; N, 22.8; F, 10.0

The infrared spectrum of the compound is shown in Figure 27.

f. 2,2-Dinitro-2-fluoroethyldimethylamine Hydrochloride

2-2-Dinitro-2-fluoroethyldimethylamine hydrochloride was prepared from the amine and concentrated hydrochloric acid in ethanolic solution following the procedure described in paragraph II,D,2,d. In this case most of the material precipitated from the solution without addition of diethyl ether. The compound is a white solid, m.p. 110-112°C.

Anal. Calc'd for $C_4H_9FClN_3O_4$: C, 22.08; H, 4.17; N, 19.31; F, 8.73

Found: C, 22.0; H, 4.4; N, 18.7; F, 8.9

g. 2,2-Dinitro-2-fluoroethylethylcarbonate

A solution of 6.0 g of 28% ammonium hydroxide ($\cong$ 0.1 mole NH_3) in 25 ml water was added (with stirring at room temperature) to a solution of 15.4 g (0.1 mole) of dinitrofluoroethanol in 50 ml water. The reaction mixture turned yellow and gradually a yellow water-insoluble liquid deposited. The reaction mixture was stirred for 30 min and then treated with 5.4 g (0.05 mole) of ethyl chloroformate. External cooling was applied to keep the reaction temperature at 20 to 25°C. After a few minutes a solution of 4.0 g (0.1 mole) sodium hydroxide in 25 ml water was added to the reaction mixture, followed by another 5.4 g portion of ethyl chloroformate. The reaction mixture was stirred for an additional 30 min and then the water-insoluble yellow liquid was extracted with two 30-ml portions of methylene chloride. The methylene chloride extracts were worked up to give 15.0 g of a colorless liquid, b.p. 53-54°C/0.1 mm, n_D^{23} 1.4215.

Anal. Calc'd for $C_5H_7N_2FO_7$: C, 26.6; H, 3.12; N, 12.4; F, 8.4

Found: C, 25.8; H, 3.2; N, 13.5; F, 8.5

The 60-mc proton and 56.4-mc fluorine NMR spectra were obtained in carbon tetrachloride solution containing TMS and $CFCl_3$ as internal references. The proton spectrum consists of a triplet at 1.33 ppm, a quartet at 4.23 ppm, and a doublet at 5.17 ppm (splitting 15.7 cps). The triplet and quartet are characteristic of a methyl and methylene of a CH_3CH_2- group. The doublet is assigned to the $FC(NO_2)_2C\underline{H}_2$- protons.

The fluorine spectrum consists of a single broadened peak at +111.3 ppm and is assigned to the $\underline{F}C(NO_2)_2CH_2$- fluorine.

h. Ethyl 2,2-Dinitro-2-fluoroethylcarbamate

After removal of 2,2-dinitro-2-fluorethylethylcarbonate (see paragraph II,D,2,g), the distillation residue was subjected to further distillation to give 4.0 g of a colorless liquid, b.p. 85 to 95°C/0.1 mm. An analytical sample of this product, b.p. 85°C/0.1 mm, n_D^{23} 1.4425, was obtained on redistillation.

Anal. Calc'd for $C_5H_8N_3FO_6$: C, 26.67; H, 3.58; N, 18.67; F, 8.44

Found: C, 26.6; H, 3.9; N, 17.8; F, 9.1

The infrared spectrum of the material is shown in Figure 28.

The 60-mc proton (Figure 29) and 56.4-mc fluorine (Figure 30) NMR spectra were obtained using TMS and $CFCl_3$ as internal references in carbon tetrachloride solution. The proton spectrum consists of a triplet at 1.23 ppm, a series of seven lines, and a broadened triplet at 5.93 ppm. The triplet at 1.23 ppm is assigned to the methyl protons at $-OCH_2CH_3$. The broadened triplet at 5.93 ppm is assigned to the $-CH_2\underline{NH}-$ proton. The seven lines can be resolved into two adjacent quartets whose nearest lines are overlapped. The quartet at 4.10 ppm is assigned to the $-OC\underline{H_2}CH_3$ protons. The second set of four lines is interpreted as a split doublet resulting from the NF and NH coupling for the $FC(NO_2)C\underline{H_2}NH-$ protons centered at 4.46 ppm. The fluorine proton coupling obtained with this assignment is 15.1 cps and compares favorably with 14.9 cps, the value obtained from the fluorine spectrum.

The fluorine spectrum shows a triplet at +109.47 ppm (splitting 14.9 cps). This signal is assigned to the $FC(NO_2)_2CH_2-$ fluorine.

i. Methyl 2,2-Dinitro-2-fluoroethylcarbamate

Methyl 2,2-dinitro-2-fluoroethylcarbamate, a white solid with m.p. 40 to 41°C, was synthesized by the method used for the corresponding ethyl ester (see paragraph II,D,2,h). The compound boiled at 100 to 115°C/0.1 mm and solidifed in the receiver. The material was further purified by recrystallization from carbon tetrachloride, yield 20%, m.p. 40-41°C.

Anal. Calc'd for $C_4H_6N_3FO_6$: C, 22.76; H, 2.87; N, 19.91; F, 9.00

Found: C, 22.8; H, 3.3; N, 20.1; F, 9.1

III. PERSONNEL

The experimental synthesis work was performed by F. J. Gerhart, M. Mascari, J. Cavallo, A. H. Ramanick, V. Grakauskas, and K. Baum. Analytical support was provided by H. Nelson (NMR), K. Inouye (microanalysis), D. I. Matson (IR), and K. Deuel (gas chromatography).

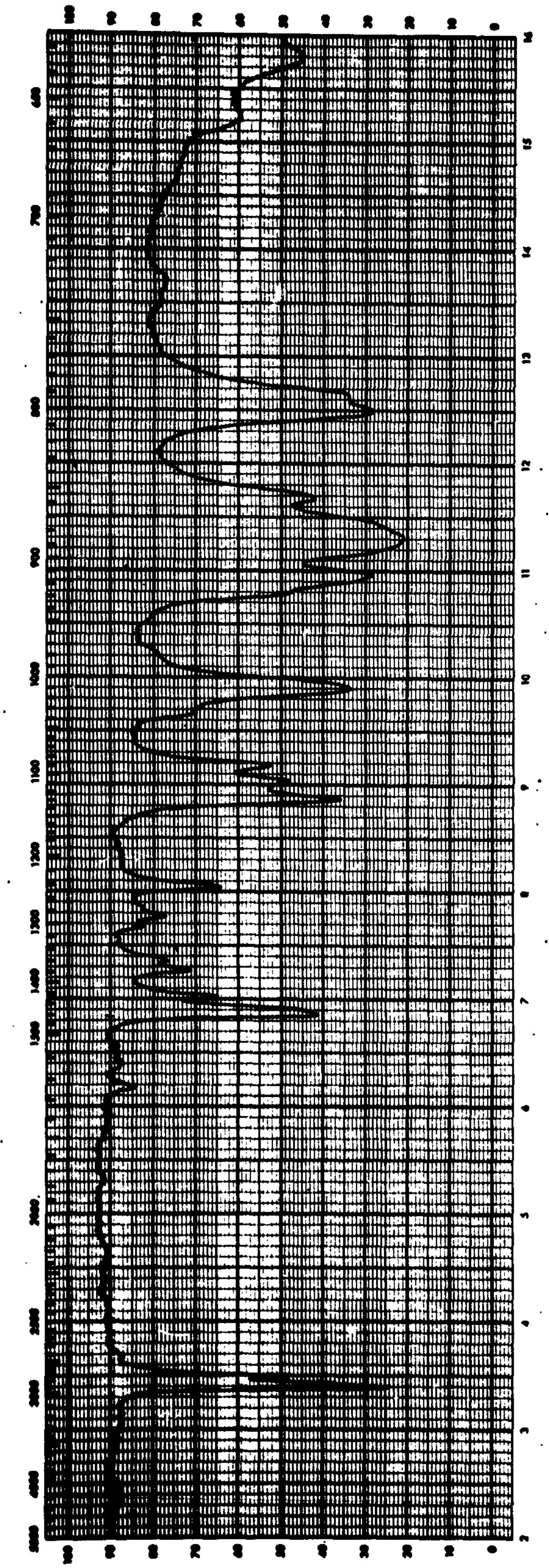

Figure 1. Infrared Spectrum of 1,1-Dichloro-1-(difluoramino)butane

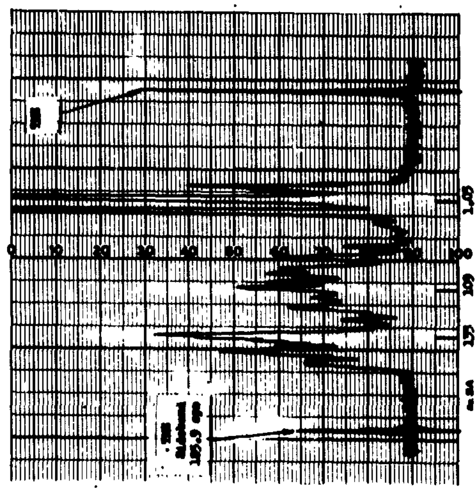

Figure 2. Proton NMR Spectrum of 1,1-Dichloro-1-(difluoramino)butane

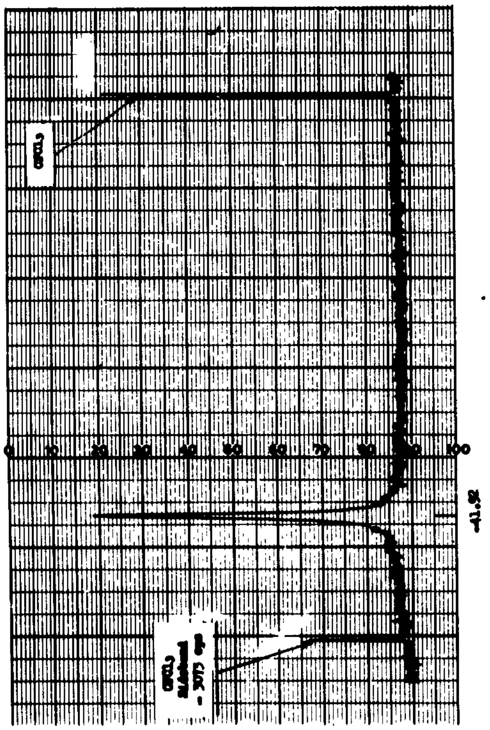

Figure 3. Fluorine NMR Spectrum of 1,1-Dichloro-1-(difluoramine)butane

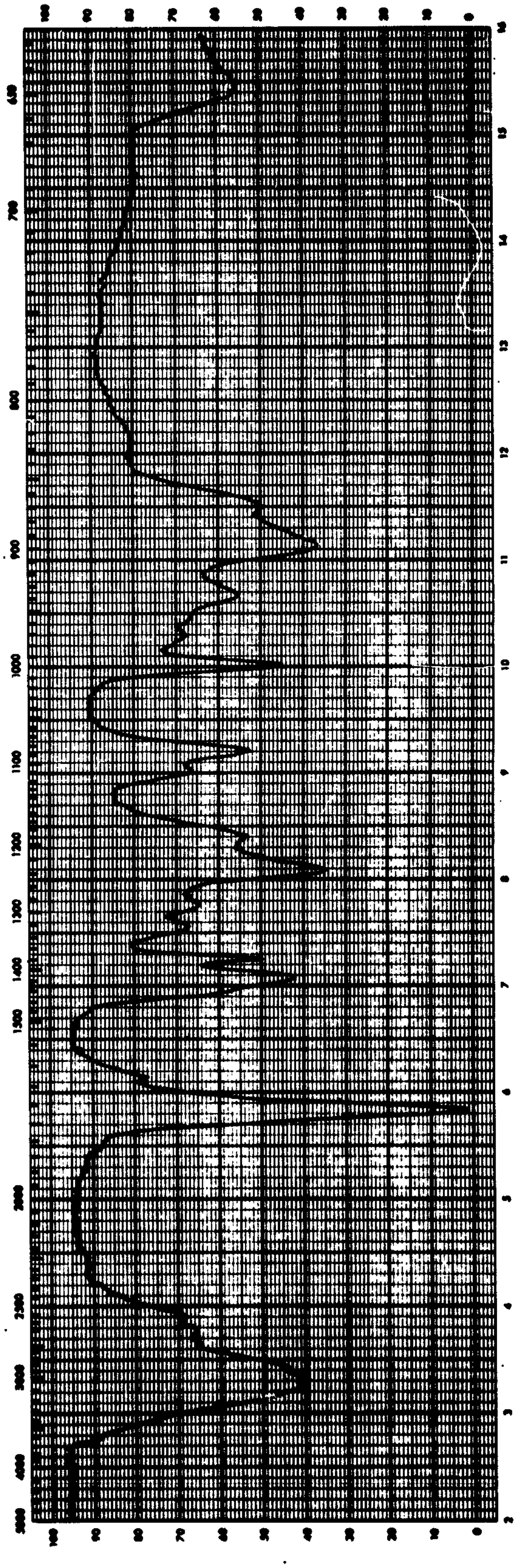

Figure 4. Infrared Spectrum of 3-Chloro-3-(difluoramino)butyric Acid

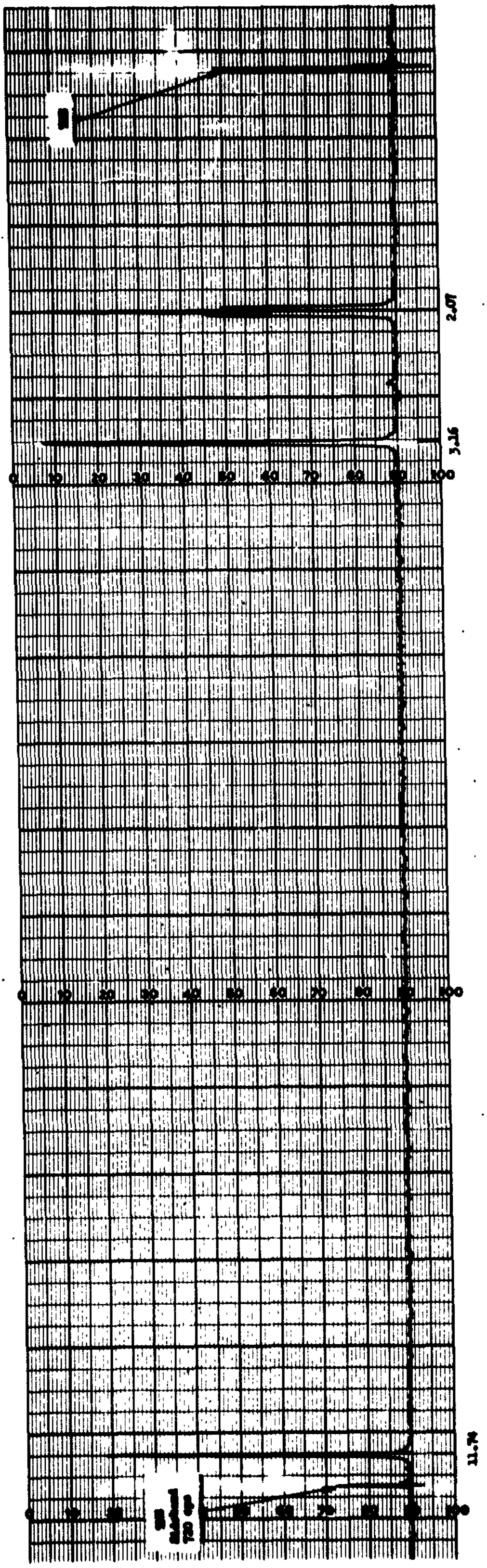

Figure 5. Proton NMR Spectrum of 3-Chloro-3-(difluoramino)butyric Acid

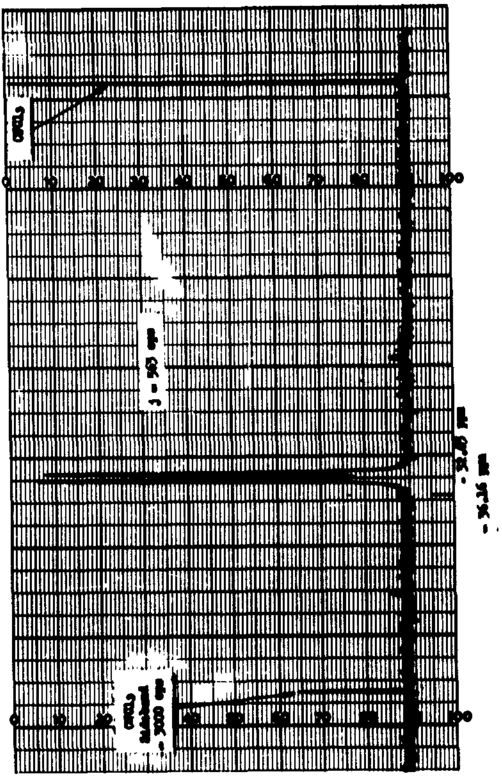

Figure 6. Fluorine NMR Spectrum of 3-Chloro-3-(difluoramino)butyric Acid

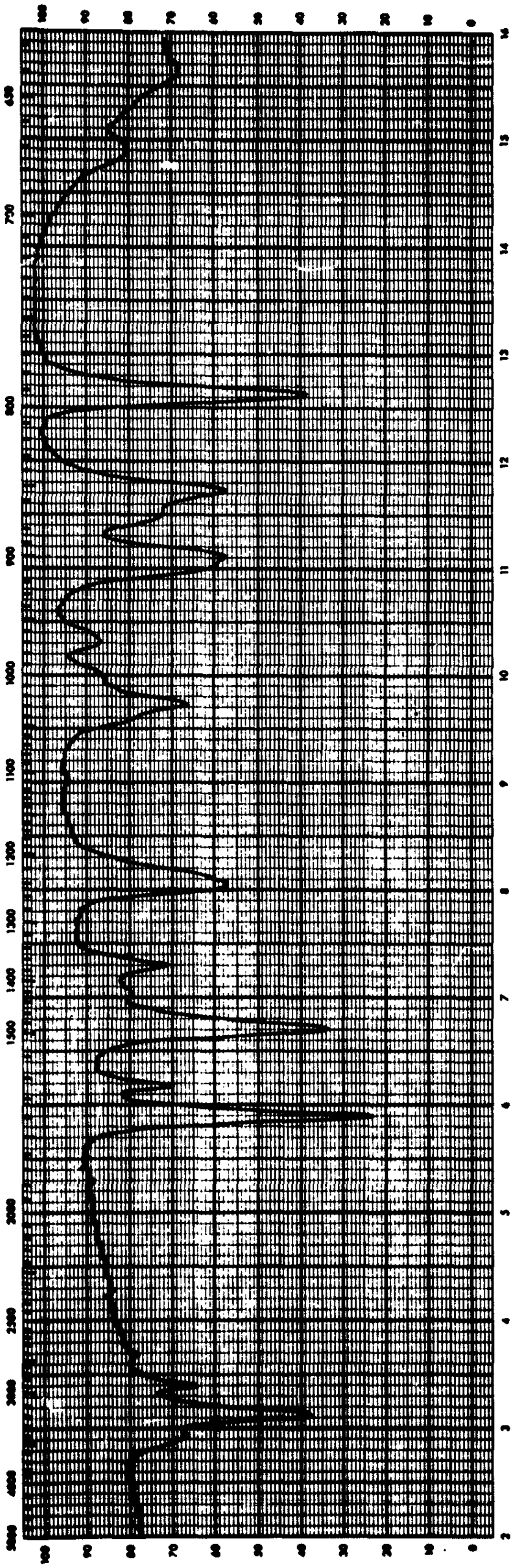

Figure 7. Infrared Spectrum of N-[2,2-Dichloro-1-fluorimino-2-(difluoramino)ethyl]acetamide

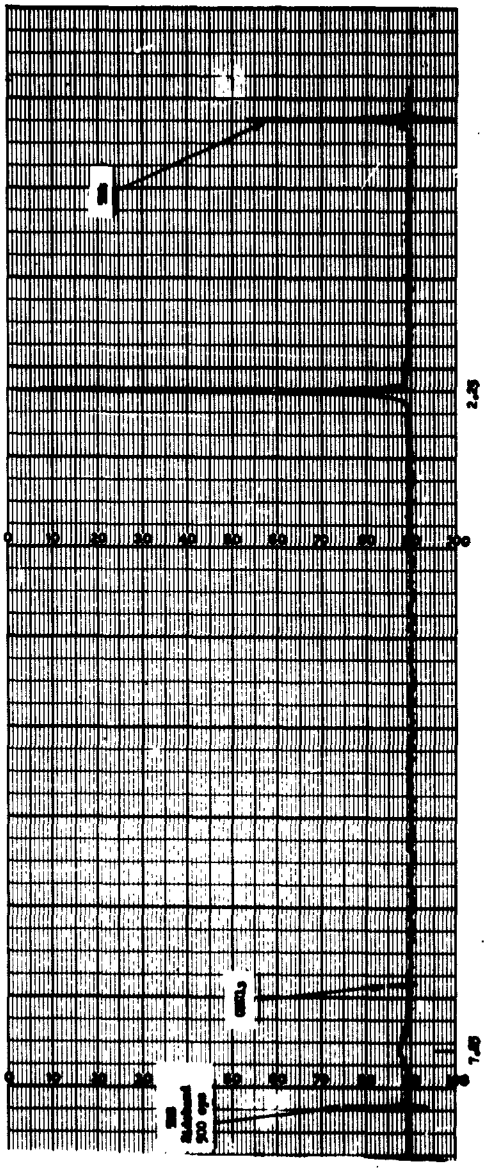

Figure 8. Proton NMR Spectrum of N-[2,2-Dichloro-1-fluorimino-2-(difluoramino)ethyl]acetamide

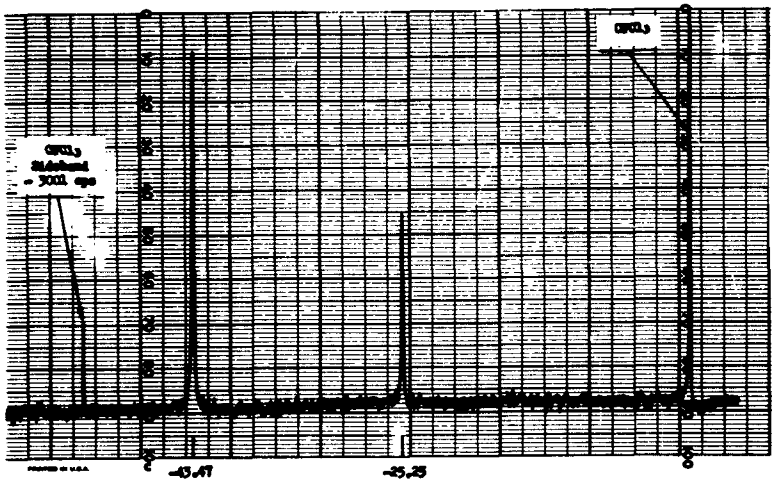

Figure 9. Fluroine NMR Spectrum of N-[2,2-Dichloro-1-fluorimino-2-(difluoramino)ethyl]acetamide

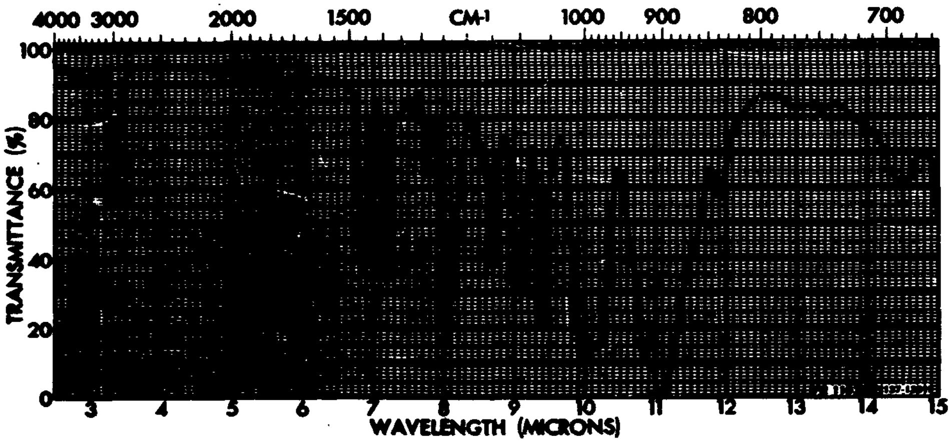

Figure 10. Infrared Spectrum of 2-Methyl-2-difluoramino-5[1,1-bis(difluoramino)ethyl]tetrahydropyran

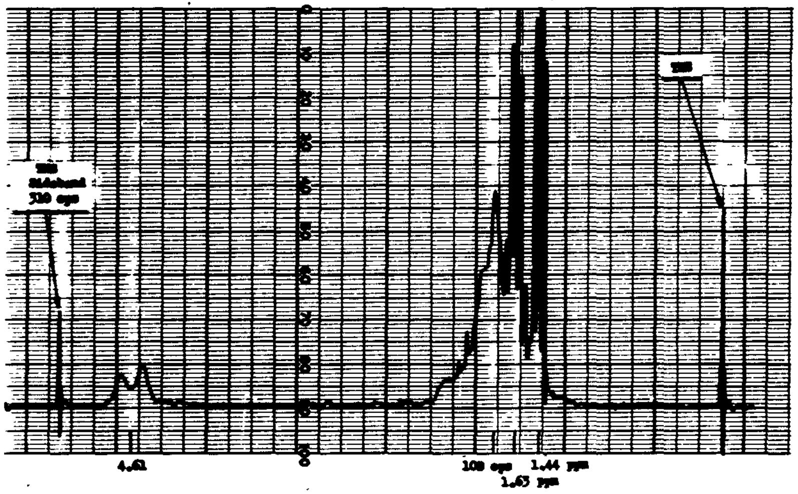

Figure 11. Proton NMR Spectrum of 2-Methyl-2-difluoramino-5-[1,1-bis(difluoramino)ethyl]tetrahydropyran

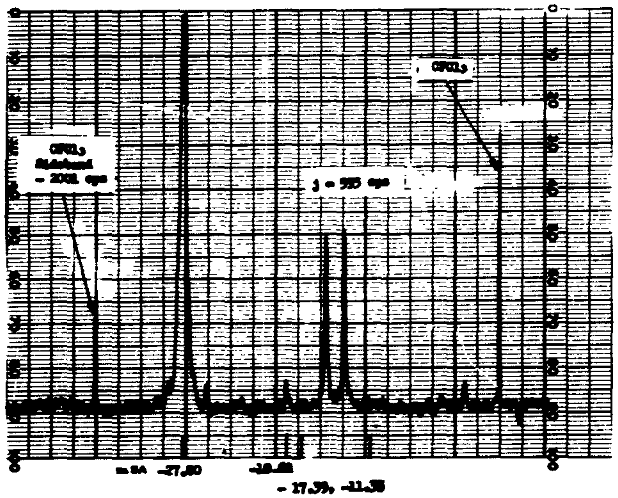

Figure 12. Fluorine NMR Spectrum of 2-Methyl-2-difluoramino-5-[1,1-bis(difluoramino)ethyl]tetrahydropyran

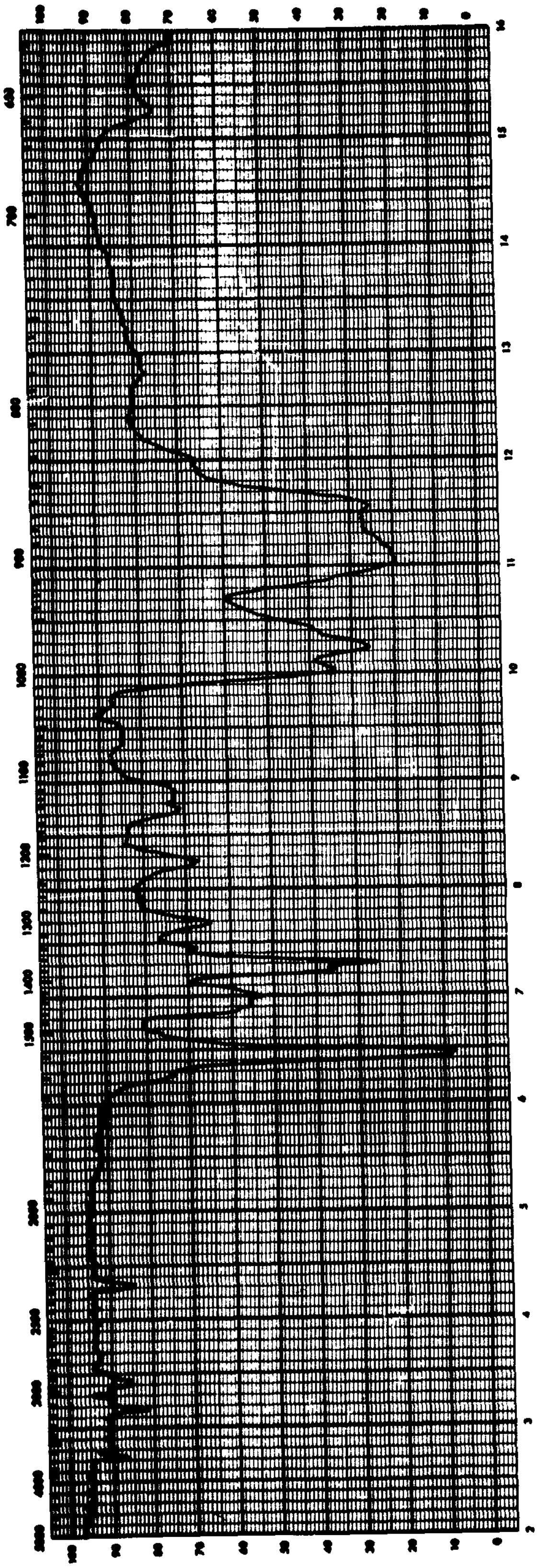

Figure 13. Infrared Spectrum of 5-Nitro-2,2-bis(difluoramino)pentane

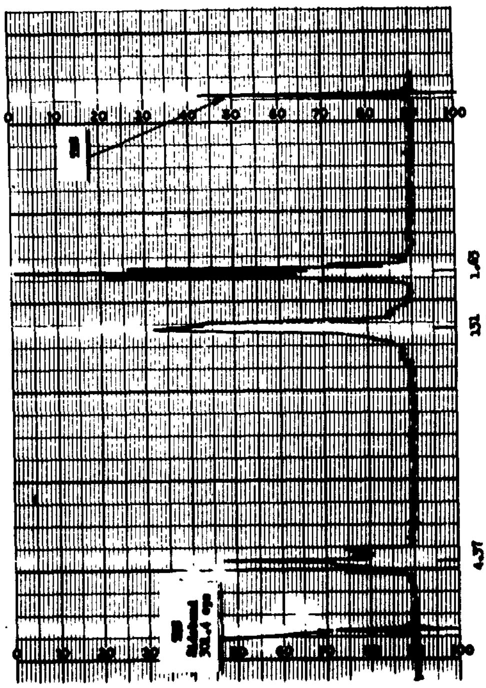

Figure 14. Proton NMR Spectrum of 5-Nitro-2,2-bis(difluoramino)pentane

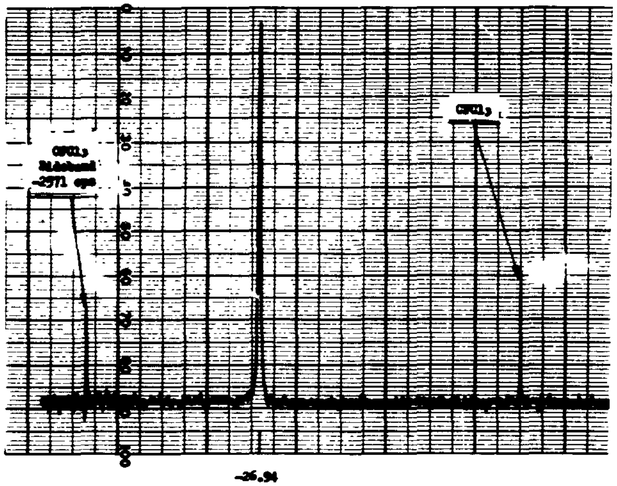

Figure 15. Fluorine NMR Spectrum of 5-Nitro-2,2-bis(difluoramino)pentane

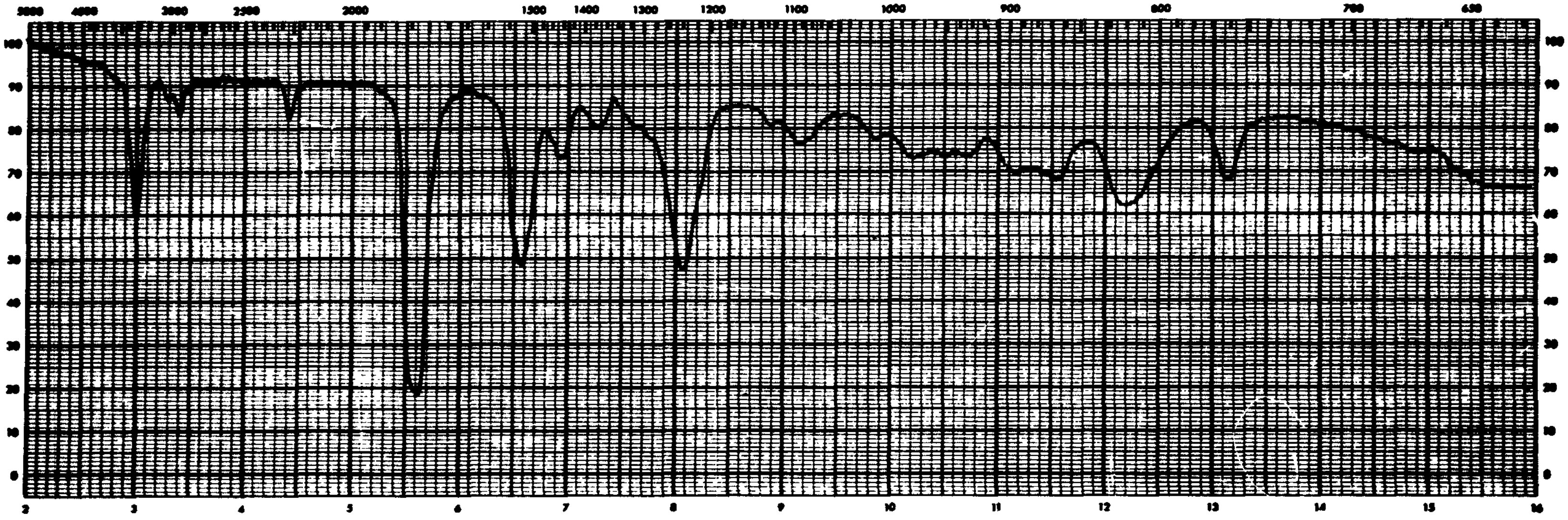

Figure 16. Infrared Spectrum of 3-Difluoraminopropylcarbamyl Fluoride

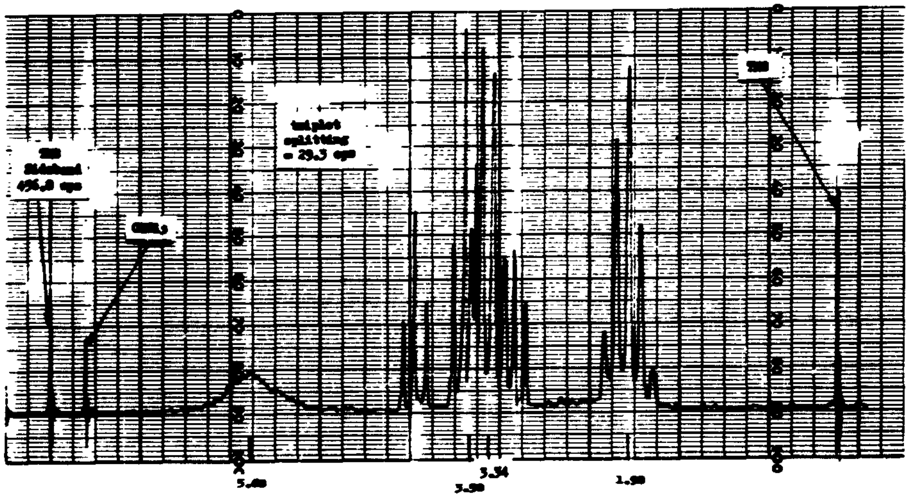

Figure 17. Proton NMR Spectrum of 3-Difluoraminopropylcarbamyl Fluoride

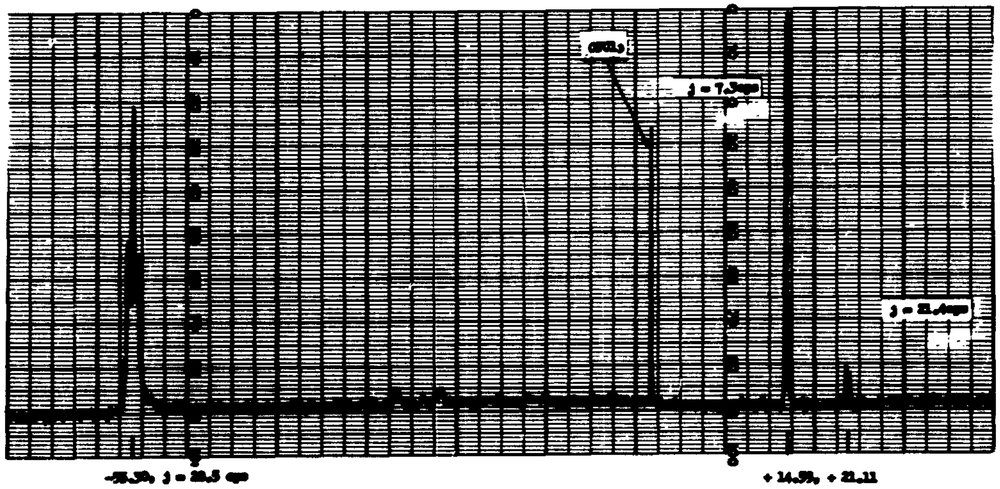

Figure 18. Fluorine NMR Spectrum of 3-Difluoraminopropylcarbamyl Fluoride

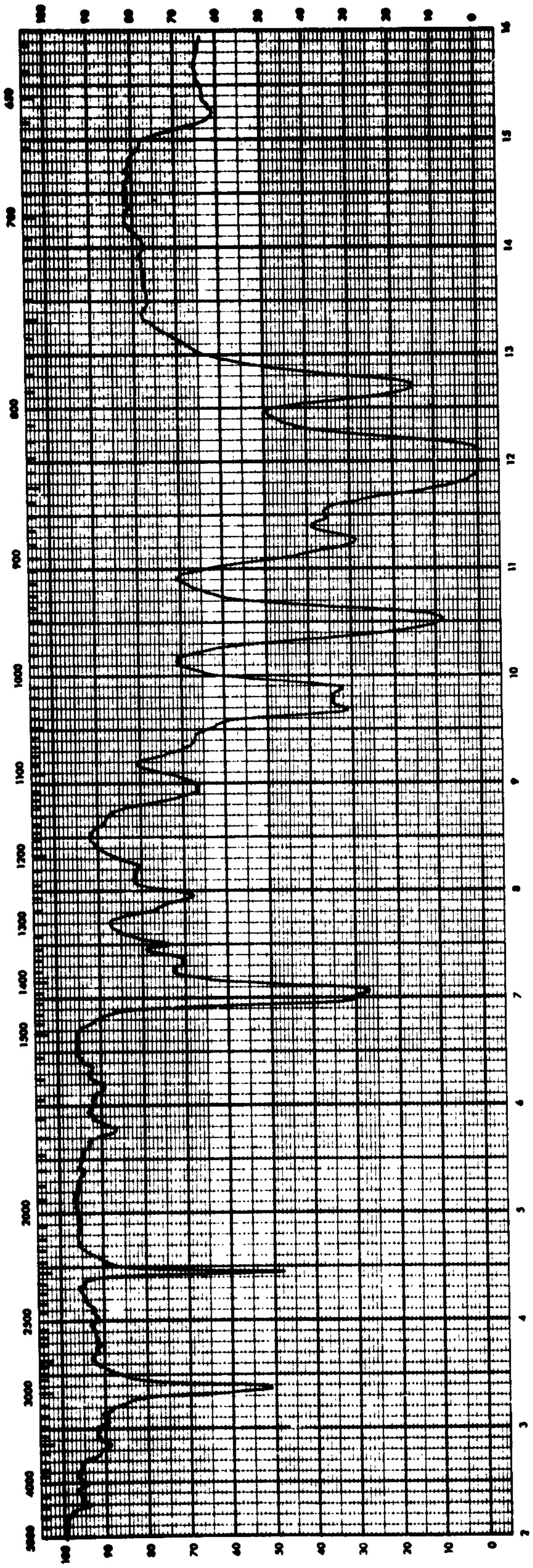

Figure 19. Infrared Spectrum of 3-Difluoraminopropionitrile

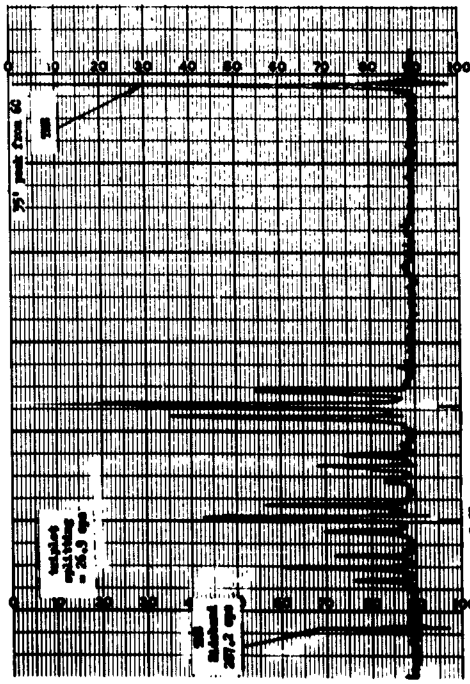

Figure 20. Proton NMR Spectrum of 3-Difluoraminopropionitrile

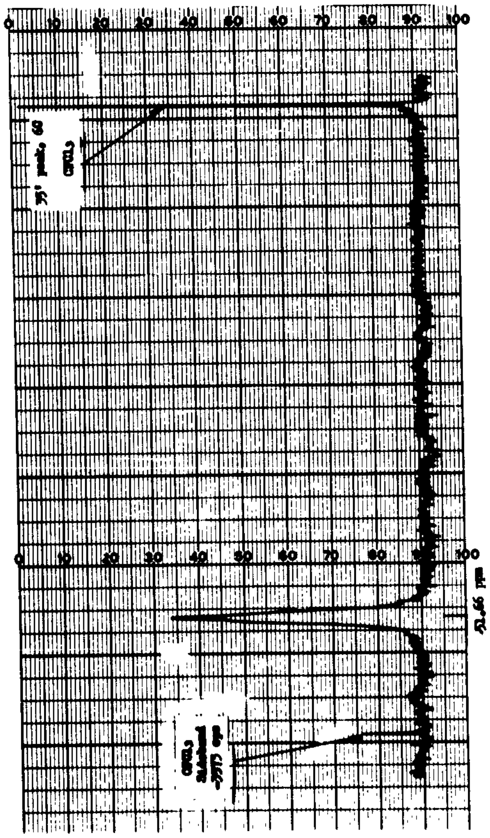

Figure 21. Fluorine NMR Spectrum of 3-Difluoraminopropionitrile

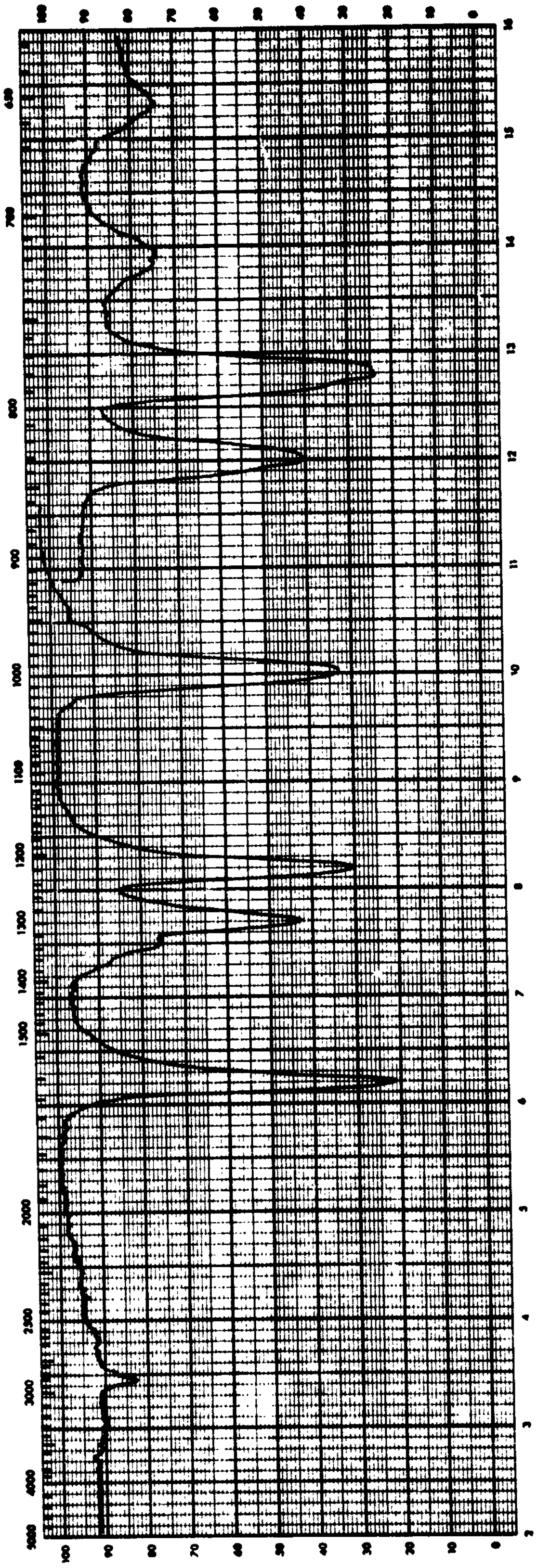

Figure 22. Infrared Spectrum of Chlorofluorodinitromethane

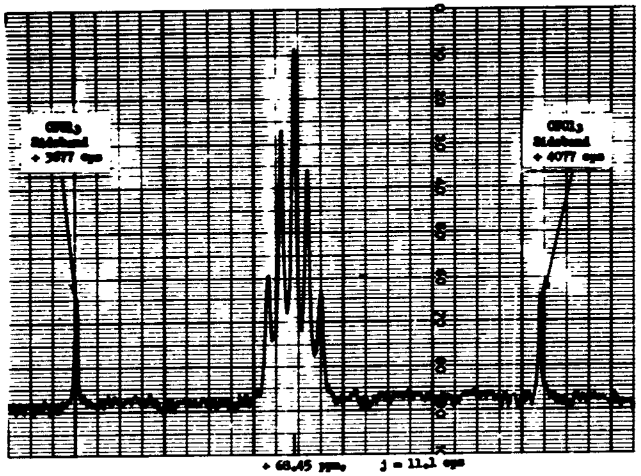

Figure 23. Fluorine NMR Spectrum of Chlorofluorodinitromethane

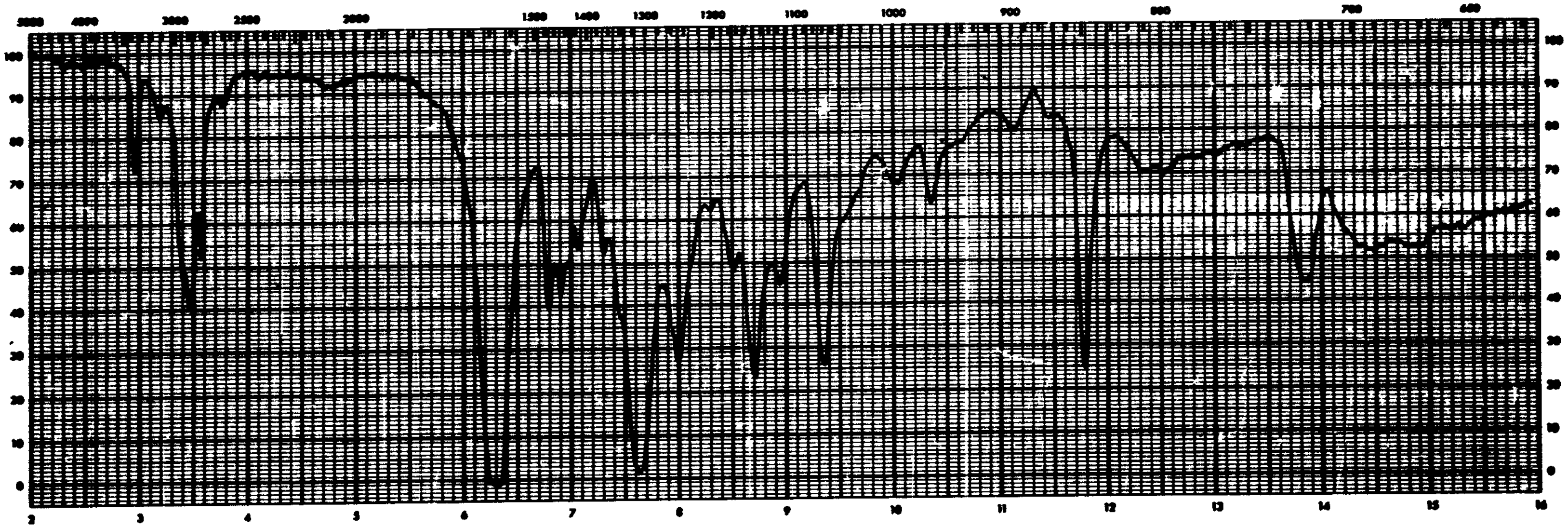

Figure 24. Infrared Spectrum of (Dinitrofluoroethyl)methylamine

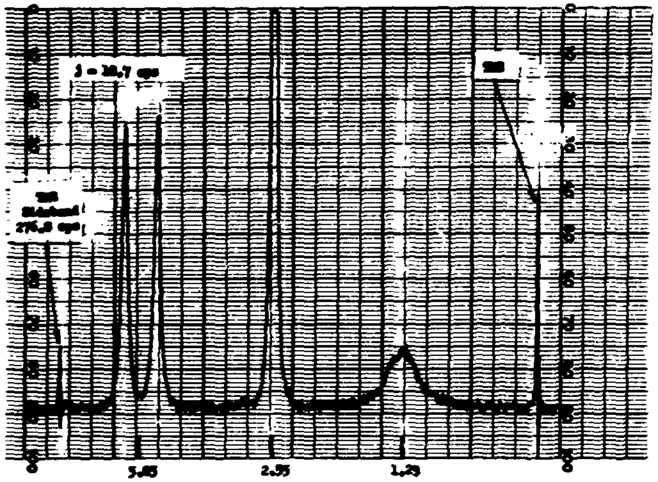

Figure 25. Proton NMR Spectrum of (Dinitrofluoroethyl)methylamine

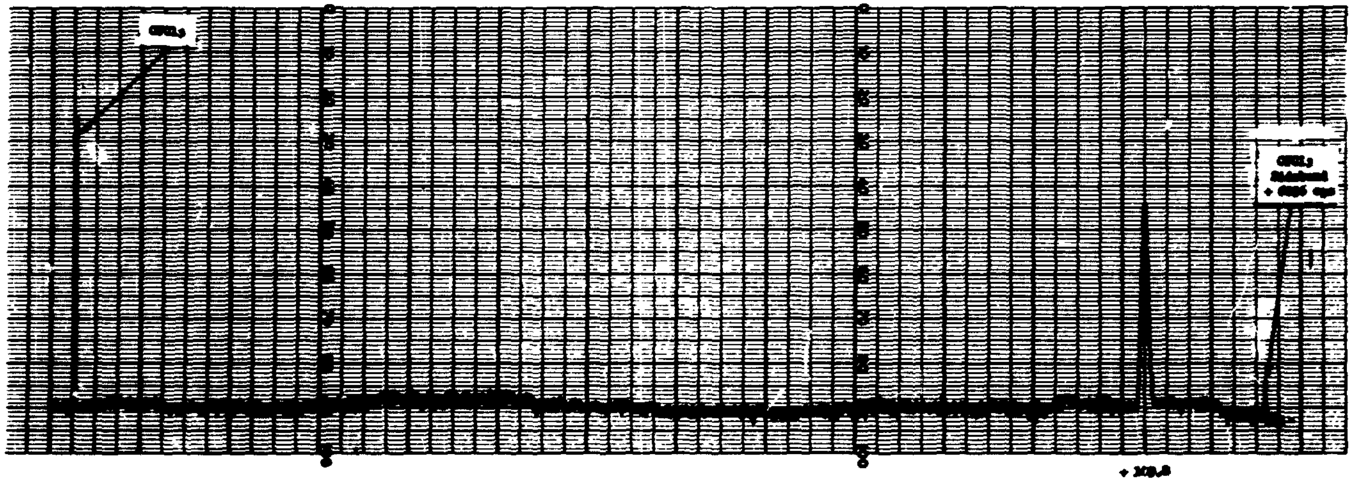

Figure 26. Fluorine NMR Spectrum of (Dinitrofluoroethyl)methylamine

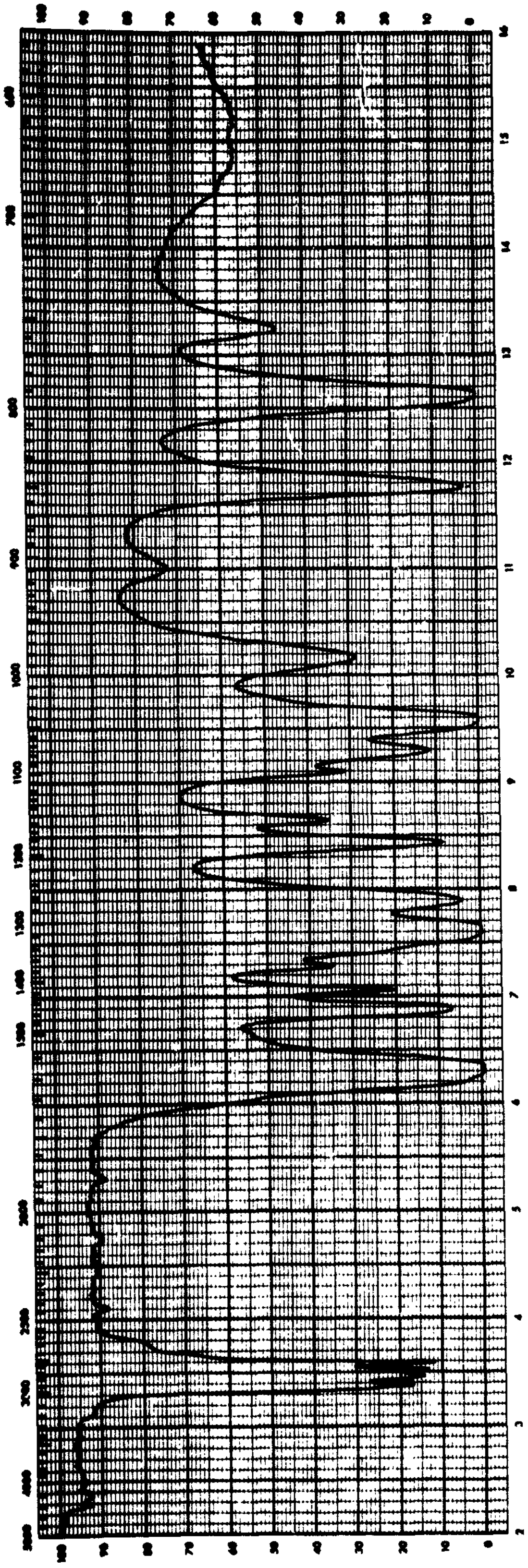

Figure 27. Infrared Spectrum of (Dinitrofluoroethyl)dimethylamine

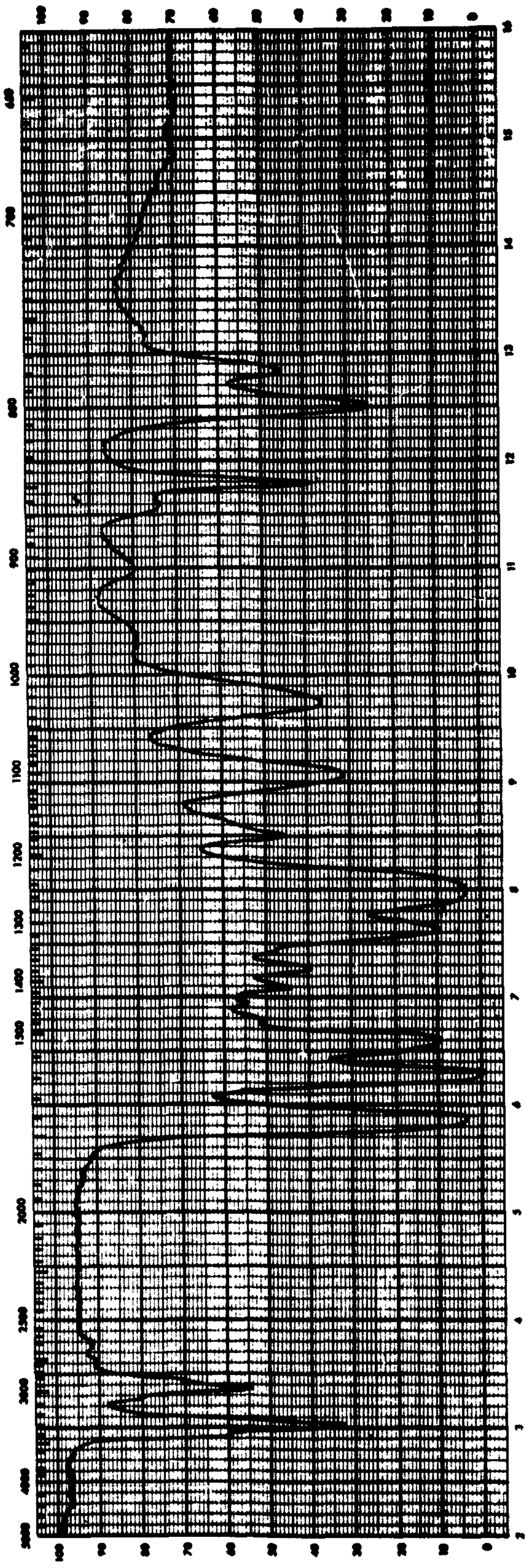

Figure 28. Infrared Spectrum of Ethyl Dinitrofluoroethylcarbamate

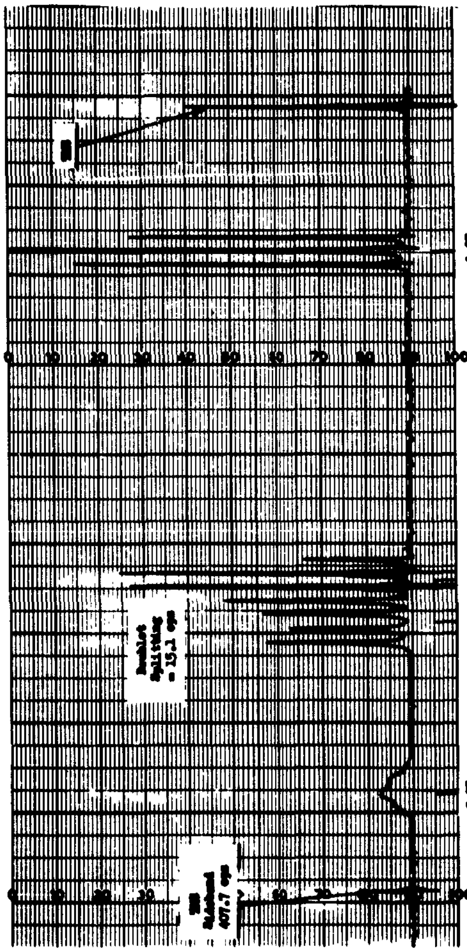

Figure 29. Proton NMR Spectrum of Ethyl Dinitrofluoroethylcarbamate

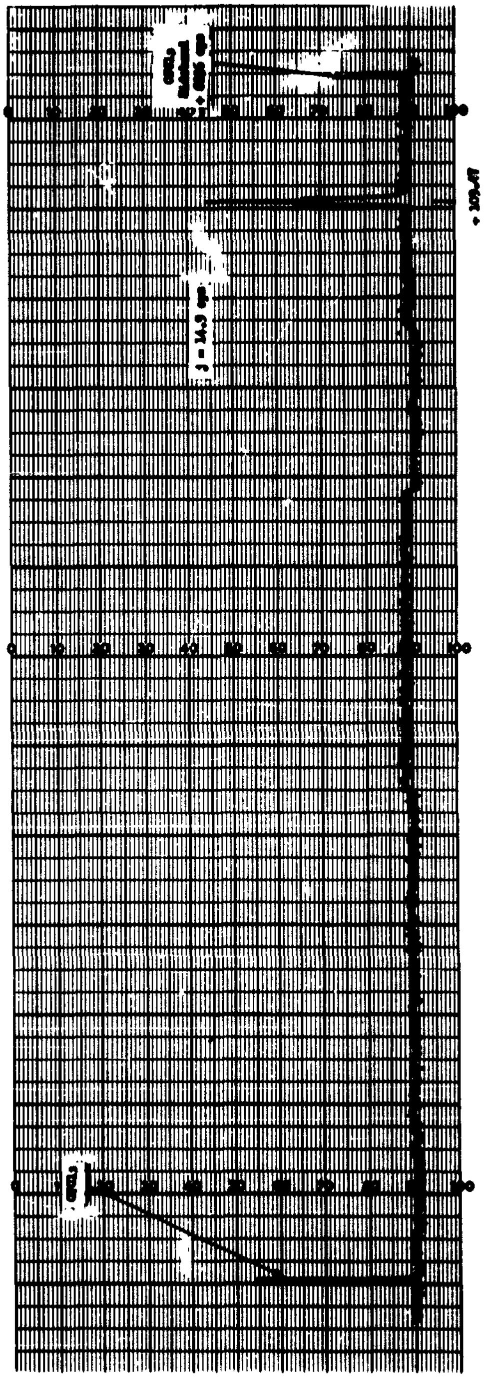

Figure 30. Fluorine NMR Spectrum of Ethyl Dinitrofluoroethylcarbamate

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