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1073.9

RESEARCH ON ULTRA-HIGH IMPULSE PROPELLANT SYSTEMS (U)

374732

DATA SHEETS

FOR COMPOUNDS PREPARED UNDER

U.S. NAVY Contracts N62558 – 2576, – 3318, – 4076, – 4272

ARPA Order 23

Program Code No. 4910

DDC AUG 9 1966 D

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1073 9

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This Document Contains 127 Pages

Copy No. 68 of 170 copies.

Research Department,
Imperial Chemical Industries Limited,
Nobel Division, Stevenston, Scotland.

Imperial Chemical Industries Limited has filed patent applications to cover compounds disclosed in this publication, and secrecy orders have been issued thereon.

IMPERIAL CHEMICAL INDUSTRIES LIMITED

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Mr.R.L. Hanson
Power Branch
Department of the Navy
Office of Naval Research
Washington D.C. 20360.
U.S.A.

Your ref:

Our ref: JP/MDS

Date: 22 July 1966

Dear Mr. Hanson,

I am sorry I omitted from our data sheets the impact sensitivity values on our apparatus for the standard explosives. Of course, the values given are of little use without these standards and I had intended to include them.

The figures for the ½ Kg. hammer are:

RDX	25 - 30 cm.
PETN	30 - 40 cm.
Tetryl	60 - 70 cm.
NG	25 - 30 cm.

TNT is very insensitive and gives a value > 200 cm. with a 2 Kg. hammer.

Yours sincerely,

(J. Peters)
Government Research Section.

This letter is a supplement to Data Sheets for Compounds Prepared under U.S. Navy Contracts N62558-2576,-3318,-4076,-4272.

CONTENTS

Introduction

This report covers the period 1st July 1960 to 30th June 1966 and summarises the important properties of compounds prepared in the Research Department laboratories of the Nobel Division of Imperial Chemical Industries Limited on behalf of the Advanced Research Projects Agency under A.R.P.A. Order 23. The work sponsored by A.R.P.A. was monitored by the Office of Naval Research and was carried out under U.S. Navy Contracts N62558-2576, -3318, -4076 and -4272.

The report is divided into three sections. Section 1 deals with all NF-containing compounds first prepared or prepared by new routes under the above contracts. Section 2 deals with compounds containing the NO_2-group only and prepared under these contracts. Section 3 describes briefly the instruments and methods employed in determining the physical characteristics of these compounds.

Compounds have been listed in elemental order as in Chemical Abstracts. Infra-red and n.m.r. traces have not been reproduced but are retained on file in Research Department, Nobel Division, for reference purposes. Infracord 137 spectra are available for all NF-compounds listed and Infracord 337 spectra for some of these compounds. Both Infracord 137 and 337 spectra are available for the NO_2- compounds.

SECTION 1

NF Containing Products

Data Sheet

1. N,N-Difluorourea (anhydrous) (DFU)

Structure : NF_2CONH_2

Physical State: White solid, m.p. 42-42.5°C

Analysis: Found: C, 12.0; H, 2.2; F, 36.5; N, 27.8%

Calc. for $CH_2F_2N_2O$: C, 12.5; H, 2.1; F, 39.5; N, 29.2%

Infra-red absorptions at: 3.0(s), 3.1(m), 5.6(s), 6.3(s), 7.4(s), 8.3(m), 9.0(w), 10.9(s), 12.0(w), 14.(m)/μ.

Impact Sensitivity: 10-20 cm

Other Properties: Moisture content when prepared 0.3%, non-hygroscopic on storage in the atmosphere. Attempts to chlorinate, nitrate and acetylate DFU were unsuccessful. Attempts to prepare lithium, sodium and silver derivatives of DFU were also unsuccessful.

ΔH_{f298} calc. -41.0; ΔH_{f298} meas. (Dow) -66.0 kcal/mole

Preparation: Fluorination of 5% urea in 0.1N NaOH solution followed by ether extraction:

$NH_2CONH_2 + F_2 \longrightarrow NF_2CONH_2$; 56% yield

References: Aerojet-General Corp., Report 0371-02-2, July 1960

Dow Chemical Corp., Report No. AR-2Q-60, April-June 1960

I.C.I. Progress Report No. 9, July - September 1962.

Data Sheet

2. N-Nitro-N'-difluoraminomethylurea

Structure: $O_2NNHCONHCH_2NF_2$

Physical State: White solid, m.p. 83-7°C (recrystallised from alcohol/ligroin)

Analysis: Found: C, 14.4; H, 1.9; F, 23.7; N, 32.9%

$C_2H_4F_2N_4O_3$ requires: C, 14.1; H, 2.4; F, 22.4; N, 32.9%

Infra-red absorptions at: 2.8(m), 3.1(m), 3.2(m), 3.3(s), 5.8(s), 6.2(s), 6.4(s), 7.1(m), 7.4(m), 7.8(m), 8.2(s), 9.6(s), 12.1(m), 12.5(m), 13.4, 13.6(m)μ.

Impact Sensitivity: 10-20 cm

Explosion Point: 136°C

Other Properties: ΔH_{f298} calc. -134.4kcal/mole

Preparation: Reaction of HNF_2 with nitrourea in the presence of 37% aqueous formalin and H_2SO_4:

$$O_2NNHCONH_2 + CH_2O \xrightarrow[H_2SO_4]{HNF_2} O_2NNHCONHCH_2NF_2 \quad (50\% \text{ yield})$$

Reference: I.C.I. Progress Report No. 15, January - March 1964.

Data Sheet

3. Bis(difluoraminomethyl)nitramine (BDMN)

Structure: $(F_2NCH_2)_2NNO_2$

Physical State: Yellow liquid

Analysis: Found: C, 13.9; H, 3.1; F, 33.7; N, 30.2%

Calc. for $C_2H_4F_4N_4O_2$: C, 12.5; H, 2.1; F, 39.6; N, 29.2%

Infra-red absorptions at: 3.0(s), 5.9(m), 6.4(vs), 7.1(vs), 7.9(vs), 8.8(s), 9.1-9.4(m), 10.5(s), 11.0(s), 12.2(s), 13.8(s)μ.

Impact Sensitivity: 10-20 cm

Explosion Point: 140°C

Other Properties: ΔH_{f298} calc. -30.1 kcal/mole (Esso ΔH_{f298} calc. -27.0) Monopropellant S.I. 297.5 calc.

Vapour pressure measured:

0°	5.8 mm	40°	28.5
10°	6.6	50°	41.1
20°	12.2	60°	57.1
30°	18.5	159° (est)	760

Vacuum thermal stability test at 60° showed an autocatalytic decomposition (initial gas evolution 19.5 ml/g/100 hr). Slightly swelled OIO and BDI/D1 casting powders.

4

Preparation: Reaction of HNF_2 with nitramine and paraformaldehyde in the presence of 96% H_2SO_4.

$$NH_2NO_2 + (CH_2O)_x + HNF_2 \xrightarrow{H_2SO_4} (F_2NCH_2)_2NNO_2; \quad 26\% \text{ yield}$$

References: Esso Research & Engineering Co. QPR 62-4, Sept.-Dec. 1962 I.C.I. Progress Report No. 14, July 1, 1962 - December 31, 1963, No. 21, July 1 - September 30, 1965.

Data Sheet

4. **Methane N-difluoraminomethylsulphonamide**

Structure: $MeSO_2NHCH_2NF_2$

Physical State: m.p. 74-76°C

Analysis: Found: C, 15.0; H, 3.7; F, 25.7; N, 17.6%

$C_2H_6F_2N_2O_2S$ requires: C, 15.0; H, 3.8; F, 23.8; N, 17.5%

Infra-red absorptions at: 3.0(s), 7.15(m), 7.6(s), 8.0(w), 8.7(s), 9.3(w), 9.9(w), 10.2(s), 10.95(s), 11.5(w), 11.95(s), 12.2(s), 12.4(s), 13.25(m)μ.

Impact Sensitivity: >200 cm

Preparation: Treatment of methane sulphonamide with 37% aqueous formalin, HNF_2 and H_2SO_4: (Soluble in water)

$$MeSO_2NH_2 + CH_2O + HNF_2 \xrightarrow{H_2SO_4} MeSO_2NHCH_2NF_2;$$

75% yield

Reference: I.C.I. Progress Report No. 18, January 1 - December 31, 1964.

Data Sheet

5. N,N'-Bis(difluoraminomethyl)sulphamide

Structure: $F_2NCH_2NHSO_2NHCH_2NF_2$

Physical State: Clear, colourless oil

Analysis: Found: C, 11.1; H, 3.1; F, 33.9; N, 24.8%

$C_2H_6F_4N_4O_2S$ requires: C, 10.6; H, 2.7; F, 33.6; N, 24.8%

Infra-red absorptions at: 3.0(s), 6.5(m), 6.85(s), 6.95(s), 7.05(s), 7.5(s), 8.3(m), 8.6-8.8(s), 9.3(m), 9.9(m), 10.2(m), 11.0(s), 12.2(s)μ.

Preparation: Reaction of HNF_2 with sulphamide and paraformaldehyde in the presence of 96% H_2SO_4, followed by Et_2O extraction.

$$NH_2SO_2NH_2 + (CH_2O)_x + HNF_2 \xrightarrow{H_2SO_4} F_2NCH_2NHSO_2NHCH_2NF_2;$$ 31% yield

Reference: I.C.I. Progress Report No. 18, January 1 - December 31, 1964.

Data Sheet

6. 4,5-Bis(difluoramino)-1,3-dinitroimidazolidin-2-one

Structure: $F_2NCHN(NO_2)CON(NO_2)CHNF_2$

Physical State: White solid m.p. 69-70°

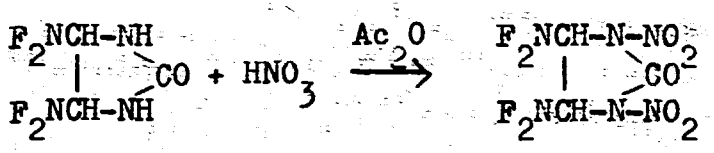
Analysis: Found: C, 13.2; H, 0.4; F, 27.5; N, 29.6%

$C_3H_2F_4N_6O_5$ requires: C, 12.9; H, 0.7; F, 27.3; N, 30.2%

Infra-red absorptions at: 5.4(s), 6.2(s), 7.8(w), 8.1(s), 9.0(s), 9.2(m), 9.75(w), 10.7(w), 11.6(m), 12.4(w), 13.5(w)μ.

^{1}HNMR Spectrum (MeCN solution): Triplet centred at 3.1τ (J=16 c/sec)

Preparation: Nitration of 4,5-bis(difluoramino)imidazolidin-2-one with HNO_3/Ac_2O for 2½ hr at -10° followed by evaporation of the acid before addition of water.



Very small yield.

Reference: I.C.I. Progress Report No. 23, January 1 - March 31, 1966.

Data Sheet

7. 4,5-Bis(difluoramino)-1-nitroimidazolidin-2-one

Structure: $F_2NCHN(NO_2)CONHCHNF_2$

Physical State: White solid, m.p. 85-89 (decomp.) (recrystallised from iPrOH/hexane)

Analysis: Found: C, 15.2; H, 0.8; F, 31.8; N, 30.4%

$C_3H_3F_4N_5O_3$ requires: C, 15.5; H, 1.3; F, 32.6; N, 30.1%

Infra-red absorptions at: 5.7(s), 5.6(s), 6.25(s), 7.75(m), 7.9(s), 8.1(s), 8.9(m), 9.3(m), 9.8(m), 10.8(m), 11.35(m), 12.1(w), 12.4(w), 12.8(m), 13.1(w), 13.7(w)

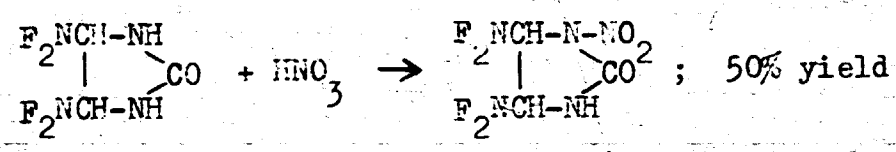
HNMR Spectrum (MeCN solution): Triplet centred at 4.35 τ (J=18 c/sec) and at 3-45 τ (J = 18 c/sec)
Broad singlet at 1.74 τ (NH)

^{19}FNMR Spectrum (MeCN solution): Triplet at -32.5 δ (J=18 c/sec)

Impact Sensitivity: <5 cm

Explosion point: 152°C

Preparation: Nitration of 4,5-bis(difluoramino)imidazolidin-2-one with 100% HNO_3 at 20° for 2 days



; 50% yield

Reference: I.C.I. Progress Report No. 15, January 1 - March 31, 1964, No. 23, January 1 - March 31, 1966.

Data Sheet

8. 4,5-Bis(difluoramino)imidazolidin-2-one

Structure: $F_2NCHNHCONHCHNF_2$

Physical State: White solid, m.p. 172° (recrystallised from benzene)

Analysis: Found: C, 19.4 H, 1.9; F, 39.9; N, 29.8%

$C_3H_4F_4N_4O$ requires: C, 19.2; H, 2.1; F, 40.4; N, 29.8%

Infra-red absorptions at: 3.1(s), 3.2(s), 5.8(s), 6.9(s), 7.7(m), 7.9(s), 8.6(m), 9.9(m), 10.5(m), 11.3(m), 11.5(s), 13.1(m)μ.

'HNMR (Acetone solution): Triplet centred at 4.39τ, J=18 c/sec (CH) each peak split by ^{14}N, J=1.8 c/sec. Broad singlet at 2.12τ (N_H)

^{19}FNMR (Acetone solution): Triplet at -31.6 δ, J=15 c/sec.

Impact Sensitivity: 10-20 cm

Explosion Point: >300°

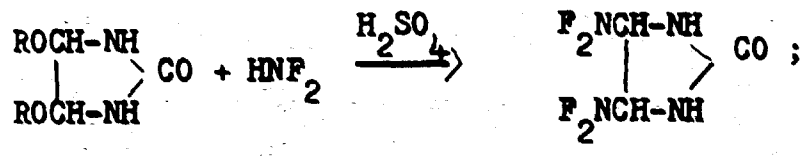
Other Properties: Can be sublimed under vacuum at 100°

0.2 g sample lost 1.6% by wt. on storage at 70° for 14 days in open tube.

ΔH_{f298} calc. -153.8 kcal/mole

Vacuum thermal stability 0.3 ml/g/100 hr at 60°C

Preparation: 1. Reaction of HNF_2 with 4,5-dihydroxy-, 4,5-dimethoxy-, or 4,5-diethoxyimidazolidin-2-one in the presence of 96% H_2SO_4

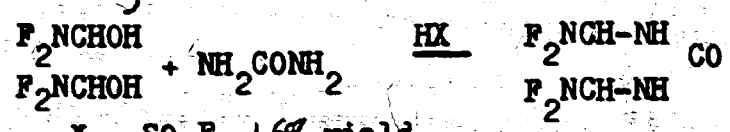


R=H, 78% yield

R=Me, 78% yield

R=Et, 84% yield

2. Condensation of 1,2-bis(difluoramino)ethane-1,2-diol with urea in the presence of H_2SO_4 or HSO_3F:



X = SO_3F, 46% yield

X = HSO_4, 16% yield

References: I.C.I. Progress Report No.14, July 1, 1962 - December 31,1963; No. 15, January 1 - March 31,1964; No.17, July 1 - September 30, 1964. No.23, January 1 - March 31,1966.

Data Sheet

9. N,N'-Bis(difluoraminomethyl)-N-nitrourea

Structure: $F_2NCH_2N(NO_2)CONHCH_2NF_2$

Physical State: White solid, m.p. 69-72°C (recrystallised from ethanol/ligroin)

Analysis: Found: C, 16.2; H, 2.7; F, 32.3; N, 31.1%

$C_3H_5F_4N_5O_3$ requires: C, 15.3; H, 2.1; F, 32.3; N, 29.8%

Infra-red absorptions at: 2.85(m), 5.8(s), 6.0(m), 6.2(s), 6.4(s), 7.0(m), 7.1(m), 7.4(m), 7.8(m), 8.2(s), 9.6(s), 9.8(m), 10.7(m), 10.9(s), 12.2(s), 12.55(s), 13.45(s), 13.65(s)μ.

Impact Sensitivity: <5 cm

Explosion Point: 143°C

Other Properties: ΔH_{f298} calc. -139.2 kcal/mole. Monopropellant I295

S.I. 245 calc.

Preparation: Reaction of HNF_2 with nitrourea in the presence of 37% aqueous formalin and H_2SO_4

$$NH_2CONHNO_2 + CH_2O \xrightarrow[H_2SO_4]{HNF_2} F_2NCH_2N(NO_2)CONHCH_2NF_2;$$ 36% yield

Reference: I.C.I. Progress Report No. 15, January 1 - March 31, 1964

Data Sheet

10. N-Acetyl-N-difluoraminomethylhydroxylamine

Structure: $AcN(OH)CH_2NF_2$

Physical State: White solid, m.p. 93-94°C

Analysis: Found: C, 25.8; H, 4.5; F, 27.4; N, 19.1%

$C_3H_6F_2N_2O_2$ requires: C, 25.7; H, 4.3; F, 27.1; N, 20.0%

Infra-red absorptions at: 3.15(s), 6.1(s), 7.1(s), 7.9(m), 8.0(m), 9.8(m), 10.0(m), 10.9(m), 12.2(s), 12.8(m)μ.

Preparation: The action of HNF_2 on a mixture of acetohydroxamic acid and paraformaldehyde in the presence of 96% H_2SO_4

$$AcNHOH + (CH_2O)_x + HNF_2 \xrightarrow{H_2SO_4} AcN(OH)CH_2NF_2;$$ 8% yield

Reference: I.C.I. Progress Report No. 12, July 1, 1962 - June 30, 1963

Data Sheet

11. N,N'-Bis(difluoraminomethyl)urea (BDMU)

Structure: $F_2NCH_2NHCONHCH_2NF_2$

Physical State: White solid, m.p. 162°C (recrystallised from ligroin/ethanol)

Analysis: Found: C, 19.4; H, 3.1; F, 39.8; N, 29.6%

$C_3H_6F_4N_4O$ requires: C, 18.9; H, 3.2; F, 40.0; N, 29.5%

Infra-red absorptions at: 3.0(s), 6.1(s), 6.6(m), 7.5(m), 8.0(m), 9.0(m), 10.0(m), 11.0(s), 12.35(s), 13.0(m), 13.5(m)μ.

Impact Sensitivity: 10-20 cm

Explosion Point: 168°C

Other Properties: ΔH_{f298} calc. -128.7 kcal/mole. BDMU was recovered unchanged from:

(i) Storage at 70°C for 7 days

(ii) A mixture with aluminium powder and ammonium perchlorate heated at 100°C for 1 hour

(iii) A mixture with nitrocellulose (12.6% N) maintained at 70°C for 1 hour

(iv) A mixture with Casting Liquid (nitroglycerine/triacetin/2-nitrodiphenylamine = 80/19/1) maintained at 70°C for 7 days

Vacuum Thermal Stability test, 0.3 ml/g/100 hrs at 60°.

BDMU was decomposed by base and by nitration, and was recovered unchanged from attempts at difluoramination, halogenation, and fluorination.

Preparation: (i) Reaction of HNF_2 with a mixture of urea and paraformaldehyde, in the presence of 96% H_2SO_4 or other dehydrating agents

$$NH_2CONH_2 + (CH_2O)_x + HNF_2 \xrightarrow{-H_2O} F_2NCH_2NHCONHCH_2NF_2$$

89% yield

(ii) Reaction of difluoraminomethanol with urea in the presence of 96% H_2SO_4 or other dehydrating agents

$$NH_2CONH_2 + F_2NCH_2OH \xrightarrow{-H_2O} F_2NCH_2NHCONHCH_2NF_2$$

(iii) Reaction of N,N'-dimethylolurea or of N,N'-di(methoxymethyl)urea with HNF_2 in the presence of 96% H_2SO_4, HSO_3F or HSO_3Cl

$$ROCH_2NHCONHCH_2OR + HNF_2 \rightarrow F_2NCH_2NHCONHCH_2NF_2$$

With H_2SO_4: R=H, 98% yield; R=Me, 76% yield

With HSO_3F: R=H, 95% yield

With HSO_3Cl: R=H, 95% yield

References: I.C.I. Progress Reports Nos. 11, January 1 - March 31, 1963; 12, July 1, 1962 - June 30, 1963; 14, July 1, 1962 - December 31, 1963; 15, January 1 - March 31, 1964; 23, January 1 - March 31, 1966.

Data Sheet

12. N,N'-Bis(difluoraminomethyl)methylene dinitramine (BDM)

Structure: $CH_2[N(CH_2NF_2)NO_2]_2$

Physical State: White solid, m.p. 89°C (Esso Report m.p. 78-80)

Analysis: Found: C, 16.0; H, 3.0; F, 31.2; N, 30.2%

Calc. for $C_3H_6F_4N_6O_4$: C, 13.5; H, 2.3; F, 28.6; N, 31.6%

Infra-red absorptions at: 3.5(m), 6.4(s), 7.0(m), 7.4(m), 7.6(m), 7.9(s), 8.7(s), 9.7(s), 10.3(s), 10.6(s), 10.9(s), 11.4(m), 12.2(s), 13.1(s)μ.

Other Properties: ΔH_{f298} -29.6 kcal/mole calc. Esso estimated ΔH_{f298} -31.05 kcal/mole, and monopropellant S.I. 284.8.

Preparation: The reaction of HNF_2 with methylene dinitramine and 37% aqueous formalin, in the presence of H_2SO_4

$$CH_2(NHNO_2)_2 + CH_2O + HNF_2 \xrightarrow{H_2SO_4} CH_2[N(CH_2NF_2)NO_2]_2;$$ 31% yield

References: Esso Research & Engineering Co. QPR 62-4, Sept. - Dec. 1962.

I.C.I. Progress Report No. 14, July 1, 1962 - December 31, 1963; No. 15, January 1 - March 31, 1964.

Data Sheet

13. Tris(difluoraminomethyl)amine, (TDMA)

Structure: $N(CH_2NF_2)_3$

Physical State: Colourless liquid, b.p. 166°/760 mm

Analysis: Found: C, 17.2; H, 2.9; F, 53.5; N, 26.5%; M.W. (cryoscopic in benzene), 234.

$C_3H_6F_6N_4$ requires: C, 17.0; H, 2.8; F, 53.8; N, 26.4%; M.W. 212.

Infra-red absorptions at: 3.4(w), 6.9(s), 7.2(s), 7.3(s), 8.2(s), 9.4(s), 10.0(m), 11.0(s), 12.2(s), 13.7(m), 16.7(m), 18.7(m)μ.

^{1}HNMR Spectrum (CCl_4 solution): Triplet centred at 5.43τ, J=24 c/sec.

^{19}FNMR Spectrum (CCl_4 solution): Triplet centred at -42.7δ, J=24 c/sec.

Impact Sensitivity: 10-20 cm

Explosion Point: >166°

Other Properties: ΔH_{f298} calc. -25.3 kcal/mole. Monopropellant S.I. 287 calc. Refractive Index (18°), 1.378. Soluble in Et_2O, $CHCl_2$, C_6H_6. Insoluble in water. No decomposition after storage in 'Pyrex' at room temperature for 3 months.

Vapour pressure measured:

13. (contd)

0°	6.4 mm	40°	34.4 mm
10°	10.3	50°	47.1
20°	17.6	60°	61.1
30°	25.7	166°	760.0

D.T.A. endotherm, 180°. Storage at 60° showed a slow initial pressure rise followed by an accelerating rate of increase. Did not form quaternary salts, decomposed by HNO_3, $HClO_4$, O_3, H_2O_2 base.

Preparation: Treatment of the following with HNF_2 and 96% H_2SO_4, HSO_3F or HSO_3Cl.

(i) Dinitropentamethylenetetramine; 50% yield

(ii) Hexamethylenetetramine; 10% yield

(iii) Hexamethylenetetramine dinitrate; 38% yield

(iv) Liquid NH_3, NF_2CH_2OH; 13% yield

(v) NF_2CH_2OH, NH_2SO_3H; 34% yield

(vi) NF_2CH_2OH, $(NH_4)_2SO_4$; 18% yield

(vii) NF_2CH_2OH, NH_4Cl; 43% yield

References: I.C.I. Progress Reports No. 15, January 1 - March 31, 1964; No. 16, April 1 - June 30, 1964; No. 18, January 1 - December 31, 1964; No. 19, January 1 - March 31, 1965; No. 20, April 1 - June 30, 1965; No. 21, July 1 - September 30, 1965.

14. Methane N,N-bis(difluoraminomethyl)sulphonamide

Structure: $MeSO_2N(CH_2NF_2)_2$

Physical State: White solid, m.p. 44-46°C

Analysis: Found: C, 15.5; H, 3.4; F, 34.0; N, 17.4%

$C_3H_7F_4N_3O_2S$ requires: C, 16.0; H, 3.1; F, 33.8; N, 18.7%

Infra-red absorptions at: 7.3(s), 7.4(s), 7.7(m), 8.2(m), 8.5(s), 8.6(s), 9.9(m), 10.1(m), 10.3(s), 10.8(s), 11.0(s), 11.7(m), 12.1(s), 12.2(s), 12.5(s), 13.3(m)μ.

Impact Sensitivity: 30-40 cm

Preparation: Treatment of methane sulphonamide with paraformaldehyde, $HNF_2 . H_2SO_4$ (Insoluble in water).

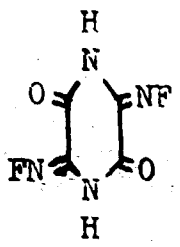
$$MeSO_2NH_2 + (CH_2O)_2 + HNF_2 \xrightarrow{H_2SO_4} MeSO_2N(CH_2NF_2)_2;$$ 58% yield.

Reference: I.C.I. Progress Report No. 18, January 1 - December 31, 1964.

Data Sheet

15. 2,5-Difluorimino-3,6-diketopiperazine

Structure:



(or isomer)

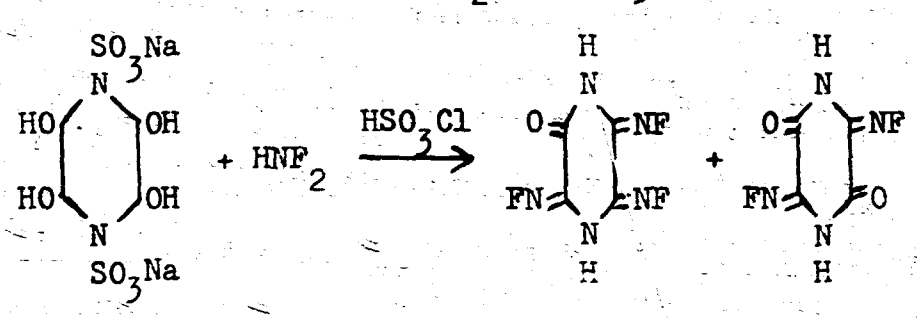
Physical State: White solid, m.p. 156-7°, recrystallised from isopropanol

Analysis: Found: C, 28.4; H, 2.6; F, 21.6; N, 33.9%

$C_4H_2F_2N_4O_2$ requires: C, 27.3; H, 1.1; F, 21.6; N, 31.8%

Infra-red absorptions at: 2.95(s), 5.75(s), 5.95(s), 6.2(s), 6.3(s), 7.2(s), 7.6(m), 7.9(s), 8.3(m), 9.2(m), 11.0(s), 11.15(s), 11.5(m), 11.55(m), 12.0(m), 12.7(m), 13.4(m), 14.0(m)μ.

Preparation: The reaction of disodium 2,3,5,6-tetrahydroxypiperazine-1,4-disulphonate with HNF_2 and HSO_3Cl (minor product)



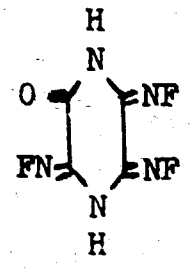
50% yield 15% yield

Reference: I.C.I. Progress Report No. 20, April 1-June 30, 1965.

Data Sheet

16. 2,3,5-Trifluorimino-6-ketopiperazine

Structure:



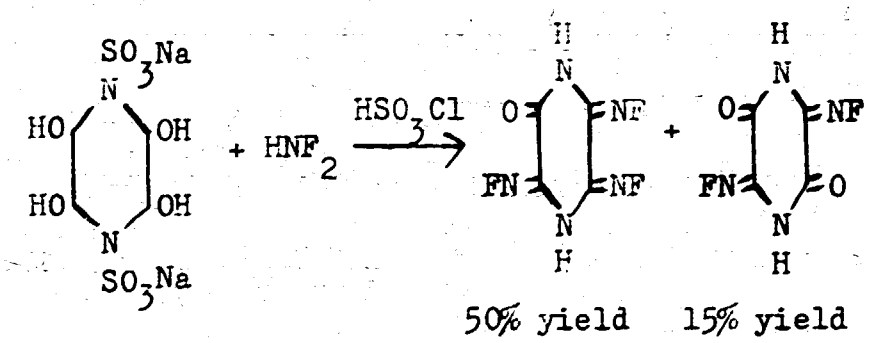
Physical State: White solid, m.p. 206-7°, recrystallised from isopropanol

Analysis: Found: C, 25.0; H, 1.9; F, 28.6; N, 37.5%;
M(ebullioscopic in acetone), 182

$C_4H_2F_3N_5O$ requires: C, 24.9; H, 1.1; F, 29.5; N, 36.3%;
M, 193.

Infra-red absorptions at: 2.95(s), 3.1(s), 5.8(s), 6.2(s), 6.3(s), 7.15(s), 7.85(w), 8.1(w), 10.8(s), 11.0(s), 11.15(s), 13.1(m), 13.3(m), 14.0(m), 14.6(m)μ.

Preparation: (i) The reaction of disodium 2,3,5,6-tetrahydroxypiperazine-1,4-disulphonate with HNF_2 and HSO_3Cl, or with 96% H_2SO_4 in the presence of paraformaldehyde.

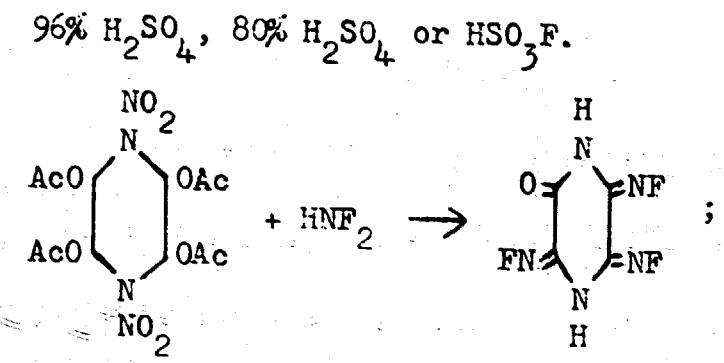


50% yield 15% yield

With 96% H_2SO_4, $(CH_2O)_x$, the yield was 39%.

16. (contd.)

(ii) The reaction of 2,3,5,6-tetraacetoxy-1,4-dinitropiperazine with HNF_2 and 96% H_2SO_4, 80% H_2SO_4 or HSO_3F.



;

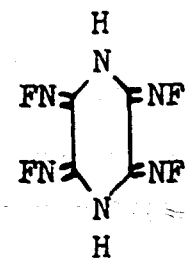
40% yield

Reference: I.C.I. Progress Report No. 20, April 1 - June 30, 1965.

Data Sheet

17. 2,3,5,6-Tetrafluoriminopiperazine (TFP)

Structure:



Physical State: White solid, m.p. >230°, recrystallised from isopropanol

Analysis: Found: C, 22.6; H, 1.0; F, 36.0; N, 40.4%
M(ebullioscopic in acetone), 209

$C_4H_2F_4N_6$ requires: C, 22.9; H, 0.95; F, 36.2; N, 40.0%;
M, 210.

Infra-red absorptions at: 2.95(m), 6.2(m), 6.8(m), 7.1(m), 10.9(m), 11.1(s), 15.9(s)μ.

Ultra-violet absorptions at: 255mμ, 327mμ (in MeOH solution)

^{1}HNMR Spectrum (Acetone solution): Peak at 6.35 (MeCN).
Peak at 6.41τ (acetone). Peak at -0.30τ (acetone)

^{19}FNMR Spectrum (Acetone solution): Peak at +24.0 δ

Impact Sensitivity: 5-10 cm

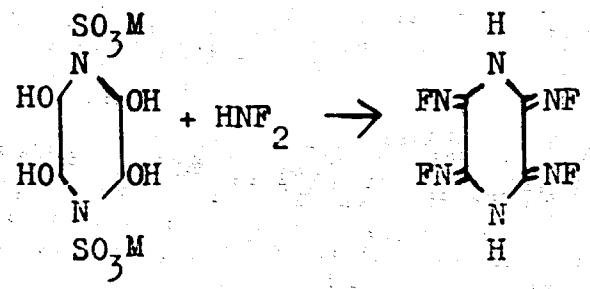
Explosion Point: 244.5°

Other Properties: TFP did not condense with difluoraminomethanol.
N_2O_5 reacted with TFP but did not give 2,3,5,6-tetrafluorimino-1,4-dinitropiperazine.

17. (contd.)

TFP was recovered unchanged from treatment with HNO_3/Ac_2O. Hydrogenation of TFP resulted in the uptake of 5 mols H_2 to give an unidentified product. Chlorination of TFP either gave recovered TFP or complete decomposition. HF did not add to TFP at room temperature. TFP was decomposed by $LiAlH_4$.

Preparation: The action of HNF_2 and 96% H_2SO_4 (4 hrs) HSO_3F, HSO_3Cl (1 hr) on salts of 2,3,5,6-tetrahydroxypiperazine-1,4,-disulphonic acid.

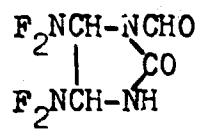


; M=Na, 77% yield (H_2SO_4)
34% yield (HSO_3F, HSO_3Cl)

References: I.C.I. Progress Reports No. 19, January 1 - March 31, 1965; No. 20, April 1 - June 30, 1965; No. 21, July 1 - September 30, 1965.

Data Sheet

18. 4,5-Bis(difluoramino)-1-formylimidazolidin-2-one

Structure: 

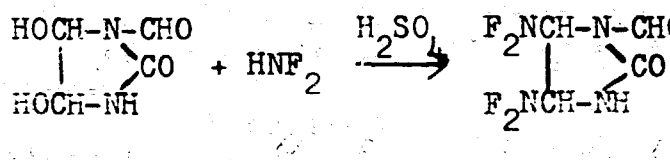
Physical State: White solid, m.p. 105-7°

Analysis: Found: C, 22.6; H, 2.2; F, 32.8; N, 25.9%

$C_4H_4F_4N_4O_2$ requires: C, 22.2; H, 1.9; F, 35.2; N, 25.9%

Infra-red absorptions at: 3.0(m), 3.1(m), 5.6(s), 5.7(s), 5.9(s), 7.0(m), 7.2(s), 7.3(m), 7.6(s), 8.1(s), 8.7(s), 10.7(m), 10.9(m), 11.5(s), 12.1(m), 13.2(m) μ.

Preparation: The reaction of 1-formyl-4,5-dihydroxyimidazolidin-2-one with HNF_2 and 96% H_2SO_4.



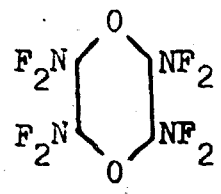
; 65% yield

Reference: I.C.I. Progress Report No. 19, January 1 - March 31, 1965.

Data Sheet

19. 2,3,5,6-Tetrakis(difluoramino)dioxan (TDD)

Structure:



Physical State: Liquid, b.p. 78-82/5 mm 100-110°/10 mm

Analysis: Found: C, 20.6; H, 2.2; F, 41.3; N, 15.0%

Calc. for $C_4H_4F_8N_4O_2$: C, 16.4; H, 1.4; F, 52.1; N, 19.2%

Infra-red absorptions at: 3.4(m), 5.8(m), 8.2(m), 8.6(s), 8.9(m), 9.6(m), 10.2(s), 11.4(s), 12.6(m)μ.

^{1}HNMR Spectrum (CCl_4 solution): Triplet at 4.49 τ, J=19 c/sec (impurity single peaks at 6.60 τ and at 2.76 τ)

^{19}FNMR Spectrum (CCl_4 solution): Doublet centred at -34.3 δ, J=20 c/sec; doublet centred at -33.6 δ, J=20 c/sec; broad band at -31.2 δ (impurity ?).

Impact Sensitivity: 5-10 cm

Other Properties: ΔH_{f298} calc. -91.4 kcal/mole. Monopropellant S.I. 266 calc. U.V. Absorption, max = 218mμ. Gas liquid chromatography indicated a complex mixture of products, the three major components

19. (contd.)

(approx. 80%) being isomers of TDD. Refractive Index of mixture (18°) 1.3960

Vapour pressure measured:

20°	2.1 mm	50°	14.2 mm
30°	4.1	60°	21.1
40°	8.1	203° (est)	760

Reaction with ethanolic base led to dehydrofluorination. TDD did not readily nitrate or methylate, and no adducts were formed with BF_3 and $HC(NO_2)_3$.

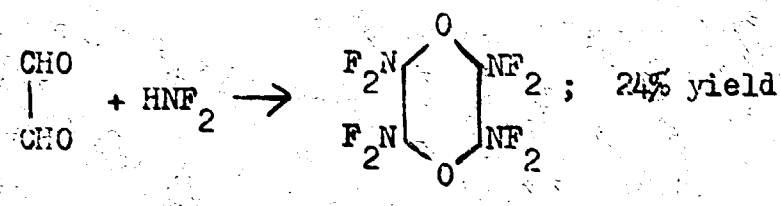
Vacuum thermal stability at 60°, 0.4 ml/g/100 hr alone, or with AP, Al, or HPVA.

Some samples of crude TDD plasticised nitrocellulose (12.6% N), a casting powder (AID) and bis(difluoramino)periodate oxycellulose. HPVA was soluble in TDD.

Crude TDD was compatible with nitrocellulose, aluminium, ammonium perchlorate maintained at 70°C for 2 days.

Preparation: Reaction of HNF_2 with glyoxal or polyglyoxal in the presence of HSO_3F, HSO_3Cl or SO_3

19. (contd.)



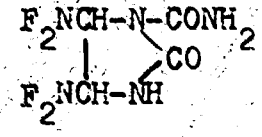
; 24% yield

References: Essc Research & Eng. Co., PR 60-3, June-Sept. 1960.

I.C.I. Progress Reports Nos. 7-11, Jan. 1, 1962 - March 31, 1963. No. 21, July 1 - September 30, 1965.

Data Sheet

20. 4,5-Bis(difluoramino)-1-ureidoimidazolidin-2-one

Structure: 

Physical State: White solid, m.p. 159-163°

Analysis: Found: C, 21.9; H, 2.7; F, 32.5; N, 30.2%

$C_4H_5F_4N_5O_2$ requires: C, 20.8; H, 2.2; F, 32.9; N, 30.3%

Infra-red absorptions at: 2.9(s), 3.1(s), 5.7(s), 6.4(s), 7.7(m), 8.0(m), 8.2(s), 10.6(w), 10.8(m), 11.4(m), 11.9(w), 12.2(m), 13.2(m), 14.0(m)μ.

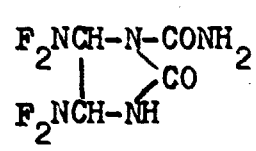
^{1}HNMR Spectrum (Acetone solution): Broad peaks at 2.45 τ, 3.18 τ(NH). Quadruplet centred at 3.98 τ, J=17 c/sec; doublet centred at 4.05 τ, J=24 c/sec (CH)

^{19}FNMR Spectrum (Acetone solution): Doublet centred at -28.7 δ, J=27 c/sec; quintuplet centred at -30.8 δ, J=17 c/sec.

Other Properties: Nitration with HNO_3 gave a solid, m.p. 65-70°. Nitrous acid decomposed the compound. The infra-red and n.m.r. spectrum support the imidazolidin-2-one structure.

Data Sheet

20. 4,5-Bis(difluoramino)-1-ureidoimidazolidin-2-one

Structure: 

Physical State: White solid, m.p. 159-163°

Analysis: Found: C, 21.9; H, 2.7; F, 32.5; N, 30.2%

$C_4H_5F_4N_5O_2$ requires: C, 20.8; H, 2.2; F, 32.9; N, 30.3%

Infra-red absorptions at: 2.9(s), 3.1(s), 5.7(s), 6.4(s), 7.7(m), 8.0(m), 8.2(s), 10.6(w), 10.8(m), 11.4(m), 11.9(w), 12.2(m), 13.2(m), 14.0(m)μ.

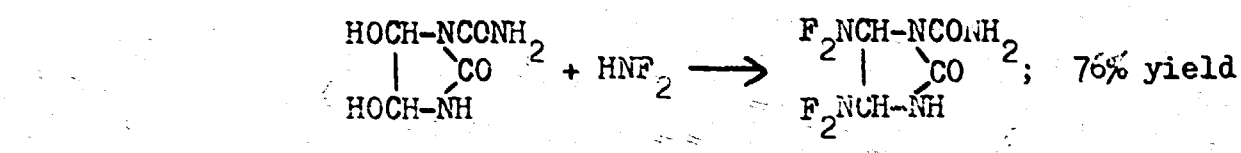
^{1}HNMR Spectrum (Acetone solution): Broad peaks at 2.45 τ, 3.18 τ(NH). Quadruplet centred at 3.98 τ, J=17 c/sec; doublet centred at 4.05 τ, J=24 c/sec (CH)

^{19}FNMR Spectrum (Acetone solution): Doublet centred at -28.7 δ, J=27 c/sec; quintuplet centred at -30.8 δ, J=17 c/sec.

Other Properties: Nitration with HNO_3 gave a solid, m.p. 65-70°. Nitrous acid decomposed the compound. The infra-red and n.m.r. spectrum support the imidazolidin-2-one structure.

20. (contd.)

Preparation: Treatment of 1:1 glyoxal:biuret adduct or its acetate with HNF_2 and H_2SO_4 alone, or in the presence of paraformaldehyde or of glyoxal



76% yield

Reference: I.C.I. Progress Report No. 20, April 1 - June 30, 1965; No. 21, July 1 - September 30, 1965.

21. N-Difluoraminomethyl acrylamide

Structure: $CH_2:CH.CONHCH_2NF_2$

Physical State: White solid m.p. 46-8° (recrystallised from acetone/hexane)

Analysis: Found: C, 34.8; H, 4.3; F, 26.0; N, 20.8%

$C_4H_6F_2N_2O$ requires: C, 35.3; H, 4.4; F, 27.9; N, 20.6%

Infra-red absorptions at: 3.1(s), 6.05(s), 6.2(s), 6.5(s), 7.1(s), 7.65(m), 8.1(s), 8.95(m), 9.1(m), 10.1(s), 10.3(s), 10.9(s), 11.55(m), 12.4(s), 14.1(m)μ.

Impact Sensitivity: >200 cm

Preparation: Reaction of HNF_2 and 96% H_2SO_4, HSO_3F on N-methylol acrylamide:

$$CH_2:CH.CONHCH_2OH + HNF_2 \xrightarrow{\text{acid}} CH_2:CH.CONHCH_2NF_2;$$ 90% yield

Reference: I.C.I. Progress Report No. 23, January 1 - March 31, 1966.

22. N-Difluoraminomethyl-N'-(2,2,2-trinitroethyl)urea

Structure: $F_2NCH_2NHCONHCH_2C(NO_2)_3$

Physical State: White solid m.p. 170-1° (recrystallised from MeOH/H_2O)

Analysis: Found: C, 17.3; H, 1.9; F, 12.9; N, 30.6%

$C_4H_6F_2N_6O_7$ requires: C, 16.7; H, 2.1; F, 13.2; N, 29.2%

Infra-red absorptions at: 5.0(m), 6.1(s), 6.3(s), 6.4(s), 7.15(m), 7.8(s), 8.05(m), 9.1(w), 9.9(w), 11.05(w), 11.5(m), 11.7(w), 12.4(m), 12.9(m), 13.6(m), 13.9(m)μ.

Other Properties: Vacuum Thermal Stability test, 0.2 ml/g/100 hr at 60°

Preparation: Difluoramination of N-hydroxymethyl-N'-(2,2,2-trinitroethyl)urea with HNF_2 and 96% H_2SO_4:

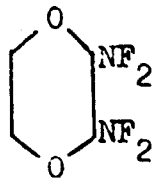
$$HOCH_2NHCONHCH_2C(NO_2)_3 + HNF_2 \xrightarrow{H_2SO_4} F_2NCH_2NHCONHCH_2C(NO_2)_3;$$ 49% yield

Reference: I.C.I. Progress Report No. 22, October 1 - December 31, 1965; 23, January 1 - March 31, 1966.

Data Sheet

23. 2,3-Bis(difluoramino)dioxan

Structure:



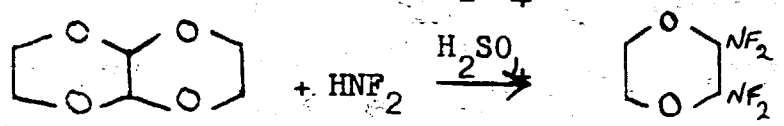
Analysis: Found: C, 25.3; H, 4.6; F, 40.3; N, 15.0%

$C_4H_6F_4N_2O_2$ requires: C, 25.3; H, 3.2; F, 40.0; N, 14.7%

Infra-red absorptions at: 3.3(w), 6.8(m), 7.9(s), 8.4(s), 9.6(m), 9.9(m), 10.3(m), 10.8(s), 11.6(s), 12.6(s), 13.7(m)μ.

Impact Sensitivity: 40-60 cm

Preparation: Reaction of 2,3-ethylenedioxydioxan with HNF_2 in the presence of 96% H_2SO_4.



; 43% yield

Reference: I.C.I. Progress Report No. 10, October 1 - December 31, 1962.

24. 1,2-Bis(difluoramino)-1,2-diformamidoethane

Structure: $(F_2NCHNHCHO)_2$

Physical State: White solid, m.p. 184-185°C (recrystallised from isopropanol) (Esso Report 195-6°)

Analysis: Found: C, 21.9; H, 2.9; F, 35.2; N, 24.5%

Calc. for $C_4H_6F_4N_4O_2$: C, 22.0; H, 2.8; F, 34.9; N, 25.7%

Infra-red absorptions at: 3.0(s), 3.4(m), 5.9(s), 6.6(s), 7.2(m), 7.9(s), 8.2(m), 9.8(m), 11.4(s), 11.8(m), 12.4(m), 13.6(s), 14.7(m), 17.5(m), 19.6(w)μ.

Impact Sensitivity: 20-30 cm

Explosion Point: 169°C

Other Properties: Intermediate in the preparation of 1,2-bis(difluoramino)ethane-1,2-dinitramine by the process:

$$\begin{matrix} F_2NCHNHCHO \\ | \\ F_2NCHNHCHO \end{matrix} \xrightarrow[Ac_2O]{HNO_3} \begin{matrix} F_2NCHNNO_2CHO \\ | \\ F_2NCHNNO_2CHO \end{matrix} \xrightarrow{EtOH} \begin{matrix} F_2NCHNHNO_2 \\ | \\ F_2NCHNHNO_2 \end{matrix}$$

57% yield

Preparation: The reaction of 1,2-diformamidoethane-1,2-diol with HNF_2 and 96% H_2SO_4:

$$\begin{matrix} HOCHNHCHO \\ | \\ HOCHNHCHO \end{matrix} \xrightarrow[H_2SO_4]{HNF_2} \begin{matrix} F_2NCHNHCHO \\ | \\ F_2NCHNHCHO \end{matrix} \quad ; \quad 50\% \text{ yield}$$

24. (contd.)

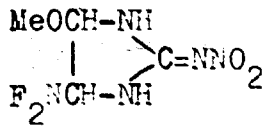
References: Esso, Q.P.R. 62-1, December 1961 - March 1962

I.C.I. Progress Report No. 16, April 1 - June 30, 1964; No. 17, July 1 - September 30, 1964.

Data Sheet

25. 4-Difluoramino-5-methoxy-2-nitriminoimidazolidine

Structure:



Physical State: White solid, m.p. 152°

Analysis: Found: C, 22.9; H, 3.5; F, 17.3; N, 32.4%

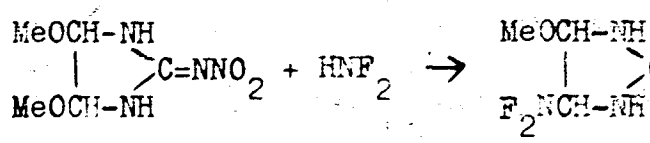
$C_4H_7F_2N_5O_3$ requires: C, 22.8; H, 3.3; F, 17.9; N, 33.2%

Infra-red absorptions at: 2.95(s), 3.1(s), 6.2(s), 6.6(s), 7.8-7.9(s), 8.15(s), 8.9(m), 9.1(m), 9.35(s), 10.4(s), 11.3(m), 12.1-12.2(m), 12.85μ.

'HNMR spectrum (Acetone solution): NH absorptions at 0.72 and 1.21 τ. Complex series of peaks in the region 4.0 to 5.5 τ associated with ring CH. Peaks due to CH_3 groups obscured by solvent.

^{19}FNMR spectrum (Acetone solution): Two doublets centred at -38.8 δ (J=27 c/sec) and -41.6 δ (J=18 c/sec)

Preparation: Treatment of 4,5-dimethoxy-2-nitriminoimidazolidine with HNF_2 and 96% H_2SO_4 in the presence of 37% formalin, or of 80% H_2SO_4



with formalin, 14% yield.
with 80% H_2SO_4, 10% yield

Reference: I.C.I. Progress Report No. 21, July 1 - September 30, 1965; No. 22, October 1 - December 31, 1965.

Data Sheet

26. Ethyl N-difluoraminomethyl-N-fluorocarbamate

Structure: $F_2NCH_2NFCOOEt$

Physical State: Colourless liquid

Analysis: Found: C, 31.3; H, 5.2; F, 27.7; N, 17.3%

$C_4H_7F_3N_2O_2$ requires: C, 27.9; H, 4.1; F, 33.1; N, 16.3%

Infra-red absorptions at: 3.0(s), 3.35(m), 5.9(s), 6.6(s), 7.15(s), 7.3(s), 7.55(s), 8.1(s), 8.5(m), 9.15(s), 9.7(s), 11.1(s), 11.45(m), 12.3(s), 12.85(s), 13.6(m)μ.

Preparation: Reaction of HNF_2 and paraformaldehyde with ethyl N-fluorocarbamate in the presence of 96% H_2SO_4

$$NHFCOOEt + (CH_2O)_x + HNF_2 \xrightarrow{H_2SO_4} F_2NCH_2NFCOOEt;$$ 25% yield

Reference: I.C.I. Progress Report No. 14, July 1, 1962 - December 31, 1963.

Data Sheet

27. Tris(difluoraminomethyl)urea

Structure: $(F_2NCH_2)_2NCONHCH_2NF_2$

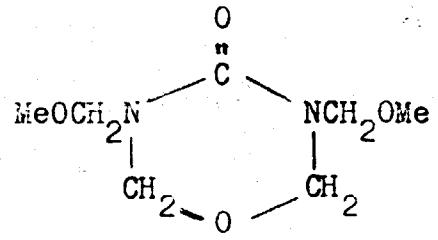
Physical State: White solid, m.p. 70-74° (purified by sublimation at 100°C)

Analysis: Found: C, 19.0; H, 3.5; F, 44.6; N, 27.9%

$C_4H_7F_6N_5O$ requires: C, 18.8; H, 2.7; F, 44.7; N, 27.4%

Infra-red absorptions at: 2.9(m), 6.0(s), 6.5(m), 8.0(m), 10.0(m), 10.9(s), 12.3(s), 12.9(m)μ.

Preparation: Action of excess HNF_2 in the presence of 96% H_2SO_4 on crude N,N'-bis(methoxymethyl)uron



$\xrightarrow[H_2SO_4]{HNF_2}$ $(F_2NCH_2)_2NCONHCH_2NF_2$; 45% yield

Reference: I.C.I. Progress Report No. 12, July 1, 1962 - June 30, 1963; No. 20, April 1 - June 30, 1965.

Data Sheet

28. Ethyl N-difluoraminomethylcarbamate

Structure: $F_2NCH_2NHCOOEt$

Physical State: Liquid

Analysis: Found: C, 30.7; H, 4.8; F, 26.2; N, 18.0%

Calc. for $C_4H_8F_2N_2O_2$: C, 31.2; H, 5.2; F, 24.7; N, 18.2%

Infra-red absorptions at: 2.95(s), 3.3(m), 5.85(s), 6.5(s), 6.9(m), 7.1(m), 7.3(m), 7.5(m), 8.0(s), 8.45(m), 8.9(m), 9.1(s), 9.7(s), 11.0(s), 11.4(m), 12.2(s), 12.8(m), 13.7(m)μ.

Other Properties: Did not give difluoraminomethyl ammonium ion on reaction with $HClO_4$

Preparation: Reaction of HNF_2 on ethyl carbamate and paraformaldehyde in the presence of 96% H_2SO_4

$$NH_2COOEt + (CH_2O)_x + HNF_2 \xrightarrow{H_2SO_4} F_2NCH_2NHCOOEt$$

29% yield

References: Aerojet-General Corp. Report No. 0235-01-12, Sept. 1 - Nov. 30, 1961.

I.C.I. Progress Report No. 14, July 1, 1962 - Dec. 31, 1963; No. 16, April 1 - June 30, 1964.

Data Sheet

29. **1,2-Bis(difluoramino)-1,2-dimethoxyethane**

Structure: $CH_3OCHNF_2CHNF_2OCH_3$

Physical State: Colourless liquid

Analysis: Found: C, 25.5; H, 5.4; F, 39.5; N, 13.5%

$C_4H_8F_4N_2O_2$ requires: C, 25.0; H, 4.2; F, 39.6; N, 14.6%

Infra-red absorptions at: 3.4(s), 6.9(s), 7.35(s), 8.25(s), 8.7(s), 8.9(s), 9.65(s), 10.1(m), 10.4(m), 11.5(s), 12.1(s), 13.1(m), 13.9(s)μ.

Impact Sensitivity: 40-60 cm

Preparation: Reaction of HNF_2 with glyoxal tetramethylacetal in the presence of 96% H_2SO_4

$$\begin{matrix}(MeO)_2CH\\|\\(MeO)_2CH\end{matrix} + HNF_2 \xrightarrow{H_2SO_4} \begin{matrix}MeOCHNF_2\\|\\MeOCHNF_2\end{matrix} \quad ; \text{ 48\% yield}$$

Reference: I.C.I. Progress Report No. 10, October 1 - December 31, 1962

Data Sheet

30. N,N'-Bis(difluoraminomethyl)-N-methoxyurea

Structure: $F_2NCH_2N(OMe)CONHCH_2NF_2$

Physical State: Gum

Analysis: Found: C, 22.7; H, 4.5; F, 31.9; N, 24.7; OCH_3, 14.1%

$C_4H_8F_4N_4O_2$ requires: C, 21.8; H, 3.6; F, 34.6; N, 25.4; OCH_3, 14.1%

Preparation: Reaction of methoxyurea with paraformaldehyde and HNF_2 in the presence of 96% H_2SO_4

$$MeONHCONH_2 + (CH_2O)_x + HNF_2 \xrightarrow{H_2SO_4} F_2NCH_2N(OMe)CONHCH_2NF_2$$

Low yield

Reference: I.C.I. Progress Report No. 12, July 1, 1962 - June 30, 1963.

Data Sheet

31. 1,7-Bis(difluoramino)-2,4,6-trinitro-2,4,6-triazaheptane

Structure: $F_2NCH_2N(NO_2)CH_2N(NO_2)CH_2N(NO_2)CH_2NF_2$

Physical State: White solid, m.p. 156-7° (recrystallised from isopropanol)

Analysis: Found: C, 15.4; H, 2.7; F, 19.[illegible]; N, 31.7%; M(ebullioscopic in acetone), 357

$C_4H_8F_4N_8O_6$ requires: C, 14.1; H, 2.4; F, 22.3; N, 32.9%; M, 340

Infra-red absorptions at: 6.3(s), 6.5(m), 7.0(s), 7.15(m), 7.85(s), 7.95(s), 8.65(m), 9.0(m), 9.9(m), 10.35(s), 10.6(s), 10.8(m), 12.4(m), 13.05(m), 13.25(m)

Preparation: Action of HNF_2 and 96% H_2SO_4 on 2,4,6-trinitro-2,4,6-triazaheptane-1,7-diacetate:

$$AcO\left[(CH_2N(NO_2)\right]_3CH_2OAc + HNF_2 \xrightarrow{H_2SO_4} F_2N\left[CH_2N(NO_2)\right]_3CH_2NF_2;$$

83% yield

Reference: I.C.I. Progress Report No. 20, April 1 - June 30, 1965.

Data Sheet

32. 2-Difluoraminobutan-2-ol

Structure: $MeC(OH)NF_2Et$

Physical State: Colourless liquid

Analysis: Found: C, 38.5; H, 7.0; F, 30.1; N, 8.6%

$C_4H_9F_2NO$ requires: C, 38.4; H, 7.2; F, 30.4; N, 11.2%

Infra-red absorptions at: 2.9(s), 3.35(s), 6.9(s), 7.1(s), 7.3(s), 7.8(m), 8.3(s), 8.5(s), 9.5(s), 9.7(s), 10.2(s), 10.4(s), 11.4(s)μ.

Preparation: Reflux of HNF_2 over methylethyl ketone

$$MeCOEt + HNF_2 \longrightarrow MeC(OH)NF_2Et$$

Quantitative

Reference: I.C.I. Progress Report No. 6, October 1 - December 31, 1961

Data Sheet

33. 1,2-Bis(difluoramino)-1,2-di(methanesulphonamido)ethane

Structure: $(F_2NCHNHSO_2Me)_2$

Physical State: Solid

Analysis: Found: C, 18.0; H, 3.0; F, 20.65; N, 15.9; S, 23.0%

$C_4H_{10}F_4N_4O_4S_2$ requires: C, 15.4; H, 3.1; F, 23.9; N, 17.6; S, 20.1%

Infra-red absorptions at: 3.1(m), 7.4(s), 7.5(s), 7.65(s), 7.8(m), 8.6(s), 8.75(m), 9.3(m), 9.75(m), 10.35(m), 10.7(s), 11.4(s), 11.7(s), 13.1(s), 13.3(m), 14.0(m)μ.

Preparation: Treatment of 1,2-di(methanesulphonamido)ethane-1,2-diol with HNF_2 and H_2SO_4:

$$\begin{matrix} HOCHNHSO_2Me \\ | \\ HOCHNHSO_2Me \end{matrix} + HNF_2 \xrightarrow{96\%\ H_2SO_4} \begin{matrix} F_2NCHNHSO_2Me \\ | \\ F_2NCHNHSO_2Me \end{matrix} \quad ; \quad 78\%\ \text{yield}$$

Reference: I.C.I. Progress Report No. 21, July 1 - September 30, 1965.

Data Sheet

3+. N,N'-Bis(2,2,2-tribromo-1-difluoraminoethyl)urea

Structure: $(CBr_3CHNF_2NH)_2CO$

Physical State: Prisms, m.p. 145°, recrystallised from ethanol

Analysis: Found: C, 8.5; H, 0.75; Br, 65.0; F, 11.2; N, 9.9%

$C_5H_4Br_6F_4N_4O$ requires: C, 8.7; H, 0.6; Br, 69.4; F, 11.0; N, 8.1%

Infra-red absorptions at: 2.90(m), 3.01(s), 5.97(s), 6.06(m), 6.54(s), 8.07(m), 8.33(m), 8.70(m), 9.17(m), 9.80(m), 10.8(m), 11.76(s), 12.8(s), 13.9(s)μ.

Other Properties: No replacement of bromine by NF_2, NO_2 or ONO_2 on further treatment with HNF_2/118% H_2SO_4, HNF_2/HSO_3F, $AgNO_2$ or $AgNO_3$.

Preparation: The reaction of bromal, urea, HNF_2 and 96% H_2SO_4

$$CBr_3CHO + HNF_2 + NH_2CONH_2 \xrightarrow{H_2SO_4} CBr_3CHNF_2NHCONHCHNF_2CBr_3;$$

41% yield

Reference: I.C.I. Progress Report No. 22, October 1 - December 31, 1965.

Data Sheet

35. N,N'-Bis(2,2,2-trichloro-1-difluoraminoethyl)urea

Structure: $(CCl_3CHNF_2NH)_2CO$

Physical State: Prisms, m.p. 160°, recrystallised from ethanol

Analysis: Found: C, 14.9; H, 0.98; Cl, 44.1; F, 16.6; N, 16.5%

$C_5H_4Cl_6F_4N_4O$ requires: C, 14.2; H, 0.95; Cl, 49.8; F, 18.0; N, 13.3%

Infra-red absorptions at: 2.90(m), 3.01(s), 5.97(s), 6.25(m), 6.52(s), 8.3(m), 9.2(m), 9.9(m), 10.9(m), 11.8-11.9(s), 12.8(s), 13.9(s)μ.

Other Properties: No replacement of chlorine by NF_2, NO_2 or ONO_2 on further treatment with HNF_2/118% H_2SO_4, HNF_2/ HSO_3F, $AgNO_2$ or $AgNO_3$

Preparation: The reaction of chloral, urea, HNF_2 and 98% H_2SO_4

$$CCl_3CHO + HNF_2 + NH_2CONH_2 \xrightarrow{H_2SO_4} CCl_3CHNF_2NHCONHCHNF_2CCl_3;$$

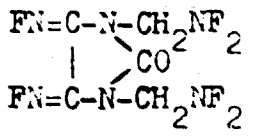
22% yield

Reference: I.C.I. Progress Report No. 22, October 1 - December 31, 1965.

Data Sheet

36. 1,3-Bis(difluoraminomethyl)-4,5-difluoriminoimidazolidin-2-one

Structure:



Physical State: m.p. 162-4° (recrystallised from EtOH)

Analysis: Found: C, 21.7; H, 1.9; F, 41.8; N, 30.4%

$C_5H_4F_6N_6O$ requires: C, 21.6; H, 1.4; F, 41.0; N, 30.2%

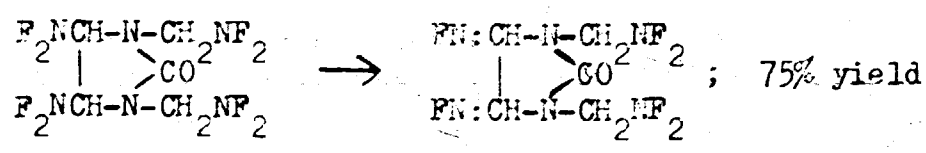
Infra-red absorptions at: 5.6(s), 6.2(s), 7.2(s), 7.7(m), 8.55(m), 9.7(m), 9.8(m), 10.0(m), 10.25(s), 10.8(s), 11.2(m), 11.8(m), 12.0(s), 12.2(s), 12.4(m), 12.9(m), 13.3(m)μ.

'HNMR Spectrum (MeCN solution): Triplet centred at 4.41τ (J=24 c/sec)

^{19}FNMR Spectrum (MeCN solution): Single peak at +31.4 δ (C:NF), triplet at -44.0 δ (J=24 c/sec) (CH_2NF_2)

Other Properties: ΔH_{f298} calc. -32.7 kcal/mole. Monopropellant S.I. 245 calc.

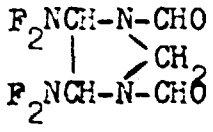
Preparation: Action of HCl in aqueous acetone on 4,5-bis-(difluoramino)-1,3-bis(difluoraminomethyl)imidazolidin-2-one



; 75% yield

Reference: I.C.I. Progress Report No.16, April 1 - June 30, 1964; No. 23, January 1 - March 31, 1966.

37. 4,5-Bis(difluoramino)-1,3-diformylimidazolidine

Structure: 

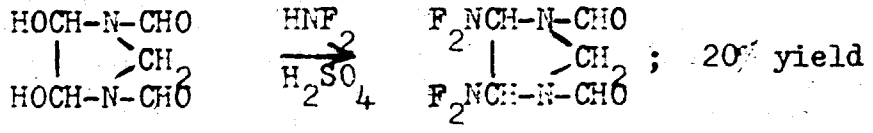
Physical State: White solid, m.p. 118°C

Analysis: Found: C, 25.5; H, 3.0; F, 31.5; N, 24.1%

$C_5H_6F_4N_4O_2$ requires: C, 26.1; H, 2.6; F, 33.0; N, 24.3%

Infra-red absorptions at: 3.4(s), 6.0(s), 6.9(s), 7.3(s), 7.5(m), 7.6(m), 7.9(m), 8.4(m), 10.9(m), 11.4(m), 12.0(m), 12.8(m), 13.1(m), 13.7(m), 14.1(m)μ.

Preparation: The action of HNF_2 and 96% H_2SO_4 on 1,3-diformyl-4,5-dihydroxyimidazolidine



; 20% yield

Reference: I.C.I. Progress Report No. 16, April 1 - June 30, 1964

Data Sheet

38. 4,5-bis(difluoramino)-1,3-bis(difluoraminomethyl)imidazolidin-2-one, (BDMBDI)

Structure: $F_2NCH-N-CH_2NF_2$ (CO) $F_2NCH-N-CH_2NF_2$

Physical State: Liquid

Analysis: Found: C, 18.9; H, 2.0; F, 47.3; N, 26.6%;
M(ebullioscopic in acetone), 324

$C_5H_6F_8N_6O$ requires: C, 18.9; H, 1.9; F, 47.8; N, 26.4; M, 318

Infra-red absorptions at: 3.3(w), 5.6(vs), 6.9(vs), 7.0(s), 7.3(s), 7.6(w), 8.0(s), 8.4(w), 9.3(w), 9.7(m), 10.0(m), 10.7(s), 11.4(s), 12.2(s), 13.3(w), 14.4(w), 16.4(w), 20.0(w)μ.

'HNMR Spectrum (CCl_4 solution): 15 peaks in the region 4.15 to 5.72 τ consisting of a triplet due to the magnetically equivalent hydrogen nuclei on the CH_2 groups, and a pair of sextuplets due to the magnetically non-equivalent ring CH-rings.

^{19}FNMR Spectrum (CCl_4 solution): Doublet centred at -30.5 δ J=18 c/sec. ($CHNF_2$). Triplet centred at -43.2 δ, J=21 c/sec (CH_2NF_2). Doublet:triplet in 1:1 ratio.

Impact Sensitivity: 5-10 cm

Explosion Point: >250°C (volatilisation occurred above 140°C)

68. (contd.)

Other h... ... $\Delta H_{f,g}$ ... kcal/mole. Monopropellant I.S. 240 sec. Vapour pressure measured:

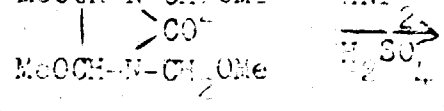
... 0.1 mm ... 0.3 mm

... 0.2 ... 0.5

... 1.5

Vacuum Thermal Stabilities at 60° alone or with HFVA, AP, Al showed a steady gas evolution rate of 0.9 ml/ /100 hr. Slightly swelled OIO and DLI/DI castin powders. DTA of sample in closed tube gave an exotherm leading to detonation, starting at 220°.

Preparation: The action of HNF_2 and 96% H_2SO_4 on 4,5-dimethoxy-1,3-di(methoxymethyl)imidazolidin-2-one.



, 90% yield

Reference: I.C.I. Progress Report No. 1., April 1 - June 30, 1964; No. [illegible], January 1 - March 31 [illegible], No. 21, July 1 - September [illegible], 196[illegible].

Data Sheet

39. 1,3-Bis(difluoraminomethyl)imidazolidin-2-one

Structure: $\overline{CH_2N(CH_2NF_2)CON(CH_2NF_2)CH_2}$

Physical State: Yellowish liquid

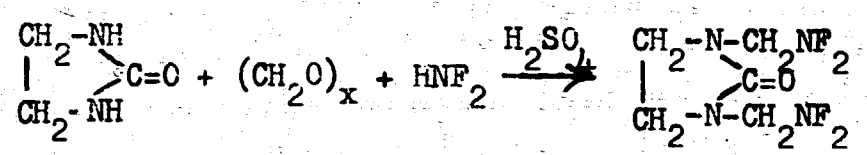
Analysis: Found: C, 28.2; H, 3.8; F, 32.8; N, 25.9%

$C_5H_8F_4N_4O$ requires: C, 27.8; H, 3.7; F, 35.2; N, 25.9%

Infra-red absorptions at: 3.0(w), 3.5(w), 5.85(s), 6.75(s), 7.0(s), 7.4(m), 7.9(s), 10.0(w), 10.4(w), 11.1(s), 12.35(s), 13.3(w)μ.

Other Properties: Vacuum Thermal Stability 0.3 ml/g/100 hr at 60°C

Preparation: The reaction of HNF_2 with a mixture of imidazolidin-2-one and paraformaldehyde in the presence of 96% H_2SO_4



approx. 50% yield

Reference: I.C.I. Progress Report No. 14, July 1, 1962 - December 31, 1963; No. 23, January 1 - March 31, 1966.

Data Sheet

40. Tetrakis(difluoraminomethyl)urea

Structure: $(F_2NCH_2)_2NCON(CH_2NF_2)_2$

Physical State: Colourless liquid

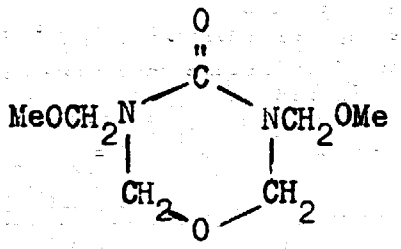
Analysis: Found: C, 18.5; H, 3.3; F, 48.1; N, 25.9%

$C_5H_8F_8N_6O$ requires: C, 18.7; H, 2.5; F, 47.5; N, 26.2%

Infra-red absorptions at: 2.9(w), 3.3(w), 5.8(s), 6.5(w), 6.8(m), 7.0(m), 7.1(m), 7.3(m), 7.7(m), 8.0(s), 8.3(m), 9.1(m), 9.6(m), 9.8(m), 10.4(m), 10.8(s), 12.1(s), 13.3(m)μ.

Other Properties: ΔH_{f298} calc. -114.8 kcal/mole. Monopropellant S.I. 265 calc.

Preparation: Action of excess HNF_2 under autogenous pressure in the presence of 96% H_2SO_4 on N,N'-bis(methoxymethyl)uron

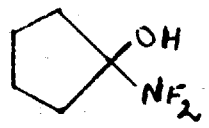


$\xrightarrow[H_2SO_4]{HNF_2}$ $(F_2NCH_2)_2NCON(CH_2NF_2)_2$; 36% yield

Reference: I.C.I. Progress Report No. 12, July 1, 1962 - June 30, 1963.

Data Sheet

41. 1-Difluoraminocyclopentan-1-ol

Structure: 

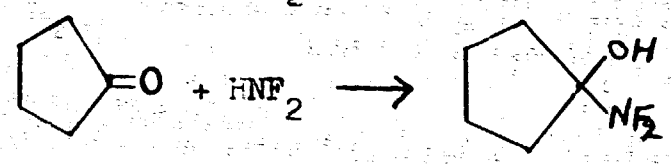
Physical State: White solid, m.p. 10°C

Analysis: Found: C, 41.7; H, 6.4; F, 24.8; N, 9.8%

$C_5H_9F_2NO$ requires: C, 43.8; H, 6.6; F, 27.7; N, 10.2%

Infra-red absorptions at: 2.9(s), 3.35(s), 3.45(m), 7.1(s), 7.5(s), 7.8(m), 8.2(m), 8.6(s), 9.1(m), 10.4(m), 10.6(m), 11.6(s)μ.

Preparation: Refluxing HNF_2 on cyclopentanone



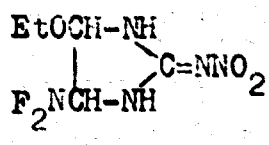
; Quantitative

Reference: I.C.I. Progress Report No. 6, October 1 - December 31, 1961

Data Sheet

42. 4-Difluoramino-5-ethoxy-2-nitriminoimidazolidine

Structure:



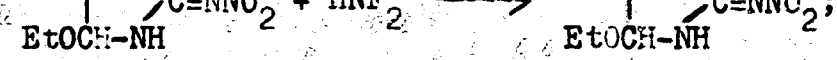
Physical State: White solid m.p. 173° (decomp.)

Analysis: Found: C, 26.1; H, 4.0; F, 17.0; N, 30.4; EtO, 20.1%

$C_5H_9F_2N_5O_3$ requires: C, 26.7; H, 4.0; F, 16.9; N, 31.1; EtO, 20.0%

Infra-red absorptions at: 2.95(s), 3.1(s), 6.3 (s), 6.5(s), 7.4(m), 7.6(m), 7.8(s), 8.1(s), 8.6(w), 9.0(s), 9.3(s), 9.8(w), 10.3(s), 11.5(m), 12.1(m), 12.3(m), 12.8(m), 13.3(w) μ.

Preparation: Action of HNF_2 and 80% H_2SO_4 on 4,5-diethoxy-2-nitriminoimidazolidine:



14% yield

Reference: I.C.I. Progress Report No. 23, January 1 - March 31, 1966.

Data Sheet

43. N,N'-Bis(difluoraminomethyl)-N-ethylurea

Structure: $F_2NCH_2NEtCONHCH_2NF_2$

Physical State: White, hygroscopic solid, m.p. 52-53°C

Analysis: Found: C, 28.1; H, 4.8; F, 31.9; N, 26.3%

$C_5H_{10}F_4N_4O$ requires: C, 27.5; H, 4.6; F, 34.9; N, 25.7%

Infra-red absorptions at: 2.95(s), 6.05(s), 6.55(s), 7.95(s), 9.1(m), 10.0(s), 11.0(s), 12.35(s), 13.0(m), 13.7(m)μ.

Preparation: The reaction of HNF_2 with a mixture of ethyl urea and paraformaldehyde in the presence of 96% H_2SO_4

$$EtNHCONH_2 + (CH_2O)_x + HNF_2 \xrightarrow{H_2SO_4} F_2NCHNEtCONHCH_2NF_2$$

81% yield

Reference: I.C.I. Progress Report No. 11, January 1 - March, 31, 1963.

Data Sheet

44. N,N'-Bis(1-difluoraminoethyl)urea

Structure: $MeCH(NF_2)NHCONHCH(NF_2)Me$

Physical State: White solid, m.p. 125° (dec.) (recrystallised from EtOH/ligroin)

Analysis: Found: C, 25.9; H, 5.0; F, 35.4; N, 26.3%

$C_5H_{10}F_4N_4O$ requires: C, 27.5; H, 4.6; F, 34.9; N, 25.7%

Infra-red absorptions at: 3.0(s), 6.1(s), 6.5(s), 7.7(w), 8.0(m), 8.6(m), 8.9(w), 9.3(w), 10.2(m), 11.8(s)μ.

Preparation: Reaction of urea with paraldehyde, HNF_2 and 96% H_2SO_4

$$NH_2CONH_2 + (MeCHO)_x + HNF_2 \xrightarrow{H_2SO_4} MeCH(NF_2)NHCONHCH(NF_2)Me$$

19% yield

Reference: I.C.I. Progress Report No. 15, January 1 - March 31, 1964.

Data Sheet

45. 1,2-Bis(difluoramino)-1,2-dioxamidoethane

Structure: $(F_2NCHNHCOCOOH)_2$

Physical State: White solid, m.p. 160° (dec.)

Analysis: Found: C, 23.6; H, 2.2; F, 22.7, N, 17.4%

$C_6H_6F_4N_4O_6$ requires: C, 23.5; H, 2.0; F, 24.8; N, 18.3%

Infra-red absorptions at: 2.95(s), 3.0(s), 5.7(s), 5.9(s), 6.5(s), 7.65(m), 8.0(s), 9.0(w), 9.8(w), 10.75(m), 11.55(m), 12.2(w), 13.3(m), 13.8(m)μ.

Preparation: Reaction of 1,2-di(sodio-oxamido)ethane-1,2-diol with HNF_2 and H_2SO_4

$$\begin{matrix} HOCHNHCOCOONa \\ | \\ HOCHNHCOCOONa \end{matrix} + HNF_2 \xrightarrow{H_2SO_4} \begin{matrix} F_2NCHNHCOCOOH \\ | \\ F_2NCHNHCOCOOH \end{matrix} \quad ; \quad 56\% \text{ yield}$$

Reference: I.C.I. Progress Report No. 19, January 1 - March, 31, 1965.

Data Sheet

46. 1,2-Bis(difluoramino)-1,2-bis(trifluoracetamido)ethane

Structure: $(F_2NCHNHCOCF_3)_2$

Physical State: White solid, m.p. 183-6°

Analysis: Found: C, 20.1; H, 1.3; F, 53.9; N, 15.5%;
M(ebullioscopic in acetone), 356

$C_6H_4F_{10}N_4O_2$ requires: C, 20.3; H, 1.1; F, 53.7; N, 15.8%; M, 354.

Infra-red absorptions at: 3.05(s), 5.9(s), 6.55(m), 8.1(m), 8.3(s), 8.55(s), 11.1(m), 11.95(m), 13.3(m), 13.8-14.0(m)μ.

Preparation: Reaction of 1,2-bis(trifluoracetamido)ethane-1,2-diol with HNF_2 and H_2SO_4

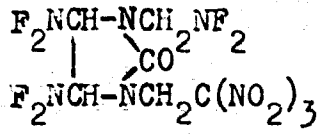
$$\begin{matrix} HOCHNHCOCF_3 \\ | \\ HOCHNHCOCF_3 \end{matrix} + HNF_2 \xrightarrow{H_2SO_4} \begin{matrix} F_2NCHNHCOCF_3 \\ | \\ F_2NCHNHCOCF_3 \end{matrix} ; \quad 72\% \text{ yield}$$

Reference: I.C.I. Progress Report No. 20, April 1 - June 30, 1965

Data Sheet

47. 4,5-Bis(difluoramino)-1-difluoraminomethyl-3-(2,2,2-trinitroethyl)-imidazolidin-2-one (BDTI)

Structure:



Physical State: Crystalline solid, m.p. 86-87° (recrystallised from CCl_4)

Analysis: Found: C, 17.5; H, 1.4; F, 27.1; N, 26.9%

$C_6H_6F_6N_8O_7$ requires: C, 17.3; H, 1.4; F, 27.4; N, 26.9%

Infra-red absorptions at: 5.6(s), 6.2-6.3(s), 6.9-7.1(s), 7.7(s), 8.1(s), 9.4(m), 9.8(m), 9.95(m), 10.1(m), 10.8(s), 11.4(s), 11.6(s), 11.75(s), 12.2-12.3(s), 12.85(s), 13.0(s)μ.

'H.MR Spectrum ($CDCl_3$ solution): 16 peaks in the region 4.03 to 5.68 τ consisting of a singlet due to the hydrogen nuclei of the $CH_2C(NO_2)_3$ group, a triplet due to the hydrogen nuclei of the CH_2NF_2 group, and a pair of sextuplets due to the magnetically non-equivalent ring CH-rings.

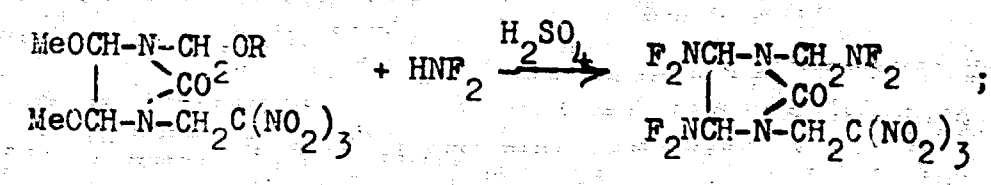
^{19}FNMR Spectrum ($CDCl_3$ solution): A triplet centred at -28.8 δ, J=21 c/sec; a doublet centred at -31.0δ, J=12 c/sec; a triplet centred at -43.6δ, J=2[illegible] c/sec; three groups in ratio 1:1:1, assigned to NF_2 groups on positions 5, 4 and 1 respectively.

47. (contd.)

Impact Sensitivity: 5-10 cm

Other Properties: ΔH_{f298} calc. -150.0 kcal/mole. Monopropellant S.I. 263 calc. Vacuum Thermal Stability 0.3 ml/g/100 hr at 60°

Preparation: Action of HNF_2 and 96% H_2SO_4 on 4,5-dimethoxy-1-methoxymethyl-3-(2,2,2-trinitroethyl)imidazolidin-2-one:



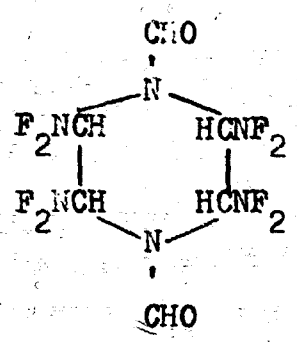
R=H, 74% yield
R=Me, 32% yield

Reference: I.C.I. Progress Reports No. 20, April 1 - June 30, 1965; No. 21, July 1 - September 30, 1965; No. 23, January 1 - March 31, 1966.

Data Sheet

48. 2,3,5,6-Tetrakis(difluoramino)-1,4-diformylpiperazine

Structure:



Physical State: White solid, m.p. 171-2°C, purified by dissolving in acetone and reprecipitating with water.

Analysis: Found: C, 21.5; H, 1.8; F, 43.3; N, 23.4%; M(ebullioscopic in acetone), 342

$C_6H_6F_8N_6O_2$ requires: C, 20.8; H, 1.7; F, 43.9; N, 24.3%; M, 346

Infra-red absorptions at: 3.3(s), 5.75(s), 6.9(m), 7.0(m), 7.5(m), 7.8(m), 8.1(s), 9.8(s), 10.3(w), 11.2(s), 12.0(w), 13.6(w), 14.75(m)μ.

'HNMR Spectrum (Acetone solution): Singlet at 1.09 τ (CHO); Triplet at 3.68 τ, J=23 c/sec (ring CH). Each peak split into doublet, J= 4 c/sec.

^{19}FNMR Spectrum (Acetone solution): Complex spectrum between -40.9 δ and -36.3 δ

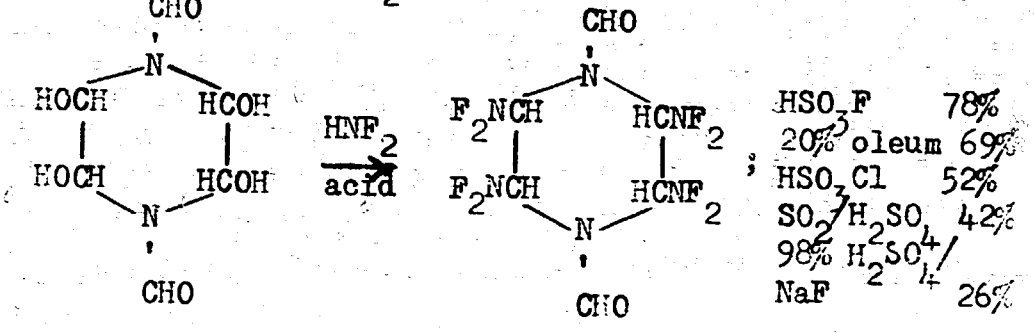
Impact Sensitivity: 5-10 cm

Explosion Point: 202°C

48. (contd.)

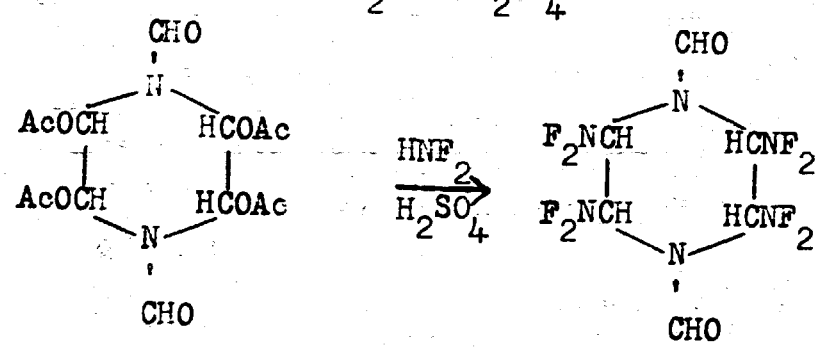
Other Properties: ΔH_{f298} calc. -71.2 kcal/mole. Monopropellant S.I. 260 calc. Decomposed by refluxing with EtOH, alone or with HCl, also by reaction with NH_3. Unchanged by HNO_3 in CF_3COOH. Unidentified products from attempted reduction with $NaBH_4$ in H_2O, and from action of $HClO_4$. Cyanogen bromide did not react. Vacuum Thermal Stability Test, 0.5 ml/g/100 hr.

Preparation: (i) Reaction of 1,4-diformyl-2,3,5,6-tetrahydroxy-piperazine with HNF_2 and conc. acid:



; HSO_3F 78%
20% oleum 69%
HSO_3Cl 52%
SO_2/H_2SO_4 42%
98% H_2SO_4/NaF 26%

(ii) Reaction of 1,4-diformyl-2,3,5,6-tetraaceto-piperazine with HNF_2 and H_2SO_4



79% yield

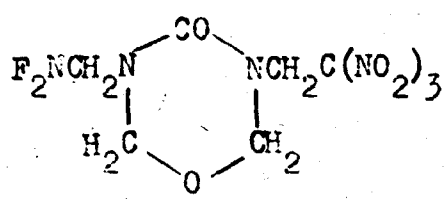
48. (contd.)

Reference: I.C.I. Progress Report No. 16, April 1 - June 30, 1964; No. 17, July 1 - September 30, 1964; No. 18, January 1 - December 31, 1964; No. 19, January 1 - March 31, 1965; No. 20; April 1 - June 30, 1965.

Data Sheet

49. N-Difluoraminomethyl-N'-(2,2,2-trinitroethyl)uron

Structure:



Physical State: White solid, m.p. 83-85° (recrystallised from i-PrOH)

Analysis: Found: C, 22.2; H, 2.1; F, 9.7; N, 24.5%

$C_6H_8F_2N_6O_8$ requires: C, 21.8; H, 2.4; F, 11.5; N, 25.4%

Infra-red absorptions at: 6.0(s), 6.3(s), 6.7(s), 7.3(w), 7.55(m), 7.7(m), 8.3(w), 9.0(w), 9.65(w), 9.8(w), 10.0(w), 10.15(w), 11.1(m), 11.6(m), 12.4(m), 12.6(m), 13.0(w), 13.4(m)μ.

'HNMR (MeCN solution): Triplet at 5.08τ ($J_{CH_2-NF_2}$ =24 c/sec), peak at 5.01τ (uron ring CH_2) and peak at 4.88τ $\left[CH_2C(NO_2)_3\right]$, in ratio 1:2:1

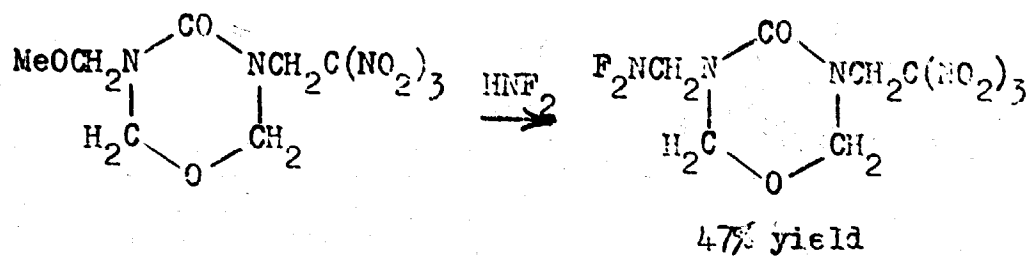
^{19}FNMR (MeCN solution): Triplet at -44.5 δ ($J_{NF_2-CH_2}$ = 24 c/sec)

Explosion Point: 153°

Other Properties: Vacuum Thermal Stability 4.7 ml/g/100 hr at 60°C

Preparation: Action of HNF_2 and 96% H_2SO_4 on N-methoxymethyl-N'-(2,2,2-trinitroethyl)uron at -23°

49. (contd.)



47% yield

Reference: I.C.I. Progress Report No. 25, January 1 - March, 31, 1966.

Data Sheet

50. Tris(difluoraminomethyl)trinitroethylurea

Structure: $(F_2NCH_2)_2NCON(CH_2NF_2)CH_2C(NO_2)_3$

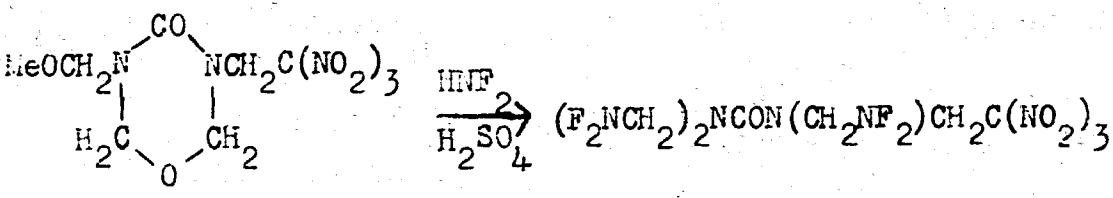
Physical State: Colourless viscous liquid

Analysis: Found: C, 16.7; H, 2.1; F, 24.0; N, 26.3%

$C_6H_8F_6N_8O_7$ requires: C, 17.2; H, 1.9; F, 27.3; N, 26.8%

Infra-red absorptions at: 3.4(.), 3.5(m). 5.8(s), 6.2-6.4(s), 6.9(s), 7.1-7.5(s), 8.1(s), 8.45(m), 9.2(s), 9.6-10.0(s), 10.6(s), 10.75-11.0(s), 11.5(s), 11.75(m), 12.-12.5(m), 13.75(w)μ.

Preparation: Action of HNF_2 and 96% H_2SO_4 under autogenous pressure at room temperature on N-methoxymethyl-N'-(2,2,2-trinitroethyl)uron



Reference: I.C.I. Progress Report No. 23, January 1 - March 31, 1966.

Data Sheet

51. 1,1,4,4-Tetrakis(difluoramino)cyclohexane (TDC)

Structure: 

Physical State: White solid, m.p. 107-108°C

Analysis: Found: C, 24.8; H, 2.8; F, 52.8; N, 19.8%

Calc. for $C_6H_8F_8N_4$: C, 25.0, H, 2.8; F, 52.8; N, 19.5%

Infra-red absorptions at: 3.4(s), 6.8(s), 7.2(m), 9.7(m), 9.9(m), 10.2(s), 10.9(s), 11.1(s), 11.4(s)μ.

'HNMR Spectrum ($CDCl_3$ solution): Single peak at 7.61 τ

^{19}FNMR Spectrum ($CDCl_3$ solution): Single peak at -27.4 δ

Impact Sensitivity: 5-10 cm

Explosion Point: Decomposes without explosion at 266°C

Other Properties: Vapour pressure:-

15°C	7.3 mm Hg	45°C	9.0 mm Hg
25	7.8	55	9.8
35	8.3	65	11.2

Heat of vaporisation: 2 kcal/mole

Density: 1.7 g/c.c.

U.V. absorption: λ_{max} = 210 mμ

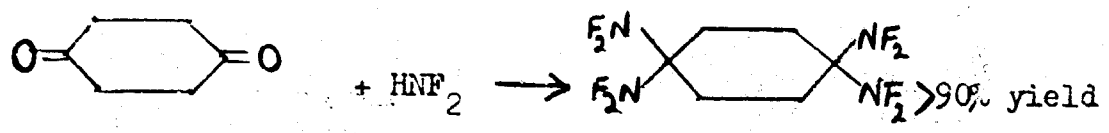
Very soluble in nitroglycerine

Attemtps to brominate, chlorinate and oxidise TDC were unsuccessful. TDC was resistant to alkali.

ΔH_{f298} calc. -55.4 kcal/mole

51. (contd.)

Preparation: Reaction of cyclohexane-1,4-dione with HNF_2 in the presence of 96% H_2SO_4, HSO_3F or HSO_3Cl

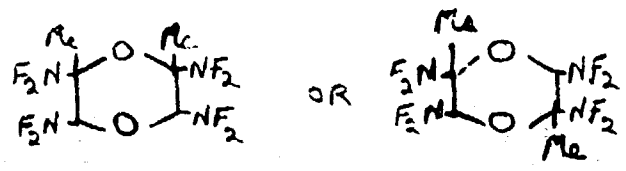


References: Rohm and Haas, QPR P-61-6, January - March, 1961

I.C.I. Progress Report No. 4, April - June, 1961

Data Sheet

52. 2,3,5,6-Tetrakis(difluoramino)-2,5,6-dimethyldioxan

Structure: 

Physical State: Pale yellow liquid

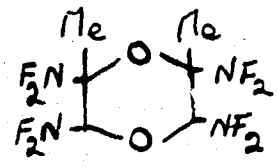
Analysis: Found: C, 23.1; H, 2.5; F, 46.3; N, 17.5;
M(Gas Density balance), 307

$C_6H_8F_8N_4O_2$ requires: C, 22.5; H, 2.5; F, 47.5; N, 17.5%. M, 320

Infra-red absorptions at: 3.4(w), 6.9(w), 7.2(m), 8.1(m), 8.4(s), 8.8(s), 9.2(m), 9.8(m), 10.1(s), 10.6(s), 11.3(s), 11.7(m)μ.

Impact Sensitivity: 5-10 cm

Preparation: Reaction of HNF_2 with monomethyl glyoxal in the presence of HSO_3F



or isomers. 25% yield

Reference: I.C.I. Progress Report No. 13, July 1, 1963 - September 30, 1963.

Data Sheet

53. 1,4-Bis(difluoramino)cyclohexane-1,4-diol

Structure: 

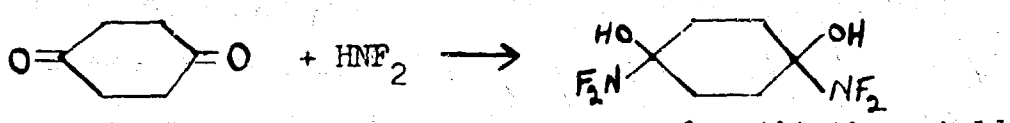
Physical State: White solid, m.p. 145°C

Analysis: Found: C, 33.5; H, 4.3; F, 35.7; N, 13.0%

$C_6H_{10}F_4N_2O_2$ requires: C, 33.0; H, 4.6; F, 34.9; N, 12.9%

Infra-red absorptions at: 2.9(s), 7.1(m), 7.8(s), 8.2(m), 8.7(w), 8.95(w), 9.3(s), 9.7(s), 10.1(m), 10.3(w), 10.5(s), 11.3(s), 11.8(s), 12.5(m)μ.

Preparation: Refluxing HNF_2 over cyclohexane-1,4-dione



Quantitative yield

Reference: I.C.I. Progress Report No. 5, July 1 - September 30, 1961

Data Sheet

54. 1,2-Diacetamido-1,2-bis(difluoramino)ethane

Structure: $(F_2NCHNHAc)_2$

Physical State: White solid, m.p. 194°C

Analysis: Found: C, 28.5; H, 4.2; F, 29.1; N, 21.8%

$C_6H_{10}F_4N_4O_2$ requires: C, 29.3; H, 4.1; F, 30.9; N, 22.8%

Infra-red absorptions at: 3.0(s), 3.4(s), 6.0(s), 6.5(s), 6.9(s), 7.3(s), 7.8(s), 8.6(m), 8.7(m), 9.7(m), 10.3(m), 11.2(m), 11.5(s), 12.1(m), 13.3(s), 13.9(m)μ.

Preparation: Reaction of HNF_2 with 1,2-diacetamidoethane-1,2-diol in the presence of 96% H_2SO_4

$$\begin{matrix} HOCHNHAc \\ | \\ HOCHNHAc \end{matrix} + HNF_2 \xrightarrow{H_2SO_4} \begin{matrix} F_2NCHNHAc \\ | \\ F_2NCHNHAc \end{matrix} \quad ; \quad 10\% \text{ yield}$$

Reference: I.C.I. Progress Report No. 15, January 1 - March 31, 1964; No. 16, April 1 - June 30, 1964.

Data Sheet

55. 1,2-Di(carbomethoxyamino)-1,2-bis(difluoramino)ethane

Structure: $(F_2NCHNHCOOMe)_2$

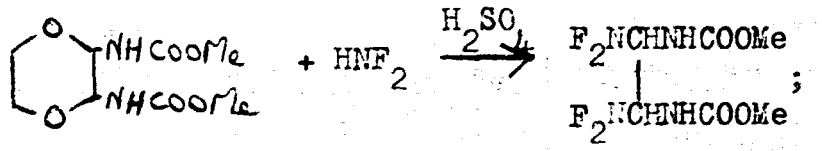
Physical State: White solid, m.p. 222-4° (dec.) (recrystallised from ethanol/ligroin)

Analysis: Found: C, 26.4; H, 3.5; F, 27.7; N, 20.2; OCH_3, 22.8%

$C_6H_{10}F_4N_4O_4$ requires: C, 25.9; H, 3.6; F, 27.4; N, 20.2; OCH_3, 22.3%

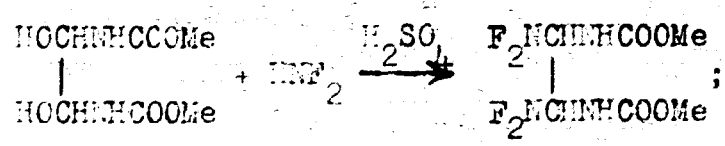
Infra-red absorptions at: 2.95(s), 5.9(s), 6.6(s), 6.9(m), 7.55(s), 7.8(s), 8.2(m), 8.5(w), 9.4(m), 9.65(m), 9.85(w), 10.5(w), 11.1(m), 11.65(s), 12.1(m), 12.8(s), 13.5(m)μ.

Preparation: (i) Action of HNF_2 and 96% H_2SO_4 on 2,3-di-(carbomethoxyamino)-1,4-dioxan:



; 67% yield

(ii) Action of HNF_2 and 96% H_2SO_4 on 1,2-di-(carbomethoxyamino)ethane-1,2-diol:



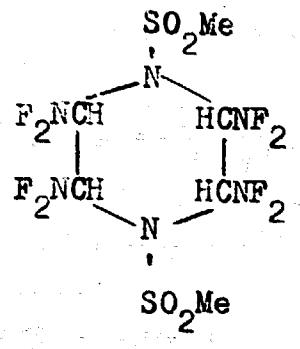
; 92% yield

Reference: I.C.I. Progress Report No. 19, January 1 - March 31, 1959.

Data Sheet

56. 2,3,5,6-Tetrakis(difluoramino)-1,4-di(methanesulphonyl)piperazine

Structure:



Physical State: m.p. 235-240°C (decomp.), recrystallised from acetonitrile

Analysis: Found: C, 16.0; H, 2.7; F, 35.4; N, 18.5; S, 15.2%

$C_6H_{10}F_8N_6O_4S_2$ requires: C, 16.1; H, 2.2; F, 34.1; N, 18.8; S, 14.4%

Infra-red absorptions at: 7.1(m), 7.3(s), 7.6(m), 7.7(s), 8.1(s), 8.6(s), 9.2(s), 9.9(m), 10.2(s), 10.3(s), 10.4(s), 11.0(s), 11.3(s), 11.6(s), 13.1(s), 14.85(s)μ.

'HNMR (Acetone solution): Triplet centred at 3.95 τ, J=21 c/sec (ring CH)

^{19}FNMR (Acetone solution): Pair of doublets at -41.3 δ (J=12 c/sec.) and -38.7 δ (J=12 c/sec)

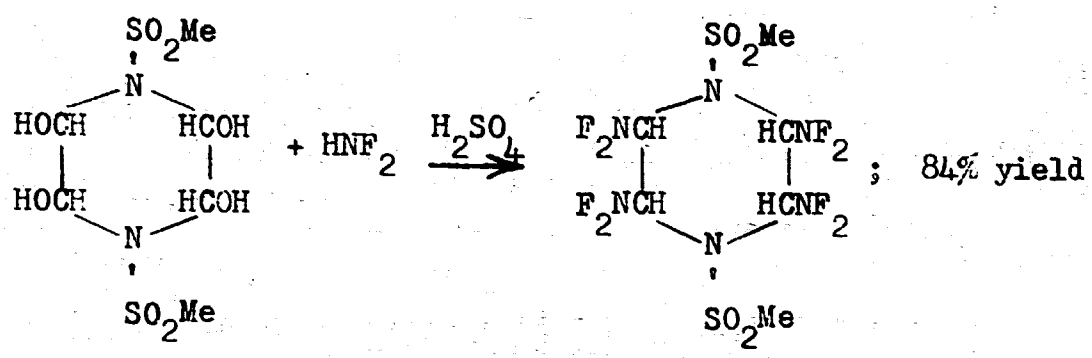
Impact Sensitivity: 20-40 cm

Explosion Point: >250°C

56. (contd.)

Other Properties: Unchanged by $HNO_3/(CF_3CO)_2O$, Raney nickel, $NaBH_4/H_2O$, or cyanogen bromide

Preparation: Action of HNF_2 and H_2SO_4 on 2,3,5,6-tetrahydroxy-1,4-di(methanesulphonyl)piperazine.



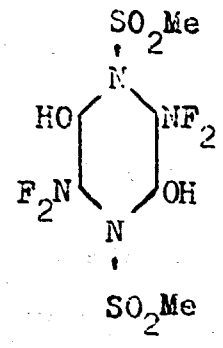
; 84% yield

Reference: I.C.I. Progress Report No. 18, January 1 - December 31, 1964; No. 19, January 1 - March 31, 1965.

Data Sheet

57. 2,5-Bis(difluoramino)-3,6-dihydroxy-1,4-di(methanesulphonyl)-piperazine

Structure:



Physical State: Crystalline solid, m.p. 188° (decomp.)

(recrystallised from MeCN, EtOH)

Analysis: Found: C, 19.8; H, 3.5; F, 21.6; N, 14.2; S, 18.1%

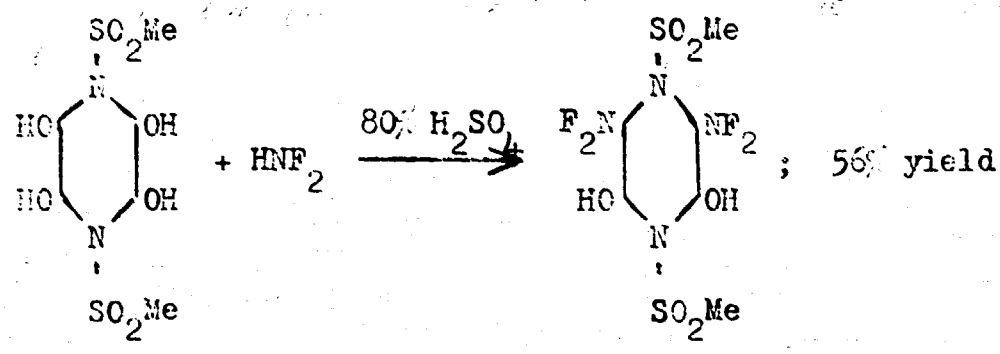
$C_6H_{12}F_4N_4O_6S_2$ requires: C, 19.2; H, 3.2; F, 20.2; N, 14.9; S, 17.0%

Infra-red absorptions at: 2.85(s), 6.9(s), 7.1(m), 7.45(s), 7.55(s), 7.9(s), 8.4(s), 8.7(s), 9.1(s), 9.3(s), 10.2(m), 10.35(s), 10.85(s), 11.45(s), 12.9(s)μ.

Other Properties: Forms adduct with dioxan. Converted to diacetate, m.p. 210-220° (decomp.) and to tetrakis-(difluoramino) derivative.

Preparation: Treatment of 2,3,5,6-tetrahydroxy-1,4-di(methane-sulphonyl)piperazine with HNF_2 and 80% H_2SO_4

57. (contd.)



; 56% yield

Reference: I.C.I. Progress Reports No. 20, April 1 - June 30, 19..5; No. 21, July 1 - September 30, 1965.

Data Sheet

58. 2-Difluoramino-1,1-diethoxypropan-2-ol

Structure: $(EtO)_2CHC(OH)NF_2Me$

Physical State: Colourless liquid

Analysis: Found: F, 20.5; N, 7.7:

$C_7H_{15}F_2NO_3$ requires: F, 19.1; N, 7.0%

Infra-red absorptions at: 2.9(m), 3.4(m), 5.9(m), 7.2(m), 8.0(s), 9.0-10.0(s), 11.5(m), 12.4(s)μ.

Preparation: Action of HNF_2 on 1,1-diethoxy acetone

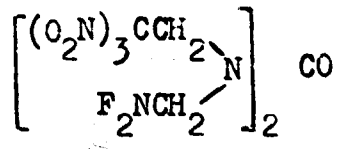
$$(EtO)_2CHCOMe + HNF_2 \longrightarrow (EtO)_2CHC(OH)NF_2Me$$

Quantitative

Reference: I.C.I. Progress Report No. 11, January 1 - March 31, 1963.

Data Sheet

59. N,N'-Bis(difluoraminomethyl)-bis(2,2,2-trinitroethyl)urea

Structure: 

Physical State: White solid, m.p. 108-9° (recrystallised from aqueous EtOH).

Analysis: Found: C, 17.0; H, 2.6; F, 14.5; N, 26.5%

$C_7H_8F_4N_{10}O_{13}$ requires: C, 16.3; H, 1.6; F, 14.7; N, 27.1%

Infra-red absorptions at: 5.9(s), 6.3(s), 7.15(s), 7.6(s), 7.8(s), 8.2(s), 9.25(s), 9.9(m), 10.9(m), 11.6(s), 11.8(m), 12.2(s), 12.5(m), 12.7(s), 13.9(s)μ.

'HNMR Spectrum (Acetone solution): Deuteration showed that no NH or OH were present. Triplet centred at 4.70 τ (J=23 c/sec) due to CH_2NF_2 groups, also three peaks at 4.84, 4.62, and 4.35 τ indicating some steric hindrance of the $CH_2C(NO_2)_3$ groups.

^{19}FNMR Spectrum (Acetone solution): Triplet centred at 45.2 δ, J=23 c/sec, consistent with N-CH_2NF_2 group.

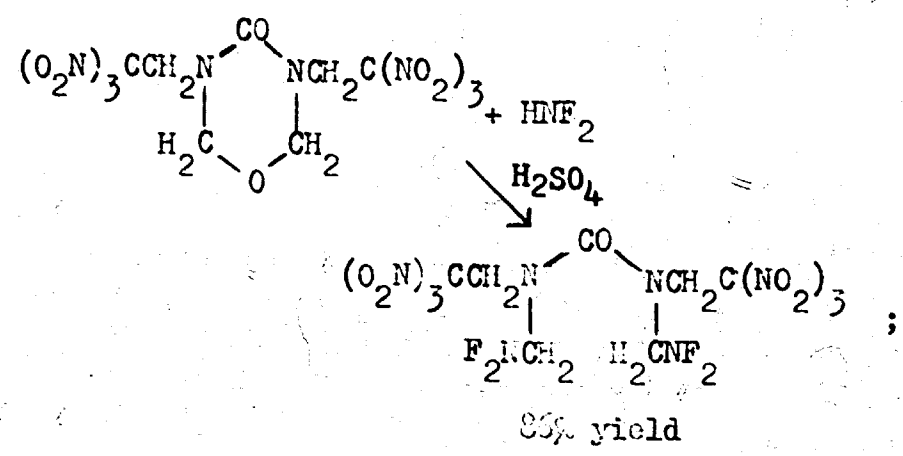
Other Properties: ΔH_{f298} calc. -111.5 kcal/mole. Monopropellant S.I. 269 calc. Vacuum Thermal Stability test, 0.5 ml/g/100 hr at 60°C.

Impact Sensitivity: 5-10 cm

Explosion Point: 169°C.

59. (contd.)

Preparation: Reaction of N,N'-bis(2,2,2-trinitroethyl)uron with HNF_2 and 96% H_2SO_4:



88% yield

Reference: I.C.I. Progress Report No. 22, October 1 - December 31, 1965; No. 23, January 1 - March 31, 1966.

Data Sheet

60. 1,2-Bis(difluoramino)-1,2-dipropiolamidoethane

Structure: $(F_2NCHNHCOC{\equiv}CH)_2$

Physical State: White solid, decomp. 160° without melting (recrystallised from iPrOH/H_2O)

Analysis: Found: C, 37.2; H, 2.8; F, 2[illegible].9; N, 21.0%

$C_8H_6F_4N_4O_2$ requires: C, 36.1; H, 2.3; F, 28.6; N, 21.1%

Infra-red absorptions at: 3.1(s), 4.7(s), 6.0(s), 6.5(s), 7.5(w), 7.8(s), 8.1(w), 8.9(w), 9.8(w), 10.45(w), 11.45(s), 13.2(s) μ.

Preparation: The action of HNF_2 and 98% H_2SO_4 on 1,2-dipropiolamidoethane-1,2-diol.

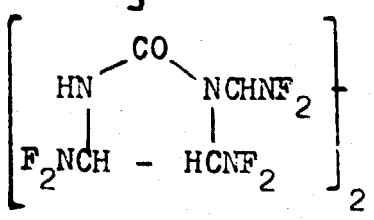
$$\begin{array}{l} HOCHNHCOC{\equiv}CH \\ | \\ HOCHNHCOC{\equiv}CH \end{array} + HNF_2 \xrightarrow{H_2SO_4} \begin{array}{l} F_2NCHNHCOC{\equiv}CH \\ | \\ F_2NCHNHCOC{\equiv}CH \end{array} \quad ; \quad 37\% \text{ yield}$$

Reference: I.C.I. Progress Report No. 24, April 1 - June 30, 1966.

Data Sheet

61. 1,2-Bis(difluoramino)-1,2-bis[4,5-bis(difluoramino)-2-oxoimidazolidin-1-yl]ethane

Structure:



Physical State: White solid, m.p. 180° approx. (decomp.)

Analysis: Found: C, 18.8; H, 2.3; F, 45.2; N, 26.3% in one case only. A more typical result is:

C. 21.5; H, 2.1; F, 38.0; N, 28.0%

$C_8H_8F_{12}N_{10}O_2$ requires: C, 19.1; H, 1.6; F, 45.2; N, 27.8%

Infra-red absorptions at: 3.1(s), 3.2(s), 5.7(s), 8.0(s), 8.6(s), 9.2(m), 9.8(s), 10.6(s), 10.9(s), 11.45(s), 12.3(s), 12.9(s), 13.4(m)μ.

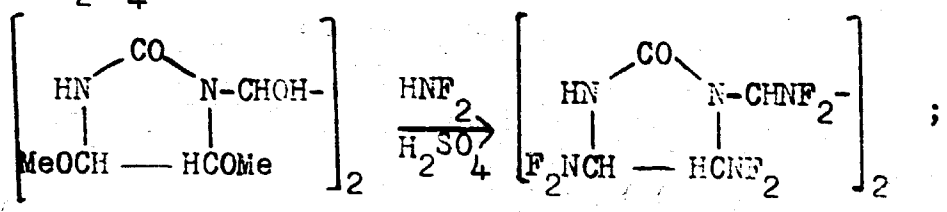
Impact Sensitivity: 5-10 cm

Explosion Point: 163-166°

Other Properties: ΔH_{f298} calc. -301.2 kcal/mole. Monopropellant S.I. 225 calc. Initially thought to be 2,3,5,6-tetrakis(difluoramino)-1,4-endoketopiperazine Vacuum Thermal Stability test at 60° gave steady gas evolution rate of 0.3 ml/g/100 hr.

61. (contd.)

Preparation: The reaction of the 2:1 adduct of 4,5-dimethoxy-imidazolidin-2-one with glyoxal with HNF_2 and H_2SO_4.



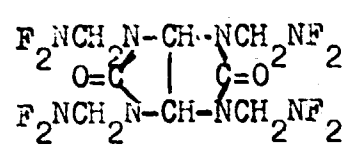
;

70% yield

Reference: I.C.I. Progress Reports No. 17, July 1 - September 30, 1964; No. 18, January 1 - December 31, 1964; No. 19, January 1 - March 31, 1965; No. 20, April 1 - June 30, 1965; No. 23, January 1 - March 31, 1966.

Data Sheet

62. Tetrakis(difluoraminomethyl)glycoluril

Structure: 

Physical State: White solid, m.p. 155°C

Analysis: Found: C, 24.1; H, 3.0; F, 36.9; N, 28.1%

$C_8H_{10}F_8N_8O_2$ requires: C, 23.9; H, 2.5; F, 37.8; N, 27.9%

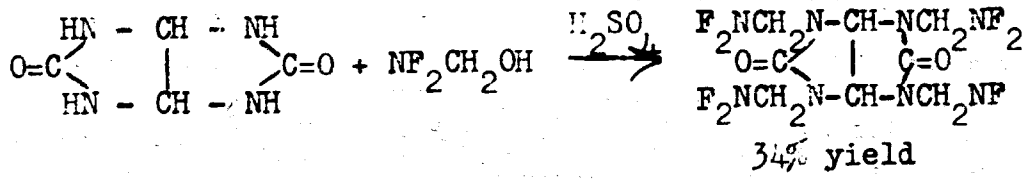
Infra-red absorptions at: 5.8(s), 7.7(m), 8.0(m), 8.4(m), 10.0(m), 10.8(m), 12.3(s), 14.6(s) μ.

Impact Sensitivity: 10-20 cm

Explosion Point: 234°C

Other Properties: ΔH_{f298} calc. -20.0 kcal/mole. Recovered unchanged from reaction with 98% HNO_3 at room temperature.

Preparation: The reaction of glycoluril with difluoraminomethanol and 96% H_2SO_4



34% yield

Reference: I.C.I. Progress Report No. 15, January 1 - March 31, 1964; No. 16, April 1 - June 30, 1964.

Data Sheet

63. 1,2-Bis(difluoramino)-1,2-(2-difluoraminopropionamido)ethane

Structure: $(F_2NCHNHCOCH_2CH_2NF_2)_2$

Physical State: Solid, m.p. 185° (decomp.) (recrystallised from $iPrOH/CCl_4$)

Analysis: Found: C, 26.3; H, 3.4; F, 40.6; N, 22.5%

$C_8H_{12}F_8N_6O_2$ requires: C, 25.6; H, 3.2; F, 40.4; N, 22.3%

Infra-red absorptions at: 3.0(s), 3.25(m), 6.05(s), 6.5(s), 7.55(m), 7.95(m), 8.05(m), 8.4(m), 8.8(w), 9.8(m), 10.3(w), 10.5(m), 11.0(s), 11.6(s), 12.0(s), 12.5(m), 12.7(m), 13.6(s)μ.

Preparation: Reaction of 1,2-diacrylamidoethane-1,2-diol or its methyl ether with HNF_2 and 96% H_2SO_4 for 8 hrs:

$$\begin{matrix} ROCHNHCOCH{:}CH_2 \\ | \\ ROCHNHCOCH{:}CH_2 \end{matrix} + HNF_2 \xrightarrow{H_2SO_4} \begin{matrix} F_2NCHNHCOCH_2CH_2NF_2 \\ | \\ F_2NCHNHCOCH_2CH_2NF_2 \end{matrix} ;$$

R=H, 54% yield
R=Me, 36% yield

Reference: I.C.I. Progress Report No. 21, July 1 - September 30, 1965.

Data Sheet

64. 1,2-Di(carbethoxyamino)-1,2-bis(difluoramino)ethane

Structure: $(F_2NCHNHCOOEt)_2$

Physical State: White solid, m.p. 200-205°C

Analysis: Found: C, 31.9; H, 4.5; F, 24.0; N, 18.3%

$C_8H_{14}F_4N_4O_4$ requires: C, 31.4; H, 4.6; F, 24.9; N, 18.3%

Infra-red absorptions at: 3.0(s), 5.9(s), 6.5(s), 7.3(m), 7.6(s), 7.8(s), 8.1(m), 9.3(m), 9.5(m), 11.5(s), 12.05(m), 12.75(m), 13.4(m), 15.4(m)μ.

^{1}HNMR Spectrum (Acetone solution): Quadruplet centred at 5.83 τ, J=7.2 c/sec (CH_2). Broad doublet at 2.17, 2.30 τ, J=7.8 c/sec (NH). Complex multiplet at 3.8-4.8 τ (CH)

^{19}FNMR Spectrum (Acetone solution); Doublet at -26.9 δ, J=27 c/sec; singlet at -31.0 δ; doublet at -35.2 δ, J=12 c/sec

Other Properties: Did not give an N-NO_2 derivative on nitration.

Preparation: Reaction of HNF_2 with 1,2-di(carbethoxyamino)ethane-1,2-diol in the presence of 96% H_2SO_4.

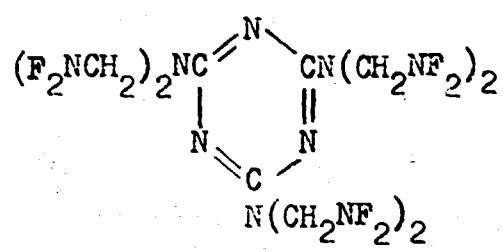
$$\begin{array}{l} HOCHNHCOOEt \\ | \\ HOCHNHCOOEt \end{array} + HNF_2 \xrightarrow{H_2SO_4} \begin{array}{l} F_2NCHNHCOOEt \\ | \\ F_2NCHNHCOOEt \end{array} ; \quad 75\% \text{ yield}$$

Reference: I.C.I. Progress Report No. 15, January 1 - March 31, 1964; No. 16, April 1 - June 30, 1964.

Data Sheet

65. Hexakis(difluoraminomethyl)melamine

Structure:



Physical State: White solid, m.p. 138-140° (recrystallised from hot CCl_4)

Analysis: Found: C, 22.2; H, 3.3; F, 39.5; N, 33.3%; M(ebullioscopic in acetone), 707

$C_9H_{12}F_{12}N_{12}$ requires: C, 21.0; H, 2.3; F, 44.2; N, 32.6%; M, 516

Infra-red absorptions at: 6.4(s), 7.8(m), 8.2(m), 9.4(m), 9.8(s), 11.0(m), 11.2(m), 12.4(m), 13.9(m)μ.

'HNMR (Acetone solution): Triplet centred at 4.4 τ, J=24 c/sec.

^{19}FNMR (Acetone solution): Triplet centred at -45.6 τ, J=24 c/sec.

Impact Sensitivity: 5-10 cm

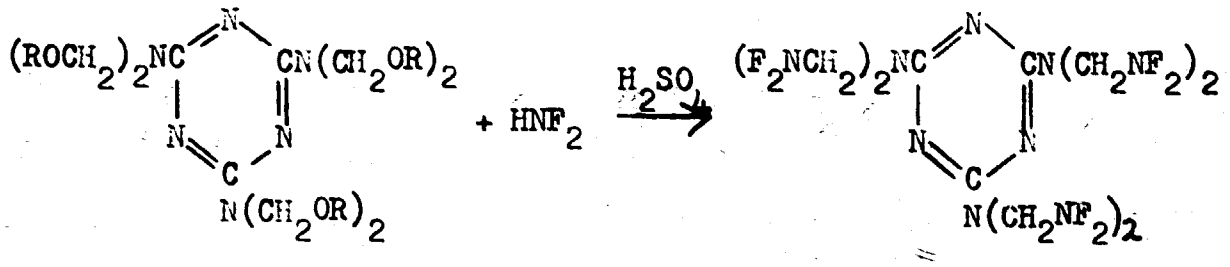
Explosion Point: >260°

Other Properties: ΔH_{f298} -47.9 kcal/mole (calc.). Monopropellant S.I. 25 calc.

Preparation: Reaction of HNF_2 with crude hexa(methoxymethyl)-melamine or with hexamethylol melamine, in the

65. (contd.)

presence of 96% H_2SO_4.



R=Me, "Low yield"

R=H, 80-90% yield

Reference: I.C.I. Progress Report No. 12, July 1, 1962 - June 30, 1963; No. 17, July 1 - September 30, 1964.

Data Sheet

66. Di[carbethoxy(difluoraminomethyl)amino]methane

Structure: $CH_2[N(CH_2NF_2)COOEt]_2$

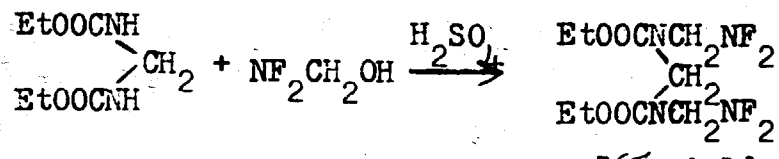
Physical State: Liquid (98% pure by GLC)

Analysis: Found: C, 32.2; H, 5.4; F, 23.2; N, 16.9%

$C_9H_{16}F_4N_4O_4$ requires: C, 33.8; H, 5.0; F, 23.7; N, 17.5%

Infra-red absorptions at: 3.0(s), 3.4(m), 5.9(s), 6.6(s), 6.8(m), 7.0(m), 7.1(m), 7.3(m), 7.6(m), 8.0(s), 8.5(m), 9.6(s), 9.7(s), 10.4(w), 11.0(s), 11.4(m), 12.2(s), 12.8(m), 13.6(m)μ.

Preparation: The action of difluoraminomethanol on methylene diurethane in the presence of 96% H_2SO_4.



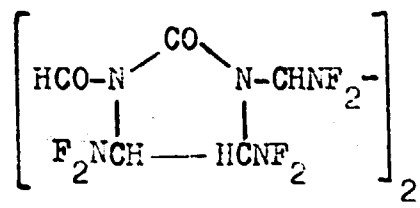
36% yield

Reference: I.C.I. Progress Report No. 16, April 1 - June 30, 1964.

Data Sheet

67. 1,2-Bis(difluoramino)-1,2-bis[4,5-bis(difluoramino)-1-formyl-2-oxoimidazolidin-3-yl]ethane

Structure:



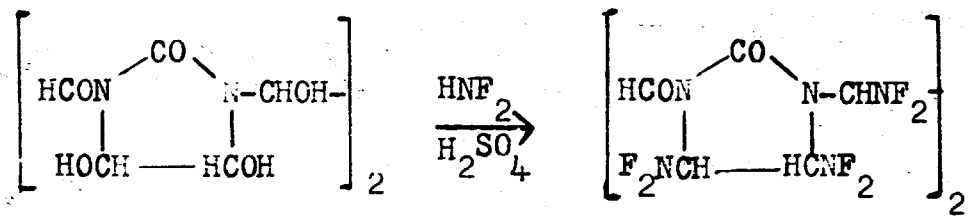
Physical State: White solid, m.p. 125° (decomp.) (reprecipitated from MeOH with H_2O).

Analysis: Found: C, 22.1; H, 1.5; F, 38.9; N, 27.2%

$C_{10}H_8F_{12}N_{10}O_4$ requires: C, 21.4; H, 1.4; F, 40.7; N, 25.0%

Infra-red absorptions at: 3.1(s), 3.2(s), 5.7(s), 7.05(s), 8.0(s), 8.6(s), 9.8(m), 10.6(m), 10.9(s), 11.4(s), 12.3(m), 12.9(s)μ.

Preparation: Difluoramination of the 3:2 adduct of formyl urea with glyoxal.



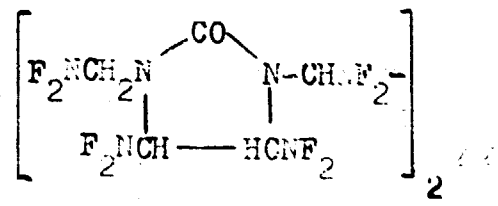
55% yield

Reference: I.C.I. Progress Report No. 23, January 1 - March 31, 1966.

Data Sheet

68. 1,2-Bis(difluoramino)-1,2-bis[4,5-bis(difluoramino)-3-difluoraminomethyl-2-oxoimidazolidin-1-yl]ethane

Structure:



Physical State: Straw coloured liquid (very impure)

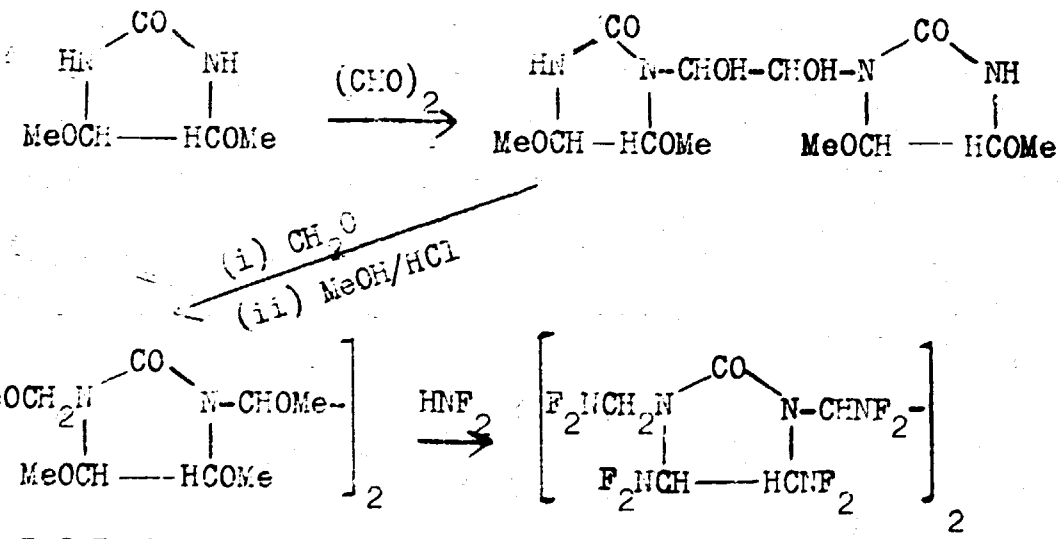
Analysis: Found: C, 22.6; H, 3.2; F, 43.0; N, 23.7%

$C_{10}H_{10}F_{16}N_{12}O_2$ requires: C, 18.9; H, 1.6; F, 47.9; N, 26.5%

Infra-red absorptions at: Not obtained

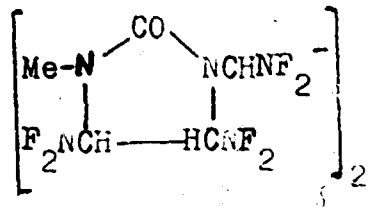
Other Properties: ΔH_{f298} calc. -311.2 kcal/mole. Monopropellant S.I. 234 calc.

Preparation: Treatment with HNF_2 and 96% H_2SO_4 of the methylated, formylated, 2:1 adduct of 4,5-dimethoxyimidazolidin-2-one with glyoxal:



Reference: I.C.I. Progress Report No. 22, October 1 – December 31, 1965.

69. 1,2-Bis(difluoramino)-1,2-bis[4,5-bis(difluoramino)-3-methyl-2-oxoimidazolidin-1-yl]ethane

Structure: 

Physical State: White solid, m.p. 208°

Analysis: Found: C, 22.6; H, 2.8; F, 41.7; N, 20.0%

$C_{10}H_{12}F_{12}N_{10}O_2$ requires: C, 22.6; H, 2.3; F, 42.9; N, 26.3%

Infra-red absorptions at: 5.8(s), 7.15(s), 7.65(s), 8.1(s), 8.5(m), 8.7(m), 9.15(m), 9.55(m), 9.8(m), 10.1(m), 10.6(s), 10.75(s), 10.95(s), 11.35(s), 11.65(s), 12.15(s), 13.15(s)μ.

^{1}HNMR Spectrum (Acetone solution): Triplet centred at 4.02 τ, J=18 c/sec. (Doublet centred at 5.50 τ, J=12 c/sec.

^{19}FNMR Spectrum (Acetone solution): Peaks at -26.7, -30.2, -32.5, -33.7, -34.2, -37.3 δ

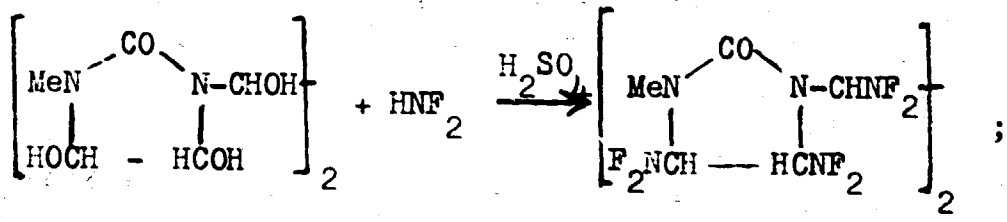
Impact Sensitivity: 10-20 cm

Torpedo Friction (1 Kg): 5-10 cm

69. (contd.)

Other Properties: ΔH_{f298} calc. -298.2 kcal/mole. Monopropellant S.I. 233 calc. DTA exotherm at 220°. Vacuum Thermal Stability test at 60°C, 0.2 ml/g/100 hr.

Preparation: Action of HNF_2 and 96% H_2SO_4 on the 3:2 glyoxal: methylurea condensate:



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Reference: I.C.I. Progress Report No. 20, April 1 - June 30, 1965; No. 21, July 1 - September 30, 1965; No. 23, January 1 - March 31, 1966.

Data Sheet

70. 1,2-Bis(difluoramino)-1,2-di(ethyloxamido)ethane

Structure: $(F_2NCHNHCOCOOEt)_2$

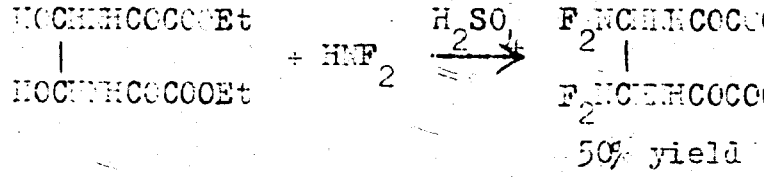
Physical State: White solid, m.p. 200-230 (decomp.)

Analysis: Found: F, 21.0; N, 15.%

$C_{10}H_{14}F_4N_4O_6$ requires: C, 21.0; N, 15.5%

Infra-red absorptions at: 3.0(s), 5.7(s), 5.9(s), 6.5(s), 7.7(s), 8.0(s), 10.8(m), 11.3(m), 11.6(m), 13.3(s)μ

Preparation: Reaction of 1,2-di(ethyloxamido)ethane-1,2-diol with HNF_2 and 96% H_2SO_4



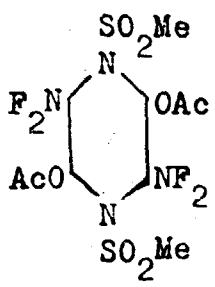
50% yield

Reference: I.C.I. Progress Report No. 19, January 1 - March 31, 1965.

Data Sheet

71. 2,5-Diacetoxy-3,6-bis(difluoramino)-1,4-di(methanesulphonyl)-piperazine

Structure:



(or isomer)

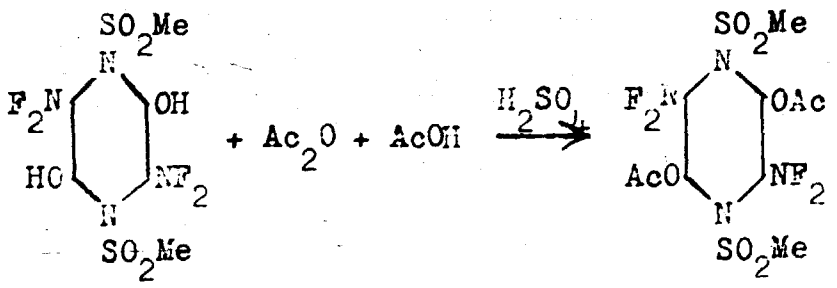
Physical State: Solid, m.p. 210-220° (decomp.) (recrystallised from MeCN)

Analysis: Found: C, 26.8; H, 3.8; F, 19.2; N, 12.5; S, 13.8%

$C_{10}H_{16}F_4N_4O_8S_2$ requires: C, 26.1; H, 3.5; F, 16.5; N, 12.2; S, 13.9%

Infra-red absorptions at: 5.7(s), 7.4(s), 7.6(m), 8.4(s), 8.6(s), 9.0(m), 9.8(s), 10.0(m), 10.2(s), 10.5(s), 10.7(s), 11.3(s), 11.5(m), 12.9(s)μ.

Preparation: Acetylation of 2,5-bis(difluoramino)-3,6-dihydroxy-1,4-di(methanesulphonyl)piperazine (or isomer)



59% yield

Reference: I.C.I. Progress Report No. 21, July 1 - September 30, 1965.

Data Sheet

72. 1,1,2-Tri(carbethoxyamino)-2-difluoraminoethane

Structure: $(EtOOCNH)_2CHCH(NF_2)NHCOOEt$

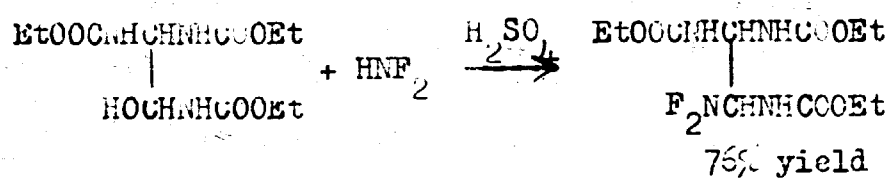
Physical State: White solid, m.p. 194-195°C

Analysis: Found: F, 9.9; N, 16.5; OEt, 39.7%

$C_{11}H_{20}F_2N_4O_6$ requires: F, 11.1; N, 16.4; OEt, 39.5%

Infra-red absorptions at: 2.9(s), 5.4(s), 5.8(s), 6.5(s), 6.8(s), 7.3(s), 7.4(s), 7.5(s), 7.7(s), 7.9(s), 8.6(m), 9.1(m), 9.6(s), 11.1(m), 11.3(s), 12.1(m), 12.7(s)μ.

Preparation: Reaction of HNF_2 with 1,1,2-tri(carbethoxyamino)ethan-2-ol in the presence of 96% H_2SO_4.



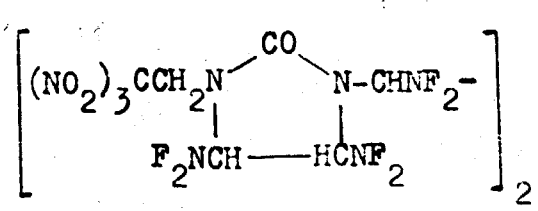
76% yield

Reference: I.C.I. Progress Report No. 15, January 1 - March 31, 1964.

Data Sheet

73. 1,2-Bis(difluoramino)-1,2-bis[4,5-bis(difluoramino)-1-(2,2,2-trinitroethyl)-2-oxoimidazolidin-3-yl]ethane

Structure:



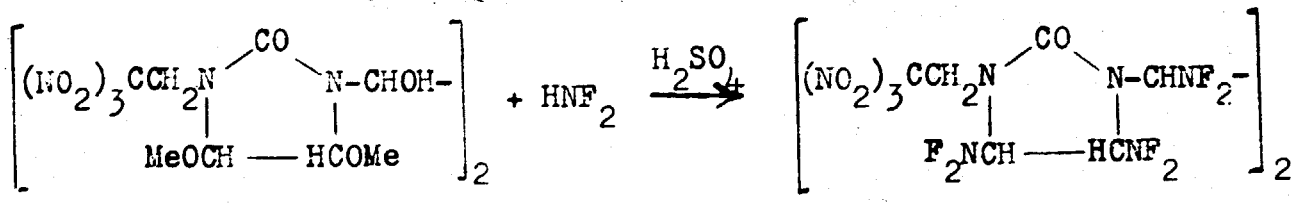
Physical State: Straw coloured viscous liquid

Analysis: Found: C, 22.6; H, 2.6; F, 19.7; N, 23.7; OMe, 2.3%

$C_{12}H_{10}F_{12}N_{16}O_{14}$ requires: C, 17.3; H, 1.2; F, 27.5; N, 27.0%

Infra-red absorptions at: 3.0(m), 3.4(w), 5.7(s), 6.25(s), 7.0(s), 7.7(s), 8.05(s), 8.55(w), 9.1(m), 9.3(m), 9.7-10.0 m), 10.8(s), 11.3-11.5(s), 12.2(s), 12.4(s), 12.8(s)μ.

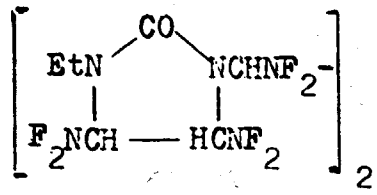
Preparation: Treatment with HNF_2 and 96% H_2SO_4 of 1,2-bis-[4,5-dimethoxy-1-(2,2,2-trinitroethyl)-2-oxo-imidazolidin-3-yl]ethane-1,2-diol:



Reference: I.C.I. Progress Report No. 23, January 1 - March 31, 1966.

Data Sheet

74. 1,2-Bis(difluoramino)-1,2-bis[4,5-bis(difluoramino)-3-ethyl-2-oxoimidazolidin-1-yl]ethane

Structure: 

Physical State: White solid, m.p. 178° (dec.)

Analysis: Found: C, 25.8; H, 3.1; F, 40.8; N, 24.8%;
M(ebullioscopic in acetone), 600

$C_{10}H_{16}F_{12}N_{10}O_2$ requires: C, 25.7; H, 2.9; F, 40.7; N, 25.0%;
M, 560.

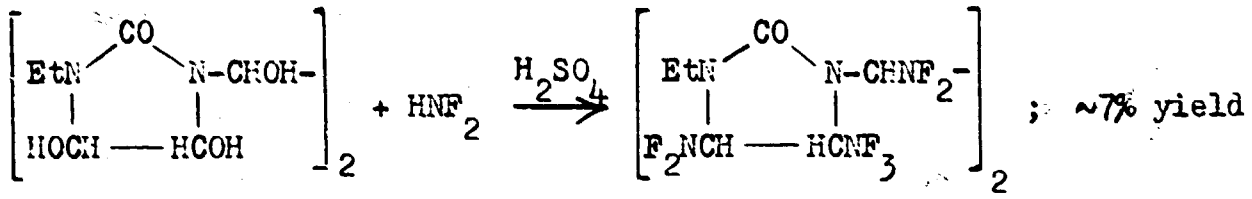
Infra-red absorptions at: 5.8(s), 7.1(s), 8.05(s), 8.3(s), 8.65(m), 9.05(m), 9.8(m), 10.65(m), 10.9(s), 11.5(s), 11.9(m), 12.1(m), 12.3(m), 12.55(m), 12.9(s)μ.

^{1}HNMR (Spectrum (Acetone solution): Triplet centred at 3.95 τ, J=19 c/sec. (CH). Quintuplet centred at 6.4 τ, J=6 c/sec. (CH_2)

^{19}FNMR Spectrum (Acetone solution): Indistinct spectrum due to solubility difficulties. Peak at -29.9 δ

Preparation: Action of HNF_2 and 96% H_2SO_4 on the 3:2 glyoxal: ethylurea adduct:

74. (contd.)



; ~7% yield

Reference: I.C.I. Progress Report No. 20, April 1 - June 30, 1965; No. 21, July 1 - September 30, 1965.

Data Sheet

75. Tri[carbethoxy(difluoraminomethyl)amino]methane

Structure: $HC[N(CH_2NF_2)COOEt]_3$

Physical State: Yellow liquid

Analysis: Found: C, 29.8; H, 5.1; F, 23.6; N, 14.9%

$C_{13}H_{22}F_6N_6O_6$ requires: C, 33.1; H, 4.7; F, 24.2; N, 17.8%

Infra-red absorptions at: 3.0(m), 3.5(m), 5.9(s), 6.6(m), 7.35(m), 8.1(s), 9.2(m), 9.5(m), 9.8(m), 11.1(m), 12.3(m), 12.9(m)μ.

Preparation: The reaction of HNF_2 with tri(carbethoxyamino)methane and paraformaldehyde in the presence of 96% H_2SO_4

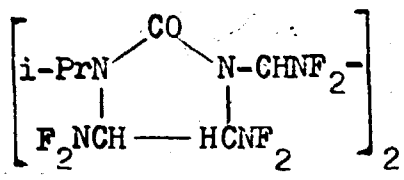
$$HC(NHCOOEt)_3 + (CH_2O)_x + HNF_2 \xrightarrow{H_2SO_4} HC[N(CH_2NF_2)COOEt]_3$$

53% yield

Reference: I.C.I. Progress Report No. 14, July 1, 1962 - December 31, 1963.

Data Sheet

76. 1,2-Bis(difluoramino)-1,2-bis[4,5-bis(difluoramino)-3-isopropyl-2-oxoimidazolidin-1-yl]ethane

Structure: 

Physical State: White solid, m.p. 170°

Analysis: Found: C, 28.2; H, 3.4; F, 36.8; N, 23.6%;

M(ebullioscopic in acetone), 610.

$C_{14}H_{20}F_{12}N_{10}O_2$ requires: C, 28.4; H, 3.4; F, 39.2; N, 23.6%;

M, 588.

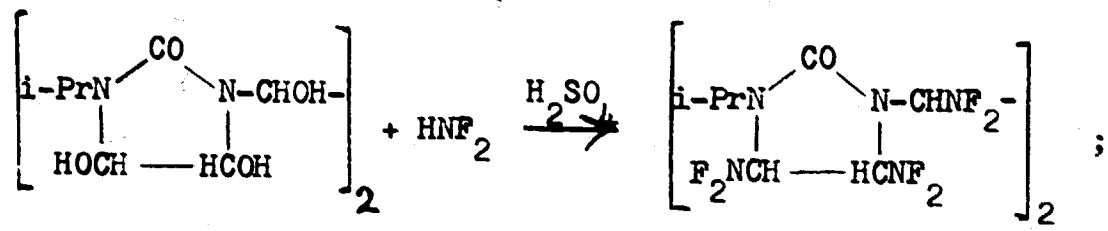
Infra-red absorptions at: 5.8(s), 7.3(s), 7.7(w), 7.9(s), 8.25(s), 8.7(m), 9.15(w), 9.8(w), 10.9(s), 11.5(s), 12.3(s), 12.7(m), 13.4(w), 14.0(w)μ.

^{1}HNMR Spectrum (Acetone solution): Indistinct spectrum, multiplet bands centred at 3.7 and 5.8τ

^{19}FNMR Spectrum (Acetone solution): Indistinct spectrum

Preparation: Reaction of 3:2 glyoxal:isopropylurea adduct with HNF_2 and 96% H_2SO_4:

76. (contd.)



;

50% yield

Reference: I.C.I. Progress Report No. 20, April 1 - June 30, 1965.

Data Sheet

77. Difluoraminated Cellulose Derivatives

Bis(difluoramino)periodate-oxycellulose, DPOC

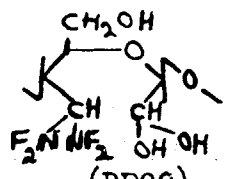
Reduced bis(difluoramino)periodate-oxycellulose, HDPOC

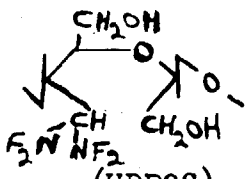
Bis(difluoramino)nitratoperiodate-oxycellulose, DNPOC

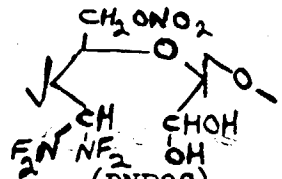
Reduced bis(difluoramino)nitratoperiodate-oxycellulose, HDNPOC

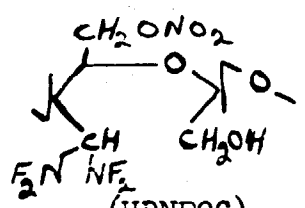
Bis(difluoramino)dinitratoperiodate-oxycellulose, D2NPOC

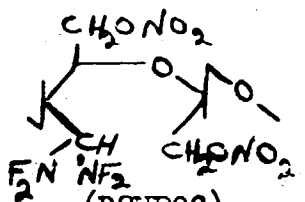
Structures:


(DPOC)


(HDPOC)


(DNPOC)


(HDNPOC)


(D2NPOC)

Physical State: White polymeric solids

Analyses:

Compound	N, %	F, %	Degree of Substitution	
			NF_2	ONO_2
DPOC	10.2	25.6	1.7	-
HDPOC	9.2	24.8	1.5	-
DNPOC	9.0	16.0	1.1	0.5
HDNPOC	8.2	13.9	0.7	0.2
D2NPOC	8.8	16.5	1.0	0.4

77. (contd.)

Impact Sensitivity: DPOC 40-60 cm

HDPOC 10-20 cm

D2NPOC 40-60 cm

Explosion Point: DPOC 146°C

HDPOC 116°C

D2NPOC 112°C

Other Properties: DPOC was plasticised by nitroglycerine and by 2,3,5,6-tetrakis(difluoramino)dioxan, (TDD). HDPOC was stable on storage at room temperature for 4 months, whereas DPOC decomposed to a significant extent in 2 months. HDPOC was shown to be compatible with, and was recovered unchanged from:

(i) aluminium and ammonium perchlorate at 100°C for 1 hour

(ii) nitrocellulose (12.6% N) maintained at 70°C for 1 hour

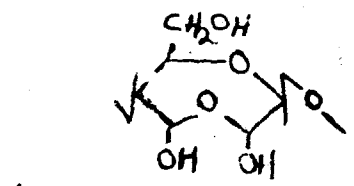
(iii) aluminium and ammonium perchlorate in the presence of water or of alcohol/acetone (2:1) at room temperature for 1 hour

(iv) aluminium, ammonium perchlorate, nitrocellulose (12.6% N) and casting liquid

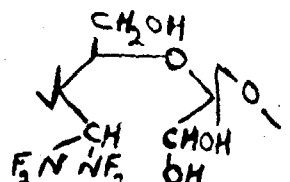
77. (contd.)

(nitroglycerine/triacetin/2-nitrodiphenylamine = 80/19/1) stored at 70°C for 2 weeks.

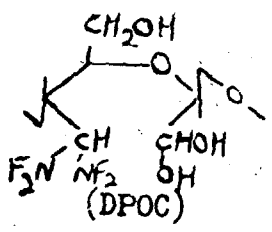
Preparation: Periodate oxidation of cellulose followed by difluoramination, reduction and nitration.


(Periodate-oxycellulose)

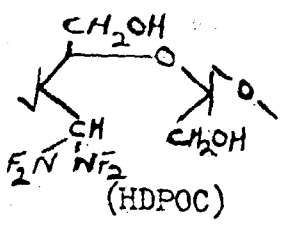
$\xrightarrow[(ii)\ HNF_2/96\%\ H_2SO_4]{(i)\ HNF_2}$


(DPOC)

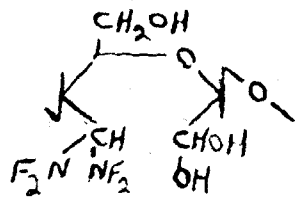
; 70% yield


(DPOC)

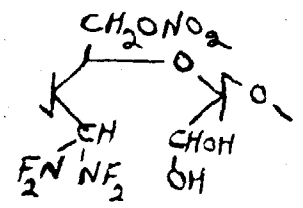
$\xrightarrow{NaBH_4}$


(HDPOC)

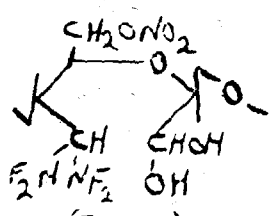
; 75% yield


(DPOC)

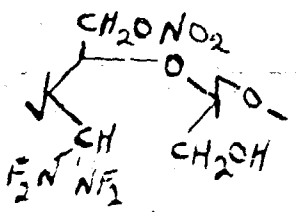
$\xrightarrow{HNO_3}$


(DNPOC)

; 50% yield

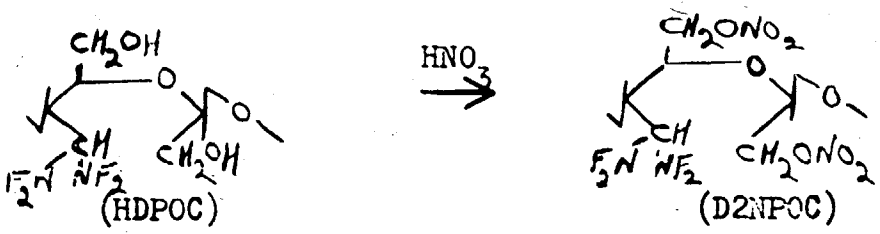

(DNPOC)

$\xrightarrow{NaBH_4}$


(HDNPOC)

; 35% yield

77. (contd.)



(HDPOC) (D2NPOC) ; 30% yield

Theoretical performances: ΔH_{f298} DNPOC -229 kcal/gm mole

ΔH_{f298} D2NPOC -207 kcal/gm mole

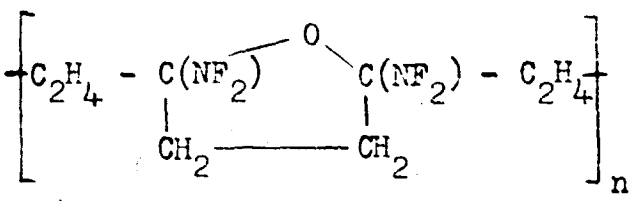
Replacement of NC by DNPOC, D2NPOC in NC/TMETN/AP/Be system results in an S.I. increase of 1.2 and 1.3 lb.sec/lb.

Reference: I.C.I. Progress Reports Nos. 8, July 1, 1961 - June 30, 1962 to 14, July 1, 1962 - December 31, 1963. Atlantic Research Corporation, December 3, 1963.

Data Sheet

78. Poly-ethylene-2,5-bis(difluoramino)-3,4-dihydrofuran

Structure:

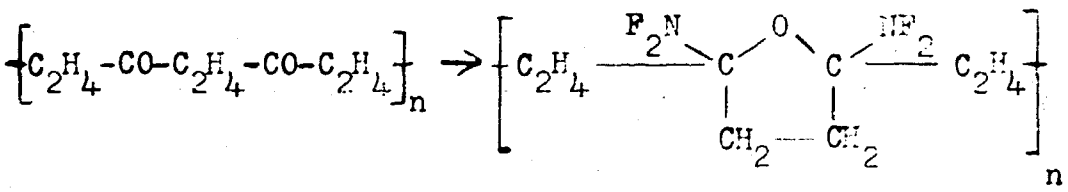


Physical State: Pale brown rubbery solid

Analysis:

Sample	C, % Found	C, % Reqd.	H, % Found	H, % Reqd.	N, % Found	N, % Reqd.	F, % Found	F, % Reqd.
Sample 1 27% CO content	43.6	55.1	7.2	7.7	7.7	10.0	18.1	27.2
Sample 2 41% CO content	43.2	42.1	5.5	5.3	15.3	12.3	27.3	33.4

Preparation: Reaction of ethylene/carbon monoxide co-polymers with HNF_2 alone and in the presence of H_2SO_4, e.g.:



; 90% yield

References: I.C.I. Progress Report No. 14, July 1, 1962 - December 31, 1963; No. 15, January 1 - March 31, 1964.

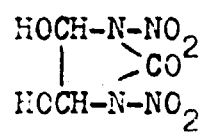
SECTION 2

NO_2 Containing Products

Data Sheet

1. 4,5-Dihydroxy-1,3-dinitroimidazolidin-2-one

Structure:



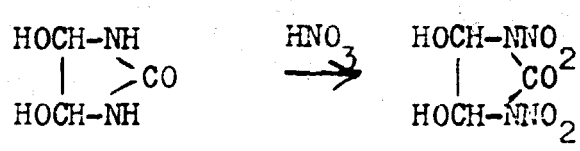
Physical State: Solid m.p. 158° (decomp.)

Analysis: Found: C, 17.3; H, 1.8; N, 26.3%

$C_3H_4N_4O_7$ requires: C, 17.3; H, 1.9; N, 26.9%

Infra-red absorptions at: 2.95(s), 5.6(s), 6.3(s), 7.6(m), 7.8(m), 8.0(m), 8.6(s), 9.1(s), 10.6(w), 12.4(w)μ.

Preparation: Action of 100% HNO_3 at 0°C, on 4,5-dihydroxy-imidazolidin-2-one



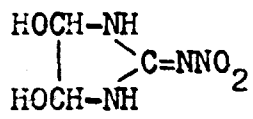
; 23% yield

Reference: I.C.I. Progress Report No. 23, January 1 - March 31, 1966.

Data Sheet

2. 4,5-Dihydroxy-2-nitriminoimidazolidine

Structure:



Physical State: White solid, m.p. 169° (decomp.)

Analysis: Found: C, 21.8; H, 4.5; N, 36.2%; M.W., 140

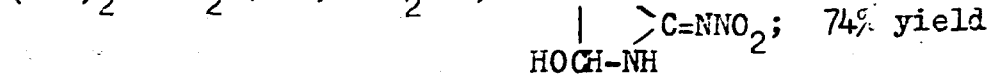
$C_3H_6N_4O_4$ requires: C, 22.2; H, 3.7; N, 34.6%; M.W., 162

Infra-red absorptions at: 3.0(s), 3.2(m), 6.3(s), 6.5(s), 7.8-8.0(s), 8.9(m), 9.2(s), 9.65(s), 11.85(m), 12.3(m), 13.3(m), 13.9-14.0(m) μ.

Impact Sensitivity: 120-160 cm

Explosion Point: 164.5°

Preparation: Addition of nitroguanidine to basic aqueous glyoxal:

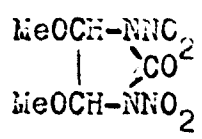


Reference: I.C.I. Progress Report No. 20, April 1 - June 30, 1965.

Data Sheet

5. 4,5-Dimethoxy-1,3-dinitroimidazolidin-2-one

Structure:



Physical State: Needles, m.p. 120-1°

Analysis: Found: C, 25.4; H, 3.35; N, 25.2%

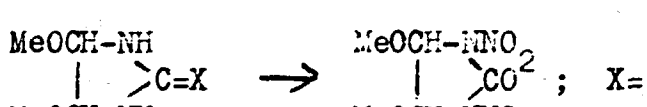
$C_5H_8N_4O_7$ requires: C, 25.4; H, 3.4; N, 23.7%

Infra-red absorptions at 5.56(s), 6.33(s), 7.54(s), 7.91(s), 8.33(s), 8.55(s), 8.85(s), 9.13(s), 9.26(s), 10.03(m), 10.75(s), 11.90(m), 12.25(s), 13.30(s), 13.51(s), 14.0(m), 14.3(m)μ.

Impact Sensitivity: >200 cm

Explosion Point: >240°

Preparation: (i) The reaction of xs HNO_3/Ac_2O on 4,5-dimethoxy-2-nitriminoimidazolidine, or on 4,5-dimethoxy-imidazolidin-2-one



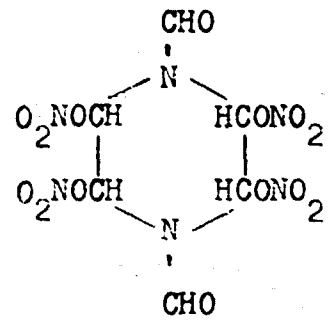
; X=:NNO_2, 80% yield
X=:O, 62% yield

Reference: I.C.I. Progress Report No. 22, October 1 - December 31, 1965.

Data Sheet

4. 1,4-Diformyl-2,3,5,6-tetranitratopiperazine

Structure:



Physical State: White solid, m.p. 152-3°C (decomp.)

Analysis: Found: C, 19.3; H, 2.7; N, 21.6%; M.W. 415

$C_6H_6N_6O_{14}$ requires: C, 18.7; H, 1.6; N, 21.8%; M.W. 386

Infra-red absorptions at: 3.4(s), 5.8(s), 6.0(s), 6.1(s), 6.9(m), 7.1(m), 7.2(s), 7.4(m), 7.7(s), 7.8(s), 7.9(s), 8.0(s), 8.2(s), 9.9(s), 10.3(m), 10.3(s), 12.2(s), 13.5(m), 14.0(m), 14.5(m)μ.

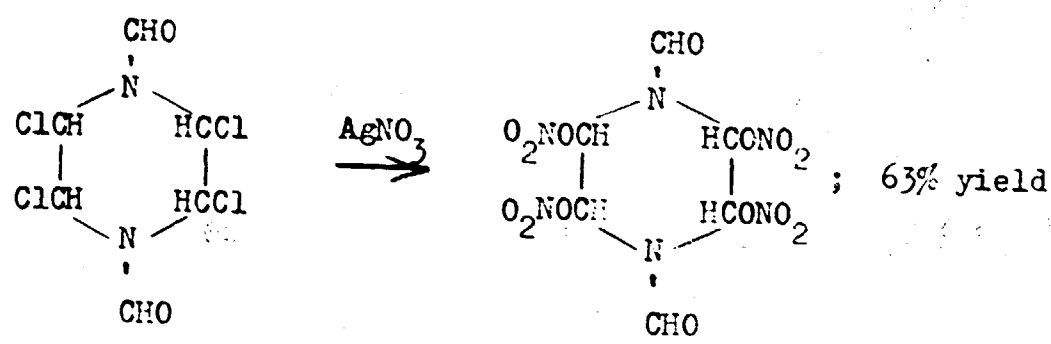
^{1}HNMR Spectrum (Acetone solution): Single peak at 1.24 τ in the ratio of 2:4 to twin peaks at 2.65, 2.80 τ, assigned to the protons of the CHO and piperazine ring respectively.

Impact Sensitivty: 20-30 cm; 10-20 cm after recrystallisation

Explosion Point: 143° (decomp.)

Preparation: The reaction of $AgNO_3$ with 1,4-diformyl-2,3,5,6-tetrachloropiperazine

4. (contd.)



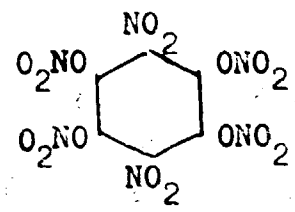
; 63% yield

Reference: I.C.I. Progress Report No. 17, July 1 - September 30, 1964.

Data Sheet

5. 1,2,4,5-Tetranitrato-3,6-dinitrocyclohexane

Structure:



Physical State: Yellow crystalline solid, m.p. 171-2° (decomp.)

Analysis: Found: C, 18.9; H, 1.6; N, 19.9%

$C_6H_6N_6O_{16}$ requires: C, 17.2; H, 1.4; N, 20.1%

Infra-red absorptions at: 5.9(s), 6.0(s), 6.[illegible](s), 7.6(m), 7.8(s), 7.9(s), 9.2(m), 9.5(m), 10.3(m), 10.5(m), 10.8(m), 11.9-12.6(s), 13.6(m), 13.7(m), 14.1(m)μ.

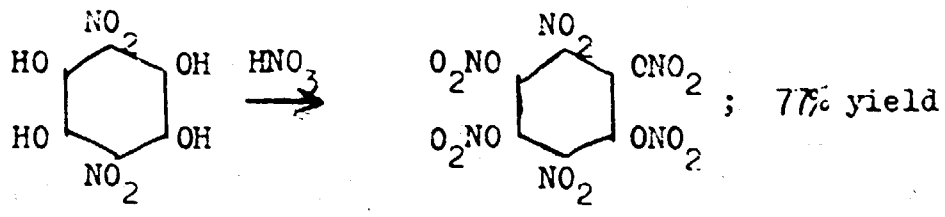
Impact Sensitivity: 10-20 cm

Explosion Point: 173°

Other Properties: ΔH_f est., 120.2 kcal/mole. Estimated heat of combustion 1708 cals/g. Monopropellant S.I., est., 261. Decomposed in acetone solution, no other solvent found for NMR study.

Preparation: Nitration of 1,2,4,5-tetrahydroxy-3,6-dinitrocyclohexane with HNO_3/Ac_2O at 0°; or with HNO_3/H_2SO_4 for 4 hours

5. (contd.)



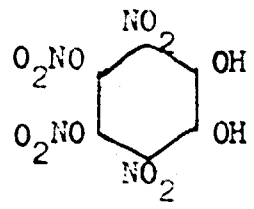
; 77% yield

Reference: I.C.I. Progress Report No. 22, October 1 - December 31, 1966.

Data Sheet

6. 1,2-Dihydroxy-4,5-dinitrato-3, -dinitrocyclohexane

Structure:



Physical State: White solid, decomp. 215°

Analysis: Found: C, 22.2; H, 2.6; N, 16.9%

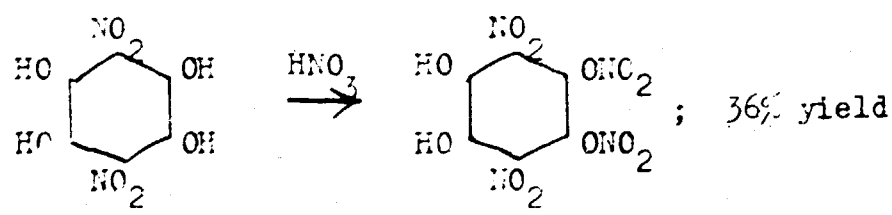
$C_6H_8N_4O_{12}$ requires: C, 22.0; H, 2.4; N, 17.1%

Infra-red absorptions at: 2.8(s), 6.0(s), 6.4(s), 7.6(s), 7.75(s), 7.85(s), 8.9(m), 9.05(m), 9.7(m), 10.3(m), 10.9(m), 11.6(s), 12.3(m), 12.7(m), 13.5(m), 14.0(s)μ.

'HNMR Spectrum (Acetone solution): 5 pairs of doublets in the region 3.7-4.8τ, indicates the structure shown is most probable one.

Impact Sensitivity: 20-30 cm

Preparation: Nitration of 1,2,4,5-tetrahydroxy-3,6-dinitrocyclohexane with HNO_3 in $CHCl_3$ at 0° for 1 hr.



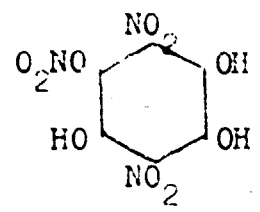
; 36% yield

Reference: I.C.I. Progress Report No. 23, January 1 - March 31, 1966.

Data Sheet

7. 1,2,4-Trihydroxy-5-nitrato-3,6-dinitrocyclohexane

Structure:



Physical State: White solid, m.p. 195-200° (decomp.)

Analysis: Found: C, 25.0; H, 3.3; N, 15.9%

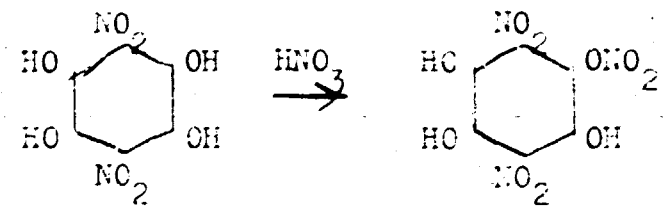
$C_6H_9N_3O_{10}$ requires: C, 25.4; H, 3.2; N, 14.9%

Infra-red absorptions at: 2.85(s), 3.1(s), 6.05(s), 6.55(s), 7.5(s), 7.65(s), 7.8(s), 7.9(s), 8.9(s), 9.1(m), 9.25(m), 9.7(m), 10.35(m), 10.8(m), 11.3-11.9(m), 12.85(m), 14.0(s)μ.

'HNMR Spectrum (Acetone solution): OH peaks at 5.2, 5.4 τ, ring peaks at 3.7τ, indistinct due to low solubility

Impact Sensitivity: >200 cm

Preparation: Nitration of 1,2,4,5-tetrahydroxy-3,6-dinitrocyclohexane with HNO_3/H_2SO_4 at 0° for 1 hr



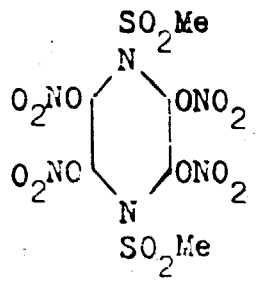
; 34% yield

Reference: I.C.I. Progress Report No. 23, January 1 - March 31, 19 .

Data Sheet

8. 1,4-Dimethanesulphonyl-2,3,5,6-tetranitratopiperazine

Structure:



Physical State: White solid, m.p. 148° (decomp.)

Analysis: Found: C, 15.0; H, 2.4; N, 17.9; S, 12.9%

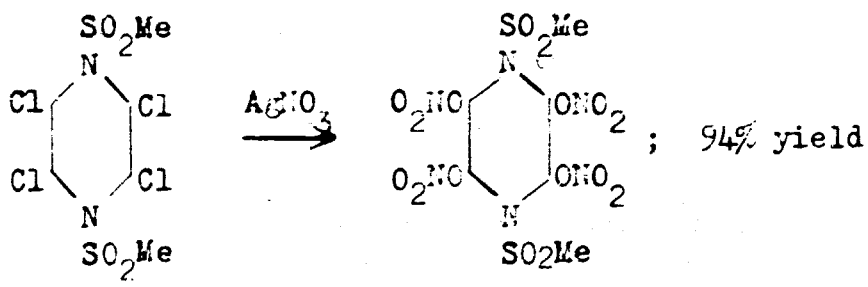
$C_6H_{10}N_6O_{16}S_2$ requires: C, 14.8; H, 2.1; N, 17.3; S, 13.2%

Infra-red absorptions at: 6.0(s), 6.1(s), 7.15(m), 7.4(s), 7.55(s),
7.8(s), 7.9(m), 8.0(s), 8.35(m), 8.6(s),
9.1(s), 9.7(w), 9.9(w), 10.3(s), 10.8(s),
12.1-12.5(s), 13.0(s), 13.5(m), 14.0(m), 14.2(m)μ.

'HNMR Spectrum (Acetone solution): Single peaks at 2.73, 6.46 τ
assigned to ring and SO_2Me protons respectively

Impact Sensitivity: 5-10 cm

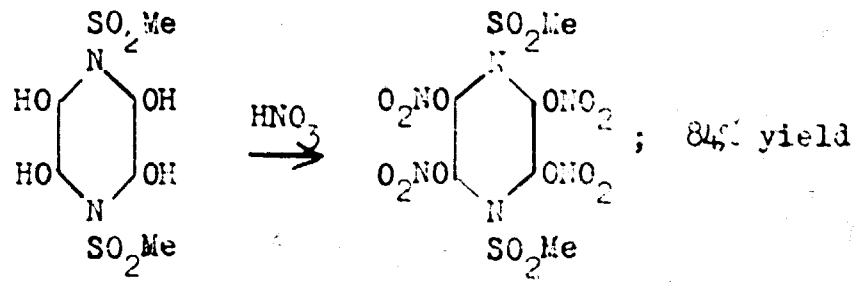
Preparation: (i) Action of $AgNO_3$ on 2,3,5,6-tetrachloro-1,4-dimethanesulphonylpiperazine:



; 94% yield

8. (contd.)

(ii) Action of HNO_3/Ac_2O on 2,3,5,6-tetrahydroxy-1,4-dimethanesulphonylpiperazine:



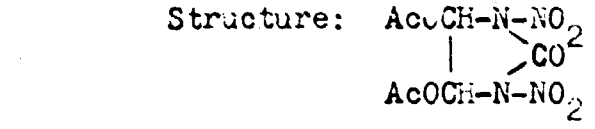
; 84% yield

Reference: I.C.I. Annual Report, Progress Report No. 18, January 1 - December 31, 1964.

Data Sheet

9. 4,5-Diacetoxy-1,3-dinitroimidazolidin-2-one

Structure:



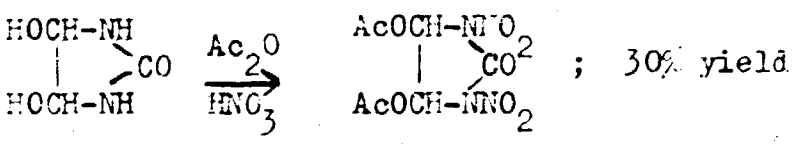
Physical State: Solid, m.p. 125-128° (recrystallised from ether)

Analysis: Found: C, 28.7; H, 2.2; N, 19.2%

$C_7H_8N_4O_9$ requires: C, 28.8; H, 2.7; N, 19.2%

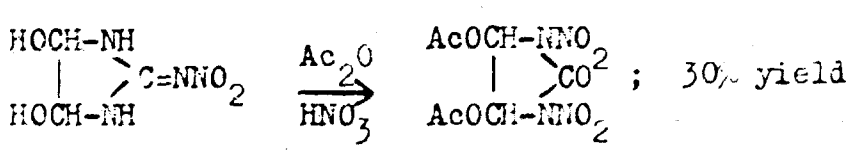
Infra-red absorptions at: 5.5(s), 5.7(s), 5.25(s), 8.0(s), 8.35(s), 8.8-9.0(s), 9.6(s), 10.5(m), 10.85(m), 12.5(m), 13.35(m)μ.

Preparation: (i) The nitration of 4,5-dihydroxyimidazolidin-2-one with HNO_3/Ac_2O



; 30% yield

(ii) The nitration of 4,5-dihydroxy-2-nitrimino-imidazolidine with HNO_3/Ac_2O



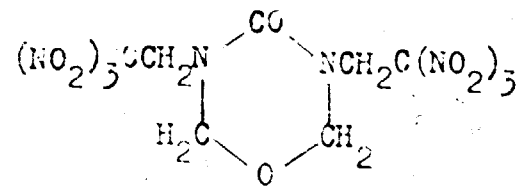
; 30% yield

Reference: I.C.I. Progress Report No. 23, January 1 - March 31, 1966.

Data Sheet

10. N,N'-Bis(2,2,2-trinitroethyl)uron

Structure:



Physical State: White solid, recrystallised from EtOH, m.p. 174-5°

Analysis: Found: C, 19.9; H, 2.5; N, 26.1%; M.W.(ebullioscopic in acetone), 343.

$C_7H_8N_8O_{14}$ requires: C, 19.6; H, 1.9; N, 26.2%; M.W., 428

Infra-red absorptions at: 6.0(s), 6.3(s), 6.75(s), 7.2(s), 7.5-7.8(s), 8.35(m), 8.55(m), 9.1(m), 9.2(m), 9.8(m), 10.15(m), 11.55(s), 11.7(s), 12.4(s), 12.6(m), 12.8(m), 13.0(s), 13.4(s), 14.0(m)μ.

'HNMR Spectrum (Acetone solution): Two single peaks at 4.31 and 4.58τ in the ratio 1:1 due to hydrogen nuclei of trinitroethyl groups and uron ring, respectively .

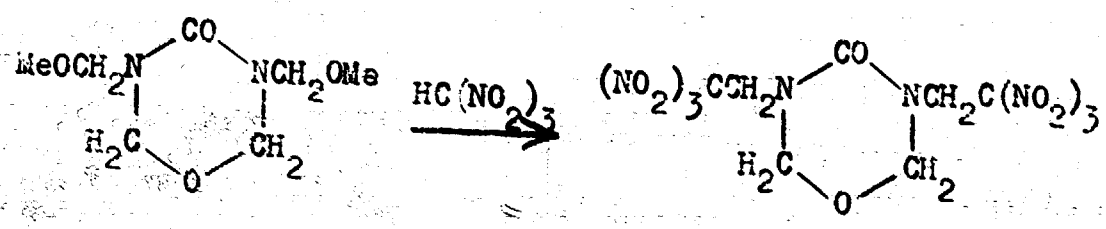
Impact Sensitivity: 10-20 cm

Explosion Point: 169°C

Other Properties: Vacuum thermal stability test, 1·1 ml/g/100 hr at 60°

Preparation: Reaction of N,N'-bis(methoxymethyl)uron with $HC(NO_2)_3$ in MeOH at 100° for 3 hrs:

10. (contd.)



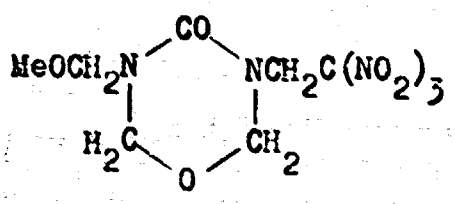
78% yield

Reference: I.C.I. Progress Report No. 22, October 1 - December 31, 1965; No. 23, January 1 - March 31, 1966.

Data Sheet

11. N-Methoxymethyl-N'-(2,2,2-trinitroethyl)uron

Structure:



Physical State: Solid, m.p. 63-65° (recrystallised from i-PrOH/hexane)

Analysis: Found: C, 27.4; H, 3.7; N, 22.7%

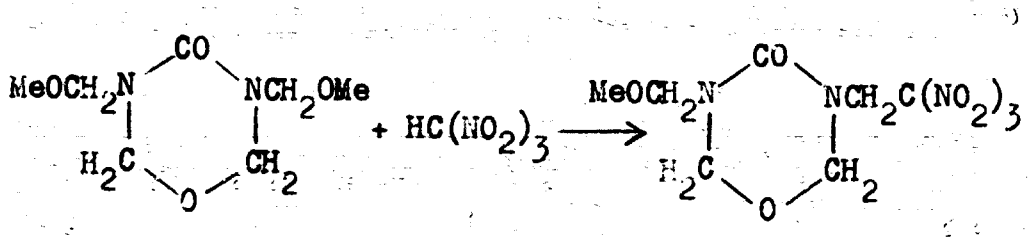
$C_7H_{11}N_5O_9$ requires: C, 27.2; H, 3.6; N, 22.7%

Infra-red absorptions at: 6.0(s), 6.25(s), 6.4(s), 6.7(m), 7.75(s), 8.1(w), 8.5(w), 9.15(m), 9.4(m), 9.9(m), 10.3(w), 11.0(w), 11.6(m), 11.75(m), 12.4(m), 12.8(m), 13.4(m)μ

Impact Sensitivity: 60-80 cm

Explosion Point: 152-5°C

Preparation: The reaction between N,N'-bis(methoxymethyl)uron and nitroform in the molar ratio 1:0.8.

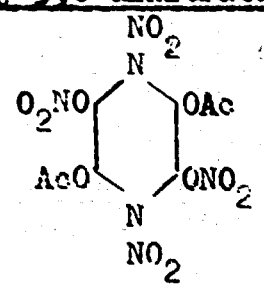


68% yield

Reference: I.C.I. Progress Report No. 23, January 1 - March 31, 1966.

Data Sheet

12. 2,5-Diacetoxy-3,6-dinitrato-1,4-dinitropiperazine

Structure:  , or isomer

Physical State: White solid, recrystallised from MeCn, m.p. 170°

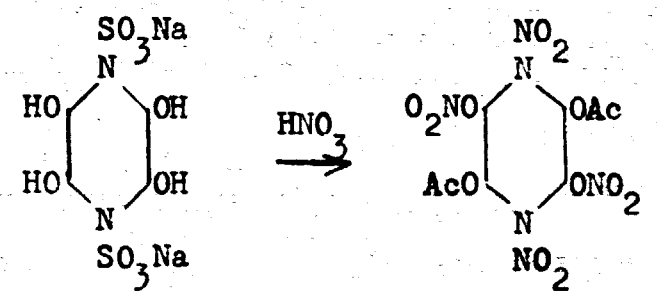
Analysis: Found: C, 23.4; H, 2.6; N, 19.4; S, nil %

$C_8H_{10}N_6O_{14}$ requires: C, 23.2; H, 2.4; N, 20.3%

Infra-red absorptions at: 3.3(m), 5.6(s), 5.9(s), 6.2(s), 7.5(m), 7.7(s), 8.4(s), 9.1(m), 9.8(s), 10.1(s), 10.6(s), 11.3(m), 11.9(m), 12.2(s), 13.0(m), 15.5(m)μ

'HNMR Spectrum (MeCN solution): Single peaks at 7.70τ (Ac-group protons) and at 2.50τ (piperazine ring protons).

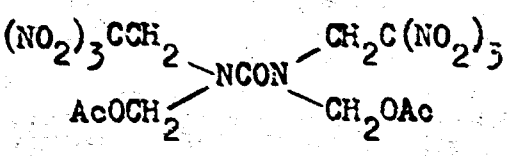
Preparation: Nitration of salts of 2,3,5,6-tetrahydroxypiperazine-1,4-disulphonic acid, using 8:3 v/v HNO_3/Ac_2O at 0°

 (or isomer); 34% yield

Reference: I.C.I. Progress Report No. 19, January 1 - March 31, 1965

Data Sheet

13. N,N'-Di(acetoxymethyl)-N,N'-bis(2,2,2-trinitroethyl)urea

Structure: 

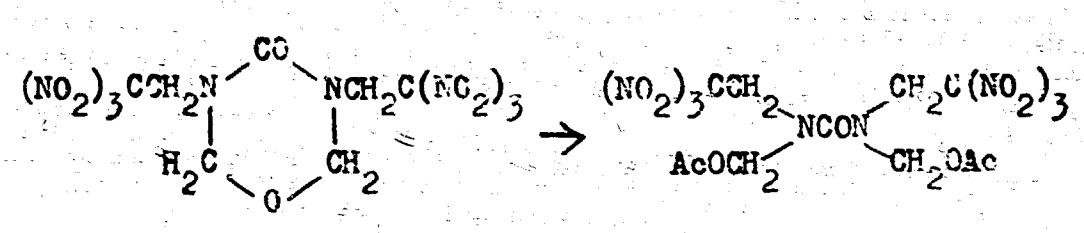
Physical State: White solid m.p. 98-100°

Analysis: Found: C, 24.5; H, 1.7; N, 21.7%

$C_{11}H_{14}N_8O_{17}$ requires: C, 24.9; H, 2.7; N, 21.1%

Infra-red absorptions at: 5.8(s), 6.0(s), 6.15(s), 6.3(s), 6.7(m), 6.95(m), 7.4(w), 7.65(s), 7.95(s), 8.1(s), 8.2(m), 8.4(m), 9.0(w), 9.5(w), 9.7(s), 10.3(w), 10.8(w), 11.5(m), 11.8(w), 12.4(m)μ.

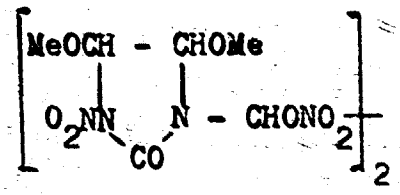
Preparation: The action of Ac_2O/H_2SO_4 (20: 1 v/v) on N,N-bis-(2,2,2-trinitroethyl)uron.



Reference: I.C.I. Progress Report No. 22, October 1 - December 31, 1965.

Data Sheet

14. 1,2-Bis(4,5-dimethoxy-1-nitro-2-oxoimidazolidin-3-yl)-1,2-dinitratoethane

Structure: 

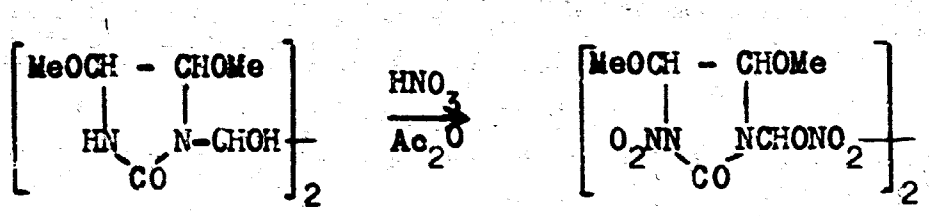
Physical State: White solid m.p. 196-7° (decomp.).

Analysis: Found: C, 27.8; H, 3.6; N, 20.5; MeO, 26.3%

$C_{12}H_{18}N_8O_{16}$ requires: C, 27.2; H, 3.4; N, 21.1; MeO, 23.4%

Infra-red absorptions at: 5.7(s), 6.05(s), 6.4(s), 7.3(m), 7.9(s), 8.2(s), 8.45(s), 9.1-9.4(s), 10.1(s), 10.35(w), 10.55(w), 12.3(s), 12.7(s), 13.3(s), 13.5(w), 14.2(w)μ.

Preparation: Nitration of 1,2-bis(4,5-dimethoxy-2-oxoimidazolidin-1-yl)ethane-1,2-diol with HNO_3/Ac_2O.



Reference: I.C.I. Progress Report No. 24, January 1 1965 - June 30, 1966.

SECTION 3

Instruments and Methods

3.1 Infra-red Spectra

Spectra of all compounds were determined on a Perkin-Elmer Infracord Model 137 spectrometer. Spectra of many compounds were also determined on a Perkin-Elmer Infracord Model 337 spectrometer. Liquids were run as thin films between rock salt plates and solids as mulls in Nujol or 'Florube' oil on rock salt plates. Gases were determined in 10 cm path-length cells with rock salt windows. In a very few cases solid were prepared in KBr discs.

3.2 NMR Spectra

^{1}H NMR and ^{19}F NMR spectra were obtained on a Perkin-Elmer Model R10 60 mc/sec instrument. ^{1}H spectra were obtained against tetramethylsilane as internal standard and ^{19}F spectra against $CFCl_3$ as internal standard.

3.3 Impact Sensitivity

The fall hammer test apparatus consists of a $\frac{1}{2}$ Kg mild steel hammer which is allowed to fall from a measured height onto a fixed volume of sample placed between the faces of two vertical Hoffmann steel roller bearings each $\frac{1}{2}$ in. diameter and $\frac{1}{2}$ in. long. The bearings are kept in place by a collar of annealed Vibrac V.45 steel $1\frac{1}{2}$ in. external diameter and $\frac{1}{4}$ in. + 1/1000 in. bore, the whole assembly resting on a steel plate of the same material $1\frac{1}{2}$ in. in diameter and 7/16 in. thick.

The maximum height at which no detonations occur out of ten attempts is recorded and also the height at which at least one detonation occurs.

3.4 Explosion Point

The explosion point was determined on a 0.1 g sample in an open round bottom Pyrex glass test tube heated in a metal block at a rate of 5°/min. The explosion point is taken as the temperature at which explosion or ignition occurs.

3.5 Vaccum Thermal Stability

Vacuum thermal stabilities were determined in an apparatus of the type described by Esso Research & Engineering (Report No. 62-3, June 11 - September 30, 1962). Approximately 0.1 g of the sample was confined under vacuum in a glass tube closed with a Fischer-Porter valve and carrying a mercury manometer side arm. The tube including side arm was immersed up to the valve seating in a thermostatically controlled water bath at 60°C. Pressure in the tube was read periodically with a cathetometer by removing it from the bath at 60° and placing in a small glass bath at 20°.

3.6 Vapour Pressure

Vapour pressures of liquids were determined in apparatus described above after thorough degassing of the sample.

3.7 Heats of Formation

All heats of formation quoted are calculated values. These were derived from the heat of formation of the closest published structure by use of bond energy values for simple bonds and group contributions for $-NF_2$, $=NF$, $-NO_2$ and $-C(NO_2)_3$ groups. The values taken were -204.5 kcal/mole for $-NF_2$, -167.6 kcal/mole for $=NF$, -24.6 kcal/mole for $-NO_2$ and +9.2 kcal/mole for replacement of $-CH_2CH_3$ by $-CH_2C(NO_2)_3$.

3.8 Specific Impulse

The approximate method developed by M.J. Harper and J.A. Hicks (Explosives Research and Development Establishment, Waltham Abbey, Report No. 24/M/60) was employed. For aluminised propellants the equation used was:

$$\log I_m = 1.3285 + 0.3400 \log Q + 0.39305 \log \left(\frac{100\ n}{C}\right)$$

For non-aluminised high energy propellants the equation used was:

$$\log I_m = 1.9355 + 0.3568 \log Q + 0.4605 \log n - 0.3336 \log C.$$

where Q is the heat of reaction in Kcal
n is the number of moles of gaseous product
C is the total heat capacity of products (both solid and gaseous) in cal.deg.$^{-1}$
} per 100 g of propellant

Q is calculated at 298°K using the most likely set of combustion products and C is calculated assuming an exhaust temperature of 2000°K.