July 25, 1977

Summary Report

15 May, 1976 to 14 May 1977

DESENSITIZATION OF EXPLOSIVE MATERIALS

By: John M. Guimont

Prepared for:

OFFICE OF NAVAL RESEARCH
800 North Quincy Street
Arlington, Virginia 22217

Attention: Dr. Richard S. Miller
Code 473

Contract No. N00014-76-C-0810; NR093-056

SRI Project PYU-5374

STANFORD RESEARCH INSTITUTE
Menlo Park, California 94025 · U.S.A.

STANFORD RESEARCH INSTITUTE
Menlo Park, California 94025 · U.S.A.

(11) 25 July 25, 1977

(9) Summary Report,
15 May 1976 to 14 May 1977,

(12) 38p.

(6) DESENSITIZATION OF EXPLOSIVE MATERIALS.

(10) By: John M. Guimont

Prepared for:

OFFICE OF NAVAL RESEARCH
800 North Quincy Street
Arlington, Virginia 22217

Attention: Dr. Richard S. Miller
Code 473

(15) Contract No. N00014-76-C-0810 NR093-056

SRI Project PYU-5374

Approved:

M. E. Hill, Director
Chemistry Laboratory

P. J. Jorgensen, Vice President
Physical and Life Sciences

1473
332 500

AB

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SRI-5374	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Desensitization of Explosive Materials		5. TYPE OF REPORT & PERIOD COVERED Summary Report 15 May, 1976 to 14 May, 1977
		6. PERFORMING ORG. REPORT NUMBER N/A
7. AUTHOR(s) J. M. Guimont		8. CONTRACT OR GRANT NUMBER(s) Contract No. N00014-76-C-0810; NR093-056
9. PERFORMING ORGANIZATION NAME AND ADDRESS SRI International 333 Ravenswood Avenue Menlo Park, CA 94025		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS N/A
11. CONTROLLING OFFICE NAME AND ADDRESS Attn Code 211 Office of Naval Research 800 North Quincy Street Arlington, VA 22217		12. REPORT DATE July 22, 1977 13. NO. OF PAGES
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
14. MONITORING AGENCY NAME & ADDRESS (if diff. from Controlling Office) N/A		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A

16. DISTRIBUTION STATEMENT (of this report)

Attached

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from report)

N/A

18. SUPPLEMENTARY NOTES

N/A

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Under the sponsorship of the Office of Naval Research, SRI has been studying the desensitization of explosive materials by replacing hydrogen with fluorine in selected explosive molecules. The objective has been to demonstrate that desensitization can be achieved by replacing hydrogen in the molecule with fluorine, and if possible to determine the mode of desensitization.

over

DD FORM 1 JAN 73 1473
EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED 332
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19. KEY WORDS (Continued)

20 ABSTRACT (Continued)

Based on our observation that FEFO is desensitized when the formal hydrogens are replaced with fluorine, we proposed to prepare and test similar nitroaliphatic formals and difluoroformals followed by introduction of fluorine into other explosive structures such as difluoraminoaliphatic formals, nitramines, and alkyl nitrates. The results, if desensitization is confirmed, would provide insight into how compounds explode and the general theory of desensitization.

Work during this research period emphasized the preparation and testing of two nitroaliphatic formals and their analogous difluoroformals, and one nitroaliphatic ether and its corresponding tetrafluoroether.

At the conclusion of the first year's work, one difluoraminoaliphatic difluoroformal was being prepared, and the technique for preparing additional difluoroformals containing sensitive functional groups was demonstrated. The physical property measurements of the difluoraminoaliphatic difluoroformal are in progress.

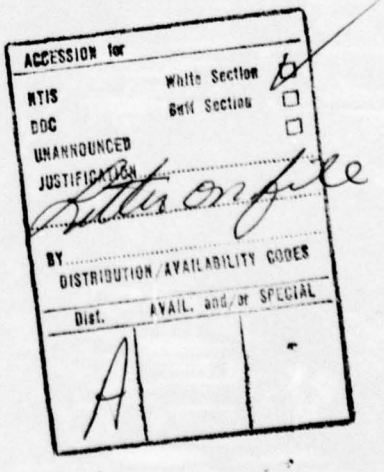
Sensitivity tests have shown that desensitization by the introduction of fluorine into nitroaliphatic formals and ethers is a general phenomenon. Replacement of hydrogen with fluorine in selected positions of the molecule has resulted in reduced sensitivity to initiation by impact and shock wave, and has also provided a decrease in melting point, an increase in density, and better thermal stability.

PREFACE

This report is submitted in partial fulfillment of the contractual obligation for Contract No. N00014-76-C-0810 entitled, "Desensitization of Explosive Materials." The report contains a summary of work performed during the period May 15, 1976 through May 14, 1977.

The research program was performed by staff of SRI's Chemistry Laboratory of the Physical Sciences Division under the supervision of M. E. Hill and Donald L. Ross, with assistance in the explosive characterization by the Poulter Laboratory. John M. Guimont was the principal investigator, and Thomas C. Goodale performed the card gap tests.

We wish to acknowledge the valuable suggestions and discussions given to this project by Dr. Richard S. Miller, Project Monitor, by Dr. Joel Schnur, Naval Research Laboratory, and by R. W. Woolfolk of SRI's Washington Office.



SUMMARY

Under the sponsorship of the Office of Naval Research, SRI has been studying the desensitization of explosive materials by replacing hydrogen with fluorine in selected explosive molecules. The objective has been to demonstrate that desensitization can be achieved by replacing hydrogen in the molecule with fluorine, and if possible to determine the mode of desensitization.

Based on our observation that FEFO is desensitized when the formal hydrogens are replaced with fluorine, we proposed to prepare and test similar nitroaliphatic formals and difluoroformals followed by introduction of fluorine into other explosive structures such as difluoraminoaliphatic formals, nitramines, and alkyl nitrates. The results, if desensitization is confirmed, would provide insight into how compounds explode and the general theory of desensitization.

Work during this research period emphasized the preparation and testing of two nitroaliphatic formals and their analogous difluoroformals, and one nitroalipnatic ether and its corresponding tetrafluoroether.

At the conclusion of the first year's work, one difluoraminoaliphatic difluoroformal was being prepared, and the technique for preparing additional difluoroformals containing sensitive functional groups was demonstrated. The physical property measurements of the difluoraminoaliphatic difluoroformal are in progress.

Sensitivity test have shown that desensitization by the introduction of fluorine into nitroaliphatic formals and ethers is a general phenomenon. Replacement of hydrogen with fluorine in selected positions of the molecule has resulted in reduced sensitivity of initiation by impact and shock wave, and has also provided a decrease in melting point, an increase in density, and better thermal stability.

CONTENTS

TABLES

GLOSSARY

ADDF	1,4,4,10,10,13-Hexafluoro-1,1,7,7,13,13-hexanitro-3,5,9,11-tetraoxatridecane
BFDEE	Bis(fluorodinitroethoxy) ethane
DDFF	Bis[5,5-bis(difluoramino)-2,2-dinitrohexyl] difluoroformal
DDNF	Bis[5,5-bis(difluoramino)-2,2-dinitrohexyl] formal
DFF	Bis(fluorodinitroethyl) difluoroformal
FDNE	Fluorodinitroethanol
FEFO	Bis(fluorodinitroethyl) formal
HADDF	1,13-Difluoro-1,1,7,7,13,13-hexanitro-3,5,9,11-tetraoxatridecane
HTD	Bis(fluorodinitroethoxy) tetrafluoroethane
NFDF	[illegible],2-difluoramino)propyl] difluoroformal
NFPF	[illegible],2-bis(difluoramino)propyl] formal
TEDFO	Bis(trinitroethyl) difluoroformal
TEFO	Bis(trinitroethyl)formal

INTRODUCTION AND BACKGROUND

The Armed Services have continuing problems with the accidental initiation of explosive materials. To reduce the hazard of handling explosives, it is necessary to know what characteristics of explosives make them sensitive to initiation under various conditions and to use this knowledge to reduce their sensitivity. Few new advances have been made in recent years toward desensitization of explosives. However, the results of our previous work for Lawrence Livermore Laboratory apply directly to the problem. During the course of that work, the compound FEFO was modified by substituting the $-CH_2-$ group with a $-CF_2-$ group to produce the compound DFF:

$FC(NO_2)_2CH_2-\underline{OCH_2}O-CH_2CF(NO_2)_2$ FEFO

$\downarrow$

$FC(NO_2)_2CH_2-\underline{OCF_2}O-CH_2CF(NO_2)_2$ DFF

To illustrate the degree of desensitization achieved, Table 1 compares the sensitivity characteristics of FEFO and DFF: other known physical properties are also given. Thus, when the difluoroformal group, $-OCF_2O-$, was incorporated into FEFO, the following improved properties were obtained:

Lowering melting point and glass transition temperatures
Higher density
Enhanced chemical and thermal stability
Decreased impact sensitivity
Decreased shock sensitivity (particularly to LVD)
Lower toxicity.

Table 1

PHYSICAL PROPERTIES OF FEFO AND DFF

	$[FC(NO_2)_2CH_2O]_2CH_2$ FEFO	$[FC(NO_2)_2CH_2O]_2CF_2$ DFF
Mol wt	320.1	356.1
bp, °C (mm)	110 (0.3)	70 (0.003)
mp, °C	+14	-17
vp, μ (25°C)	0.16	1.6
ρ, g/cc (°C)	1.59	1.67 (27)
ΔH_f^o, kcal/mol	-178	-275
DTA, °C	exotherm starts 209	exotherm starts 228 max 250
CRT, cc	0.04-0.1	0.04-0.06
LVD*	1500-1800	225-325
HVD*	80-85	77
Impact, kg-cm	6	135
Sound speed, mm/μsec	1.25	1.15
Compressibility, cm^2/dyne, ($\times 10^{11}$)	4.03	4.53
Detonation pressure, kbar†	229	213
Shock velocity, m/sec†	7272	6849

*Card gap test using 1/2-inch diameter tubes.

†Estimated using TIGER Code; C_3H_8, C_2H_6; C_2H_2, C_3H_6, CH_2, CH, F_2, NF_3, F_2O, and F rejected as possible gaseous constituents.

At the onset of this contract, the FEFO/DFF case was the most complete due to the importance of the compounds in propellant and explosive development programs. The objective of this program was to demonstrate that desensitization of explosives by the introduction of fluorine into the molecule is a general phenomenon, and our general approach, based on our original observation, has been to synthesize and test several nitroaliphatic formals and difluoroformals selected from those shown in Table 2. During the current contract, four compounds structurally similar to FEFO were prepared and tested, and additional physical property measurements and theoretical calculations were completed on FEFO and DFF.

Table 2

LINEAR FORMALS, DIFLUOROFORMALS AND HOMOLOGS

$(RO)_2CH_2$ (Formals)			$(RO)_2CF_2$ (Fluoroformals)		
Compound	No.	Structure	Compound	No.	Structure
FEFO‡	1	$[FC(NO_2)_2CH_2O]_2\overset{*}{C}H_2$	DFF‡	2	$[FC(NO_2)_2CH_2O]_2\overset{*}{C}F_2$
DNPF	3	$[H_3CC(NO_2)_2CH_2O]_2\overset{*}{C}H_2$	NPFF	4	$[H_3CC(NO_2)_2CH_2O]_2\overset{*}{C}F_2$
TDPF	5	$[CF_3OCH_2C(NO_2)_2CH_2O]_2\overset{*}{C}H_2$	OTT	6	$[CF_3OCH_2C(NO_2)_2CH_2O]_2\overset{*}{C}F_2$
TEFO‡	7	$[C(NO_2)_3CH_2O]_2\overset{*}{C}H_2$	TEDFO‡	8	$[C(NO_2)_3CH_2O]_2\overset{*}{C}F_2$
†	9	$FC(NO_2)_2CH_2\overset{*}{O}CH_2OCH_2C(NO_2)F_2$	MFF	10	$FC(NO_2)_2CH_2\overset{*}{O}CF_2OCH_2C(NO_2)F_2$
†	11	$FC(NO_2)_2CH_2\overset{*}{O}CH_2OCH_2CF_3$	TMFF	12	$FC(NO_2)_2CH_2\overset{*}{O}CF_2OCH_2CF_3$
HADDF	13	$[FC(NO_2)_2CH_2\overset{*}{O}CH_2OCH_2]_2C(NO_2)_2$	ADDF	14	$[FC(NO_2)_2CH_2\overset{*}{O}CF_2OCH_2]_2C(NO_2)_2$
BFDEE‡	15	$FC(NO_2)_2CH_2\overset{*}{O}CH_2\overset{*}{C}H_2OCH_2C(NO_2)_2F$	HTD‡	16	$FC(NO_2)_2CH_2\overset{*}{O}CF_2\overset{*}{C}F_2OCH_2C(NO_2)_2F$

* Site of change.

† Not previously reported.

‡ Subject compounds of this report.

SYNTHESIS OF EXPLOSIVES FOR SENSITIVITY TESTS

The first pair of compounds we prepared was TEFO (Compound 7) and TEDFO (Compound 8). This pair was chosen for two reasons: first, TEFO was a known compound,[1] and the synthetic route to its analog, TEDFO, involved the use of only well-known reactions; second, TEFO was known to be very sensitive to initiation, and therefore, we expected that any desensitization attributable to the presence of fluorine would be of sufficient magnitude to be easily observable.

Bis(trinitroethyl) Formal (TEFO)

TEFO was prepared using the reported[1] procedure, as shown in Equations (1) [redacted] (4):

$$C(NO_2)_4 \xrightarrow[(1)]{KOH/H_2O_2} KC(NO_2)_3 \xrightarrow[(2)]{HCl} HC(NO_2)_3$$

$$\xrightarrow[(3)]{HCHO} C(NO_2)_3CH_2OH \xrightarrow[(4)]{HCHO/H_2SO_4} [C(NO_2)_3CH_2O]_2CH_2$$

TEFO

During the course of this program, a total of 429 g (249 ml) of TEFO was prepared, most of which was consumed in card gap tests.

Bis(Trinitroethyl) Difluoroformal (TEDFO)

TEDFO was prepared as shown in Equations (5) and (6):

$$C(NO_2)_3CH_2OH \xrightarrow[(5)]{COCl_2} [C(NO_2)_3CH_2O]_2CO \xrightarrow[(6)]{SF_4/HF} [C(NO_2)_3CH_2O]_2CF_2$$

TEDFO

Bis(trinitroethyl) carbonate was prepared in 71% yield based on the procedure of T. N. Hall,[2] and the carbonate was fluorinated in 87% yield to give the difluoroformal TEDFO. Our initial attempts to fluorinate the carbonate using sulfur tetrafluoride[3] with hydrofluoric acid as a solvent and catalyst resulted in either no reaction or decomposition (Table 3). When the correct reaction time and temperature were employed as in Run 5, a 75% conversion to the desired product was obtained. The point to be made here is that the reaction temperature and time are critical. When the reaction scale was increased to 180 g of carbonate, six days were required to effect complete reaction at 105°C. A total of 390 g (232 ml) of TEDFO was prepared for card gap tests.

Bis(Fluorodinitroethoxy) Ethane (BFDEE)

The second pair of compounds prepared for testing was BFDEE/HTD. This pair was chosen because the compounds are ethers, as opposed to the formals described above, but the similarities of their structures to FEFO and DFF allowed us to compare properties not only with each other but also with FEFO and DFF. In addition, they were both known compounds, and their syntheses did not appear to present any difficulties.

Table 3

FLUORINATION OF BIS(TRINITROETHYL) CARBONATE

Trial	Carbonate (g/mmol)	HF (mmol)	SF_4 (mmol)	Temp. (^oC)	Time (hrs)	Product (g)	Remarks
1	10/48	100	157	90	20	9.5	Starting material recovered
2	10/48	1100	102	90	20	9.2	Starting material recovered
3	10/48	1300	74	120	20	9.2	Starting material plus small amount of product
4	10/48	1300	102	120	120	0.8	Primarily decomposition
5	10/48	1100	194	105	72	9.4	75% Product, 25% starting material

BFDEE has been reported previously[4,5] and was prepared by that procedure, as shown in Equations (7)-(9):

$$FC(NO_2)_2CH_2OH \xrightarrow[(7)]{\overset{O}{\diagup\diagdown}\ CH_2\text{-}CH_2/NaOH} FC(NO_2)_2CH_2OCH_2CH_2OH$$

$$\xrightarrow[(8)]{(CF_3SO_2)_2O} FC(NO_2)_2CH_2OCH_2CH_2OSO_2CF_3 \xrightarrow[(9)]{FC(NO_2)_2CH_2OH}$$

$$[FC(NO_2)_2CH_2OCH_2\text{-}]_2$$

BFDEE

Results of running the first two reactions in the sequence were essentially the same as reported in the references; however, some difficulty was encountered in obtaining a pure product from the third step. The product (BFDEE) reported in the literature was obtained in 78% yield and of sufficient purity to crystallize on cooling. BFDEE was prepared several times in our laboratory, but yields were approximately 45%, and we found it necessary to chromatograph the product to purify it. These difficulties may have been due to mixing or mass transfer problems because of the larger scale of our reactions. Rather than expending undue effort to modify the reported procedure, we accepted the poorer yield and prepared a total of 158 g (100 ml).

Bis(Fluorodinitroethoxy) Tetrafluoroethane (HTD)

HTD was a known compound[6] prepared as shown in Equations (10) and (11):

$$FC(NO_2)_2CH_2OH \xrightarrow{\overset{O\ O}{\|\ \ \|}\ ClC\text{-}CCl} [FC(NO_2)_2CH_2O\overset{O}{\overset{\|}{C}}\text{-}]_2$$

$$\xrightarrow{SF_4/HF} [FC(NO_2)_2CH_2OCF_2\text{-}]_2$$

HTD

No difficulties were encountered in the preparation of 140 g (95 ml) of HTD.

1,13-Difluoro-1,1,7,7,13,13-Hexanitro-3,5,9,11-Tetraoxatridecane (HADDF)

In addition to preparing the four compounds previously described, we expended considerable effort in an attempt to prepare HADDF. HADDF was chosen because the difluoroformal analog was known[7] and had already been shown to be relatively insensitive to initiation. We expected HADDF to be about as sensitive as FEFO, and therefore the ADDF/HADDF pair would provide a third pair of formals for which a significant difference in sensitivity could be demonstrated.

In attempts to prepare HADDF, the following synthetic routes were investigated:

1. $2FC(NO_2)_2CH_2OCH_2Cl + HOCH_2C(NO_2)_2CH_2OH \xrightarrow[(12)]{SnCl_4} HADDF$

2. $2FC(NO_2)_2CH_2OH + (ClCH_2OCH_2)_2C(NO_2)_2 \xrightarrow[(13)]{SnCl_4} HADDF$

3. $[FC(NO_2)_2CH_2OCOOCH_2]_2C(NO_2)_2 \xrightarrow[(14)]{P_4S_{10}} -OC(=S)O-$

$$\xrightarrow[(15)]{SO_2Cl_2/AlCl_3} -OCCl_2O- \xrightarrow[(16)]{[H]} HADDF$$

4. $FC(NO_2)_2CH_2OH \xrightarrow[(17)]{ClC(=S)Cl} FC(NO_2)_2CH_2OC(=S)Cl$

$$\xrightarrow[(18)]{HOCH_2C(NO_2)_2CH_2OH} [FC(NO_2)_2CH_2OC(=S)OCH_2]C(NO_2)_2$$

$$\xrightarrow[(15)]{} \xrightarrow[(16)]{} HADDF$$

Since the condensation of chloromethyl ethers with acidic alcohols was well known, routes 1 and 2 were attempted first. In both reactions, a mixture of products was obtained in which bis(fluorodinitroethyl) formal

and 5,5-dinitro-1,3-dioxane were identified; however, none of the desired product could be isolated.

Attempts to prepare the thionocarbonate, Equation (14), resulted in either no reaction or decomposition of the carbonate. The reaction of fluorodinitroethanol with thiophosgene yielded only the thionocarbonate of FDNE instead of fluorodinitroethyl chlorothioformate, Equation (17). Since it appeared that preparation of HADDF was going to be a difficult problem, and research in methods to prepare it were beyond the scope of this program, the work was discontinued.

Bis[5,5-Bis(difluoramino)-2,2-Dinitrohexyl] Difluoroformal (DDFF)

The second class of compounds we prepared for testing during this first year of the program was difluoraminoalkyl formals and difluoroformals. Table 4 shows the two pairs currently under investigation. Since 5,5-bis(difluoramino)-2,2-dinitrohexyl carbonate was available in our laboratories, and the formal was already known, we began this phase of the program with several attempts to fluorinate the carbonate, as shown in Equation 19:

$$[CH_3C(NF_2)_2CH_2CH_2C(NO_2)_2CH_2O]_2CO \xrightarrow[(19)]{SF_4/TiF_4} [CH_3C(NF_2)_2CH_2CH_2C(NO_2)_2CH_2O]_2CF_2$$

DDFF (Compound 20)

Previous work conducted at SRI for Lawrence Livermore Laboratories has shown that carbonates containing the difluoramino group are unstable in the presence of hydrofluoric acid and boron trifluoride, both of which are commonly used as catalysts for sulfur tetrafluoride fluorinations. Therefore, titanium tetrafluoride, which is a milder catalyst, was used in our attempts to prepare DDFF. The results are summarized in Table 5. The reactions, which were run at 120°C, provided a reasonable weight recovery, but spectral data indicated that the product mixture contained

Table 4

DIFLUORAMINO FORMALS

Compound	No.	Structure	Compound	No.	Structure
NFPF	17	$[CH_3C(NF_2)_2CH_2O]_2CH_2$	NFDF	18	$[CH_3C(NF_2)_2CH_2O]_2CF_2$
DDNF	19	$[CH_3C(NF_2)_2CH_2CH_2C(NO_2)_2CH_2O]_2CH_2$	DDFF	20	$[CH_3C(NF_2)_2CH_2CH_2C(NO_2)_2CH_2O]CF_2$

mostly starting material. The data also indicated that the desired product was present. When the reaction temperature was increased to 140°, mostly starting material was recovered after one day, and little product at all was recovered after three days. The product from Run 4 contained very little starting material, but the poor weight recovery would make this reaction impractical even if the product mixture were all the desired product.

Table 5

FLUORINATION OF 5,5-BIS(DIFLUORAMINO)-2,2-DINITROHEXYL CARBONATE

Run	Temp, (°C)	Time (days)	Weight* Recovered	Comments
1	120	1	0.4	Mostly starting material
2	120	5	0.3	Mostly starting material
3	140	1	0.3	Mostly starting material
4	140	3	0.1	Little starting material

*0.5-g scale reactions

The results of this series of reactions indicated that titanium tetrafluoride was not a very efficient catalyst for fluorination of carbonates. Therefore an alternate approach to the preparation of difluoraminoalkyl difluoroformals was taken and is discussed below.

Bis[2,2-Bis(Difluoramino)propyl] Difluoroformal (NFDF)

NFDF was the second difluoramino alkyl difluoroformal we attempted to prepare since the formal was already known and 2,2-bis(difluoramino) propanol (a precursor) was already on hand. In view of our unsuccessful

attempts to fluorinate bis[5,5-bisdifluoramino)-2,2-dinitrohexyl] carbonate, we prepared NFDF using the thionocarbonate, as shown in Equations (20) and (21).

$$CH_3C(NF_2)_2CH_2OH \xrightarrow[(20)]{Cl(=S)Cl} [CH_3C(NF_2)_2CH_2O]_2C=S$$

$$\xrightarrow[(21)]{SF_4/TiF_4} \underset{\text{NFDF}}{[CH_3C(NF_2)_2CH_2O]_2CF_2}$$

It has been reported[8] that thiocarbonates having the general structure RSC(=S)SR can be fluorinated without a catalyst using sulfur tetrafluoride and in some of our earlier work, a thionocarbonate ROC(=S)OR was fluorinated with sulfur tetrafluoride using titanium tetrafluoride as a catalyst.

The thionocarbonate, Equation (20), was prepared readily from 2,2-bis-(difluoramino) propanol and thiophosgene, and the fluorination proceeded smoothly at 65° in 18 hours to give an 80% conversion. Optimization of reaction parameters is now in progress and we feel that the success of this fluorination means that DDFF (discussed in the previous section) can be prepared by this method.

Details of the methods for preparing NFDF and compounds previously discussed are presented in the section Experimental Details.

CHARACTERIZATION AND SENSITIVITY TESTING

All of the compounds prepared during this program have been or will be well characterized by physical property and sensitivity measurements. Vapor pressures, densities, melting points, boiling points, thermal stabilities, sound speeds, and sensitivities to initiation were all experimentally determined in our laboratories. Heats of formation, compressibilities, detonation pressures, and shock velocities were all estimated using well-established techniques. The measured and estimated properties of the subject compounds is shown in Table 6.

Vapor Pressure

Vapor pressures were measured by the Knudsen[9] method, and, for most of the compounds, the reported value at 25° was determined by extrapolation from values measured at higher temperatures. As expected, the fluorine-substituted compounds exhibited a higher vapor pressure than the hydrogen analogs.

Density

Liquid densities were measured directly using a Fisher-Davidson Gravitometer. Solid densities were measured by suspending the material in a mixture of liquid nonsolvents and varying the ratio until the solid was dispersed evenly and the liquid and solid densities were the same. The liquid density was then measured with the gravitometer.

Table 6

COMPARISON OF PHYSICAL PROPERTIES OF TEST COMPOUND PAIRS

	FEFO	DFF	TEFO	TEDFO	BFDEE	HTD	NFPF	NFDF
mol wt	320.0	356.1	374.2	410.2	334.2	406.1	336.21	372.19
bp, °C (mm)	110(0.3)	70(0.003)	-	-	117-119 (0.01)	-	67(0.15)	48(0.15)
mp, °C	14	-17	65	16-18	30	33-35	-	-
vp, μ (25°C)	0.16	1.6	0.009	0.075	0.052	0.61	24.5	
ρ, g/cm³ (25°C)	1.59	1.67	1.72	1.68	1.54	1.68	1.45	1.51
ΔH_f°, kcal/mol (estimated)	-178	-275	-151	-243	-235	-421	-177	-269
DSC, °C, at 10°C/min	Exotherm 209	Exotherm 228	Endotherm 162	Nothing up to 207	Exotherm 167	Exotherm	Endotherm 250	
Thermal stability, cm³/g	0.16-0.4†	0.16-0.24†	0.36‡	0.25‡	0.12‡	<0.01		
LVD, cards*	1500-1800	225-325	>6400	>6400	None	None		
HVD, cards*	80-85	77	Not determined		200-400	100-200		
Impact, kg-cm	6	136	150	4-6 Liquid >250 Solid	50	>135		
Sound speed, mm/μsec	1.25	1.15	1.31	1.17	1.26	1.05		
Compressibility, cm²/dyne, (c 10^{-11})	4.03	4.53	3.39	4.35	4.09	5.40		
Detonation Pressure, kbar§	229	213	275	207	203	183		
Shock Velocity, m/sec§	7272	6849	7831	6860	7034	6384		

*Card = 10 mil (0.254 mm)

†Values are for Lawrence Livermore CRT (chemical reactivity test) run on a 0.25-g sample at 120°C for 22 hr in an atmosphere of He.

‡Values are for VTS (vacuum thermal stability test) run on a 0.25-g sample at 120°C for 22 hr at approximately 0.1 mm.

§Estimated using TIGER Code; C_3H_8, C_2H_6, C_2H_2, C_3H_6, CH_2, CH, F_2, NF_3, F_2O, and F rejected as possible gaseous constituents.

Thermal Stability (DSC, VTS)

Thermal stability of the test compounds was determined by two methods. First, differential scanning calorimetry (DSC) indicated that DFF and HTD displayed exotherms at higher temperatures than did FEFO and BFDEE. TEDFO was stable up to 207° while TEFO gave an endotherm at 162°, which was the result of decomposition and vaporization of the decomposition products. Second, gas evolution at elevated temperatures was measured by the VTS vacuum thermal stability (VTS) test at 120° (CRT for FEFO and DFF). For each pair of compounds, the fluorine-substituted compound evolved less gas than its hydrogen analog.

In general, the fluorine-substituted compounds showed better thermal stability at a fixed elevated temperature and also during heating at a constant rate.

Sound Speed and Compressibility

Sound speed measurements were made on the subject compounds to calculate their compressibility. For each of the pairs, compressibility of the fluorinated analog is greater than that calculated for the hydrogen analog. However, the value calculated for TEFO is questionable since the sound speed had to be measured on the liquid at 65°, whereas the density was measured on the solid at 25°.

Impact Sensitivity

Impact-sensitivity tests were made on a Technoproducts Dropweight Tester. Because BFDEE tended to soften at ambient temperature, the pair HTD/BFDEE was tested as liquids at 35° so that a direct comparison could be made. Because of the configuration of the sample holders and the method of testing, a comparison of results with liquids and solids cannot

be made. TEFO was the only compound that could not be tested as a liquid because of its high melting point; therefore the test equipment was cooled to test both TEDFO and TEFO as solids, again, for the purpose of direct comparison.

For each of the three pairs of compounds tested, the fluorine-substituted compound was less sensitive to impact than the hydrogen analog.

Spark Sensitivity

All of the subject compounds were tested for their sensitivity to electrostatic discharge, using a test machine constructed at SRI. None were sufficiently sensitive to detonate when subjected to a discharge of 80 millijoules (test limit) in five trials.

Shock Sensitivity

Sensitivity of the test compounds to shock initiation was measured using the card gap test. In this test a donor explosive (tetryl) is used to generate a strong shock (~200 kbar). The strength of this shock wave is reduced by placing a gap of plastic (plexiglas disks or cellulose acetate cards 0.01 in. thick) between the donor explosive and the material to be tested until a detonation no longer occurs. The larger this gap the lower the input pressure to the sample. Results are reported as the minimum number of cards or inches of gap necessary to prevent detonation in the materials (100 cards = 1 inch). The test compounds are confined in steel tubes 1/2 inch in diameter and 4 inches long. Tests on FEFO and DFF were completed prior to this program. The initial tests were run using a witness plate to determine the test results, and judgment of the results was based on fragmentation of the sample tube and witness plate. In the case of BFDEE and HTD, this method served very well since

the results were consistent and well defined. However, the initial tests of TEFO and TEDFO indicated that HVD was being initiated with attenuators as long as 6 feet and input pressures of less than 1 kbar, which hardly seems enough to initiate HVD. In addition, tests with very long attenuators resulted in extreme fragmentation of the sample holder and witness plate, whereas tests with short attenuators caused fragmentation of the witness plate without damaging the sample holder.

Since these test results were anomalous, additional tests were made using ytterbium gauges to measure the input and detonation pressures and to determine the time lapse between them (to calculate shock velocity). Tests were made using 8- and 64-inch attenuators. The results show that there is very little difference in input pressure between these lengths. At 8 inches, the pressure has dropped to about 0.9 kbar, falling to 0.75 kbar at 64 inches. In both test cases the results show that LVD is being initiated in both TEFO and TEDFO despite the fact that witness plates indicate an HVD. Based on the card gap tests to date, we are forced to conclude that LVD can be initiated in TEFO and TEDFO with attenuators at least 6400 cards in length, and that both compounds are so sensitive that we cannot determine if desensitization has occurred at this time.

We are not entirely satisfied with results obtained from the card gap test for several reasons: (1) differences in fragmentation of the sample holders is inconsistent with information obtained from the gauge measurement; (2) with the very long attenuator, transit time for LVD wave was less than the speed of sound in the sample, suggesting that initiation of the LVD may not have been due to the shock wave from the donor charge; (3) input pressures could not be reliably predicted from the length of the attenuator; and (4) gauge tests have shown that when very long attenuators are used, the input pressure is from a compression wave rather than from a true shock wave.

In view of these inconsistencies and difficulties in judging card gap test results, we are presently considering use of the wedge test to determine shock sensitivity.[10]

Detonation Pressure and Velocity

Theoretical detonation pressures and velocities were calculated using the TIGER Code. TIGER is a digital computer program in FORTRAN IV for calculating detonation parameters of condensed explosives. The central problem is the calculation of conditions in the Chapman-Jouget (C-J) detonation wave. Subsidiary problems are calculations of the properties of the detonation products along the Hugoniot curve, along isentropes (or along curves where other variables are held constant), or at specified points or grids of points. TIGER may also be used for detonations in gases and for direct solution of chemical equilibria at specified values of two state variables.

The program includes 36 subroutines whose interconnections are such that effective separation is maintained between the hydrodynamics, the thermodynamics, and the equation of state.

As presently arranged, the program can consider up to 30 gaseous constituents and up to 10 solid constituents of the product mixture. Up to 10 chemical elements may enter into the makeup of these product substances. In addition to solving chemical equilibria for the mole numbers of the constituents, the thermodynamic part of the code calculates the complete thermodynamic properties of the mixture and the first partial derivatives. Along an isentrope, the Riemann integral and the enthalpy increment are calculated for each step of expansion.

Initially, TIGER was unable to determine the C-J point because 29 gaseous constituents were being considered. We found that the computations could be done only after some of the gases were rejected as possible

constituents and the most abundant gaseous products were stipulated. Rejected gaseous products were C_3H_8, C_2H_6, C_2H_2, C_3H_6, CH_2, CH, F_2, F, F_2O, and NF_3. The gaseous products considered by TIGER were CO_2, N_2, H_2O, HF, CF_4, CO, O_2, NO, OH, H_2, O, NH_3, H, CF_3, N, CF_2, CH_4, CH_3, and C, with the first six being specified as most abundant.

Detonation pressure and velocity are both reduced by replacement of hydrogen with fluorine in the molecule. This is the expected change in view of the large negative change in heat of formation when hydrogen is replaced with fluorine.

DISCUSSION

Initiation of this research program was based on the observation that replacement of two hydrogen atoms with fluorine atoms in FEFO gave a compound (DFF) that was much less sensitive to initiation by impact and shock. Our purpose in this program has been to generalize the concept of desensitization by replacement of hydrogen with fluorine and then determine more specifically why and how the desensitization occurs.

The test data presented in the previous section on TEFO, TEDFO, BFDEE, and HTD so far confirm the desensitization concept. Card gap testing of TEFO and TEDFO did not conclusively show that desensitization was achieved for these compounds, but because of the extremely high sensitivity observed for both compounds and because of anomalies observed during testing, we prefer to reserve judgment until additional information can be obtained. Impact tests on TEFO and TEDFO do show that desensitization was achieved insofar as this test is concerned.

The test results on BFDEE and HTD are quite clear. HTD is less sensitive to initiation by impact and shock than is BFDEE. In addition to the data collected on compounds prepared and tested during this program, we surveyed SRI reports on Sensitivity Fundamentals (ONR Contract N00014-70-C-0190) to determine if any of the data would be useful for our present study. We found that LVD and HVD studies were completed on 1,1-dinitroethane (1,1-DNE) and 1,1,1-fluorodinitroethane, Table 7.

Table 7

PROPERTIES OF DINITROETHANE AND FLUORODINITROETHANE

	1,1-DNE	1,1,1-FDN
M.P. (°C)	37.5	> 0 < 25
Density (g/cm^3)	1.35	1.40
LVD (cm Plexiglas)	7.00-7.60	7.00-8.31
HVD (cm Plexiglas)	1.42-1.60	1.09-1.19
Sound Speed ($mm/\mu sec$)	1.27	1.26
Compressibility (cm^2/dyne, x 10^{-11})	4.59	4.50

Replacement of the 1-hydrogen in 1,1-DNE with fluorine resulted in an increase in density, decrease in melting point, and decrease in HVD sensitivity all of which are the anticipated trends. However, there was no significant reduction in the LVD sensitivity, and surprisingly, there was almost no decrease in the sound speed or compressibility.

Tests on the limited number of compounds in this report do not prove conclusively that an explosive will be desensitized if hydrogen is replaced by fluorine, but none of the information obtained to date contradicts the hypothesis. Additional tests on a much wider range of compounds will be necessary before any sound conclusions can be drawn regarding the generality and applicability of this method of desensitization or the mode by which it functions.

Despite the limited data available at this time, we would like to present some conjectures regarding the possible modes of desensitization to encourage thought and feedback on the subject and to demonstrate the rationale for the choice of additional compounds to be studied in this program.

It is well known that the sensitivity of an explosive to shock initiation is affected by the configuration of the test container and

also by the container materials. Therefore, the desensitization observed with our test materials could be viewed as the effect of a change in physical properties--in particular, a change in compressibility.* For each of the pairs studied, the fluorinated analog has a greater compressibility than its hydrocarbon counterpart. However, BFDEE and FEFO have nearly the same compressibility, and yet BFDEE is far more sensitive to shock initiation. If a change in compressibility is a contributing factor in desensitization, then it should be considered of prime importance only for analogs. Also, a direct relationship between compressibility and sensitivity does not necessitate a cause and effect relationship.

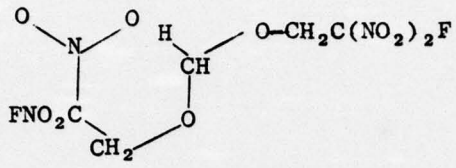
In connection with this, Dr. Joel Schnur of the Naval Research Laboratories has been investigating the conformation response of organic compounds to very high pressures. Under several kilobars pressure, hydrocarbon chains tend to assume conformations that most closely resemble a sphere, despite the fact that they are not thermodynamically favored at ambient pressure. In assuming these conformations, the molecules must be absorbing energy. In relation to explosives, it may be that the response of an explosive to high pressure is somewhat related to its ability to undergo conformational changes and absorb the energy from compression. Samples of each of our test compounds have been delivered to NRL, and high-pressure studies are planned.

In addition to the physical property effects of introducing fluorine into an explosive, there is a significant change in chemical properties. A direct intramolecular chemical interaction that could lead to the first bond breaking step should be considered as a possible influence on sensitivity. The seven-membered ring shown below is not a very probable

---

* Dr. Richard Miller suggested that a possible correlation may exist between ease of initiation and compressibility for liquids.

configuration at ambient pressure, but at several kilobars pressure, when unusual conformers predominate, it may provide a source of intramolecular action through which nitrous acid could be eliminated from the molecule:



Molecular models show that in some conformations, the formal hydrogens and nitro oxygens are in close proximity.

Replacement of the formal hydrogens with fluorine should alter the significance of this ring system considerably. For the three pairs of compounds tested, the relative position of C-F and C-NO_2 has been the same, and desensitization has been observed. Two of the difluoraminoaliphatic formals that will be tested in future work combine two distinct variations from the compounds already tested. First, DDFF has nitro groups in the same position (relative to fluorine) as the compounds already tested but at the same time it has the sensitive difluoramino group in a more isolated position. Second, NFDF contains no nitro groups and has the difluoramino groups in the same position as the nitro groups of the compounds already tested. If interaction (or lack thereof) of nitro with hydrogen as in the seven-membered ring, is an overriding factor, then the sensitivity of the NFDF may not be less than NFPF and the sensitivity difference between DDFF and DDNF may be small or insignificant. If, however, the difluoraminoaliphatic formals are desensitized, then we must assume that other chemical interactions are significant or the mode of desensitization is something other than those considered above.

The above discussion has been totally speculative and should not be considered as a presentation of the only hypotheses considered. At the present time, there are insufficient data to draw any conclusions regarding the mode of desensitization involved here. Additional tests on the subject compounds and on other explosives with a wider range of functional groups may provide a base from which we can gain an understanding of explosive sensitivity.

EXPERIMENTAL DETAILS

The following experiments are given in detail because they describe the synthesis of either new compounds or key intermediates. Elemental analyses were performed by Georgina Hum on a Perkin-Elmer Autosampler, infrared spectra were run on a Perkin-Elmer 247 Spectrophotometer, ^{1}H nmr spectra were run on a Varian EM-360 Spectrometer, and ^{19}F nmr were run on a Varian XL-100 Spectrometer.

Bis(Trinitroethyl) Carbonate

A solution of 82 g (0.83 mol) of phosgene in 500 ml of methylene chloride at 0-5° was added to a mixture of 155 g (1.63 mol) pyridine N-oxide, 300 g (1.66 mol) trinitroethanol, 400 ml chloroform, and 180 ml methylene chloride at 25° over a period of 20 min. The reaction mixture was stirred at 25° for an additional hour. Hexane (200 ml) was added to the reaction mixture, which was then cooled to 0° and filtered to remove the product. The product was washed with water and dried to yield 230 g, 71% yield, m p 114°.[11]

Bis(Trinitroethyl) Difluoroformal (TEDFO)

Bis(trinitroethyl) carbonate, 180 g (0.46 mol), was placed in a 1400-ml stainless steel autoclave and cooled to -78°C. Hydrofluoric acid, 138 g (6.9 mol), and sulfur tetrafuloride, 382 g (3.5 mol), were condensed into the reactor. The reaction was heated to 105°C in a rocker for six days. After cooling and venting the excess hydrofluoric acid and sulfur tetrafluoride, the product was washed out of the reactor with methylene chloride. The methylene chloride solution was treated with magnesium sulfate, filtered, and evaporated, leaving 178 g of pale yellow oil. The

crude product was dissolved in methylene chloride and passed through a silica-gel column, using 50% methylene chloride in hexane to elute the product: 165 g, 87% yield. Elemental analysis calculated for $C_5H_4N_6O_{14}F_2$: C, 14.64; H, 0.98; N, 20.49; F, 9.27. Found: C, 15.02; H, 1.16; N, 20.46; F, 10.00. IR (film): 1600 (s,NO_2), 1290 (s, NO_2), 1240, 1210, 1160, 1140 cm^{-1} (m, CF, or CO). Pmr ($CDCl_3$); 5.00 δ (s, CH_2). ^{19}F nmr ($CDCl_3$); -65.0 ppm (s, CF_2) (referenced to $CFCl_3$).

Bis(Fluorodinitroethoxy) Tetrafluoroethane (HTD)

Bis(fluorodinitroethyl) oxalate, 155 g (0.43 mol) was placed in a 1400-ml stainless steel autoclave and cooled to -78°. Hydrofluoric acid, 145 g (7.3 mol), and sulfur tetrafluoride, 460 g (4.3 mol) were condensed into the reactor. The reaction was heated to 100° in a rocker for four days. After cooling and venting the excess hydrofluoric acid and sulfur tetrafluoride, the product was washed out of the reactor with methylene chloride. The methylene chloride solution was treated with magnesium sulfate, filtered, and evaporated, leaving a pale yellow solid. The product was recrystallized from chloroform and hexane to yield 140 g, m p 33-35° 80% yield. IR (melt): 1600 (s, NO_2), 1310 (s, NO_2), 1200, 1 1140, 1120 cm^{-1} (s, CF, or CO). Pmr ($CDCl_3$): 5.05 δ (d, J = 15 H_2, CH_2).

Bis [2,2-Bis(Difluoramino)propyl] Thionocarbonate

A mixture of 1.62 g (10 mmol) 2,2-bis(difluoramino) propanol,[12] 0.58 g (5 mmol) thiophosgene, and 10 ml methylene chloride was placed in a three-neck flask equipped with a condenser, additional funnel, and thermometer. The mixture was cooled to 0°, and 0.79 g (10 mmol) of pyridine was added dropwise over 15 min at 0-5° with stirring. The reaction was allowed to warm to ambient temperature and stir for three hours. After the reaction mixture was evaporated to a semisolid residue, the residue was extracted

with ether. The ether solution was filtered and evaporated, leaving a pale yellow oil which was chromatographed on silica gel using 50% methylene chloride in hexane to yield 1.2 g colorless liquid, 66% yield. Elemental analysis calculated for $C_7H_{10}F_8N_4O_2S$: C, 22.96; H, 2.75; N, 15.30. Found: C, 23.10; H, 2.75; N, 15.51. Pmr ($CDCl_3$): 1.73 (quintet, CH_3CNF_2, J = 2Hz, area 3), 5.00 δ (quintet, CH_2CNF_2, J = 2 Hz, area 2).

Bis[2,2-Bis(Difluoramino)propyl] Difluoroformal (NFDF)

Bis[2,2-bis(difluoroamino)propyl] thionocarbonate, 0.5 g (1.4 mmol), and titanium tetrafluoride, 0.05 g (0.4 mmol), were placed in an 18-ml Monel high-pressure reactor. The reactor was cooled to -78° and charged with 5 g (46.3 mmol) of sulfur tetrafluoride. The reactor was then heated to 65° on a shaker for 18 hours. After the reactor was cooled and vented, the product was washed out with methylene chloride. The methylene chloride solution was stirred for 24 hours with mercury, filtered, and evaporated to a pale yellow liquid which was distilled at 48° (0.15 mm). Elemental analysis calculated for $C_7H_{10}F_{10}N_4O_2$: C, 22.59; H, 2.71; N, 15.06. Found: C, 22.02; H, 2.62; N, 14.76. Pmr ($CDCl_3$): 1.70 (quintet, CH_3CNF_2, J = 2 Hz, area 3), 4.40 δ (quintet, CH_2CNF_2, J = 2 Hz, area 2). ^{19}F nmr (referenced to $CFCl_3$) 27.6 (d, NF, J = 6 Hz), -65.9 ppm (S, CF_2).

REFERENCES

1. M. E. Hill and K. G. Shipp, U.S. Patent 3,526,667 (1970).

2. T. N. Hall, J. Org. Chem. 33, 4457 (1968).

3. P. E. Aldrich and W. A. Sheppard, J. Org. Chem. 29, 11 (1964).

4. V. Grakauskas, J. Org. Chem. 35, 3030 (1970).

5. C. D. Beard, K. Baum, and V. Grakauskas, J. Org. Chem. 38, 3673 (1973).

6. "Exploratory Research," SRI Report, Contract No. AT(04-3)-115, March 31, 1975).

7. "Exploratory Research," SRI Report, Contract No. AT(04-3)-115, May 1, 1971 to January 31, 1973.

8. R. J. Harder and W. C. Smith, J. Am. Chem. Soc., 83, 3422 (1961).

9. "Determination of Thermodynamic and Surface Properties," in Physical Mehtods of Chemistry, Part V, A. Weissberger and B. Rossiter eds. (Wiley-Interscience, New York, 1971).

10. Lawrence Livermore Laboratories Report, UCRL-78154 (May 5, 1976).

11. T. N. Hall, U.S. Patent 3,431,290 (1969).

12. W. H. Graham and J. P. Freeman, J. Org. Chem., 34, 2589 (1969).

DISTRIBUTION LIST

Addressee	No. Copies
Scientific Officer: Dr. R. S. Miller Power Program, Code 473 Office of Naval Research Arlington, VA 22217	1
Administrative Contracting Officer: Commander DCASR-San Francisco 866 Malcolm Road Burlingame, CA 94010	1
ONR Branch Office: Dr. Phillip Miller Office of Navla Research Room 447 760 Market Street San Francisco, CA 94102	1
Dr. Adolph Amster, Code SEA 0332 Head, Explosives and Pyrotechnics Branch Energy Conversion and Materials Division U.S. Naval Sea Systems Command Washington, D.C. 20362	1
Dr. Raymond McGuire, L-402 Lawrence Livermore Laboratory University of California P. O. Box 808 Livermore, CA 94550	1
Trojan Division IMC Chemical Group P. O. Box 310 Spanish Fork, UT 84660 Attention: Mr. W. J. Carroll	1

Dr. Joel Schnur, Code 5570 Naval Research Laboratory Washington, D.C. 20375	1
Jerry Smith Office of Naval Research 536 South Clark Street Chicago, IL 60605	1
Dr. H. J. Matsuguma Feltman Research Labs. ARRADCOM Dover, N.J. 07801	1
Director, Naval Research Laboratory, Attn: Code 2627 Washington, D. C. 20375	6
Office of Naval Research Department of the Navy Arlington, Virginia 22217 Attn: Code 102IP	6
Defense Documentation Center Bldg. 5, Cameron Station Alexandria, Virginia 22314	12