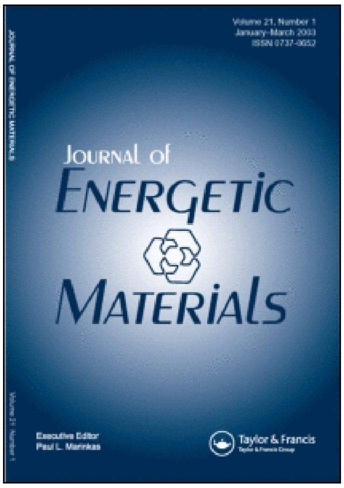

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Polynitroaliphatic explosives containing the pentafluorosulfanyl (SF_5) group: The selection and study of a model compound

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To cite this Article Sitzmann, M. E. , Gilligan, W. H. , Ornellas, D. L. and Thrasher, J. S.(1990) 'Polynitroaliphatic explosives containing the pentafluorosulfanyl (SF_5) group: The selection and study of a model compound', Journal of Energetic Materials, 8: 4, 352 — 374

To link to this Article: DOI: 10.1080/07370659008012580

URL: http://dx.doi.org/10.1080/07370659008012580

POLYNITROALIPHATIC EXPLOSIVES CONTAINING THE PENTAFLUOROSULFANYL (SF_5) GROUP: THE SELECTION AND STUDY OF A MODEL COMPOUND.

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ABSTRACT

An investigation concerning the effect of the pentafluorosulfanyl (SF_5) group on the properties of explosive nitro compounds is described. The investigation includes: (a) the preparation of several polynitro SF_5 model compounds; (b) the selection of the best model compound (based on overall properties such as melting point, stability, ease of synthesis, etc.); (c) the subjection of this compound to calorimetric determination of the heat and products of detonation. The initial results from the investigation support the hypothesis that the SF_5 group can provide explosives with improved properties (increased density, decreased sensitivity and good thermal stability) as well as produce energy in the detonation.

INTRODUCTION

Very few reports have appeared in the literature describing energetic materials based on the pentafluorosulfanyl (SF_5) group. In the late 1970's, Witucki and Frankel reported a polynitroaliphatic compound, 2-fluoro-2,2-dinitroethyl pentafluorothioacetate (1), containing the SF_5 moiety.[1,2] The ester (1) was described as a very dense, thermally stable, insensitive liquid.[1]

$$SF_5CH_2CO_2CH_2C(NO_2)_2F$$

1

Another report appeared in 1980 which connects SF_5 and NF_2 chemistry in terms of energetic materials. In this report, J. L. Bovin patented the reaction products from SF_5NF_2 and alkenes (e.g., see equation 1) as rocket fuels, but no test data was provided in the patent.[3]

$$SF_5NF_2 + C_2H_4 \longrightarrow SF_5CH_2CH_2NF_2 \qquad (1)$$

As part of a continuing search for energetic materials that combine high performance with low vulnerability towards accidental detonation, we began a more extensive investigation into the effect of the pentafluorosulfanyl group on the properties of explosive nitro compounds. The investigation was based upon the following considerations: (A) indications that the SF_5 group can provide explosive nitro compounds with improved properties, i.e., increased density, decreased sensitivity and good thermal stability; (B) the predicted energy release due to formation of HF in the detonation of SF_5 explosives [compare the average S-F bond energy (79 Kcal/mole[4]) to that of H-F (136 Kcal/mole[5])]; and (C) the predicted energy release from SF_5 compounds in metalized compositions (for example, compare the respective S-F and Al-F bond energies, 79 and 158 Kcal/mole[5]).

As stated above, there were indications that the SF_5 group would provide nitro explosives with increased density. For example, the polynitro ester (1) has a density of 1.697 g/ml (by comparison, the energetic plasticizer, bis(2-fluoro-2,2-dinitroethyl)formal, has a density of 1.60 g/ml). Although it is well established that substitution of fluorine for hydrogen in hydrocarbons leads to a significant increase in density (with the greatest change being produced by the first fluorine atom),[6] there is not nearly so much data available on the densities of compounds containing the pentafluorosulfanyl moiety. However, the data in TABLE 1 show that very high density compounds are obtained upon incorporation of the SF_5 group with incorporation of additional SF_5 groups leading to an additional, but more gradual increase in density. Thus, it was expected that the SF_5 group would provide nitro explosives with high density along with improved performance (detonation pressure as calculated by the Kamlet-Jacobs equation[7] varies with the square of the density).

TABLE 1

Liquid Densities of Pentafluorosulfanyl Derivatives

Compound	Density (g/ml)	Reference
C_6H_6	0.88	5
$C_6H_5NO_2$	1.20	5
$C_6H_5SF_5$	1.49	8
$C_3F_7SF_5$	1.80	9
$(C_2F_5)_2NCF_2CF_2SF_5$	1.86	9
$SF_5CF_2CF_2SF_5$	2.04	10
$SF_5CF_2CF_2CF_2CF_2SF_5$	2.05	10
$(SF_5)_2NCF_2CH_2SF_5$	2.13	11

Since 1 is described as an insensitive liquid, it would appear that the SF_5 group could also provide decreased sensitivity for nitro explosives. (The impact sensitivity for 1 is reported as >177cm/2.5Kg).[1]

The high intrinsic thermal stability of the SF_5 group was demonstrated by Sheppard[8], who was the first to prepare pentafluorosulfanylbenzene. He held this compound at 400°C in a sealed tube for 7 hours and found that less than 20% decomposition occurred under these rather drastic conditions. He also describes aryl SF_5 compounds as being inert to strong oxidizing and reducing conditions as well as strong acids and bases. These results certainly suggest that incorporation of the SF_5 group into nitro explosives can provide energetic materials with good chemical and thermal stability.

The approach to SF_5 explosives was to prepare several polynitro SF_5 model compounds and choose the best (based on melting point, stability, ease of synthesis, etc.) for in-depth physical evaluation. This evaluation would include determination of the impact sensitivity and thermal stability as well as the heat and products of detonation. Determination of the detonation products for the model compound was considered necessary since the SF_5 group must be converted to HF in the detonation if this group is to provide energy. Undesirable fluorine-containing detonation products would be CF_4, SF_6, SF_4, etc. It was also quite desirable that the SF_5 model compound have a reasonably high melting point (>50°C). Not only are impact sensitivity and detonation calorimetry measurements more convenient for solid samples, but use of solids would allow a more confident comparison of the impact sensitivity results from the model compound with those from similar non-SF_5 explosives.

RESULTS AND DISCUSSION

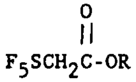
Synthesis of Polynitro SF_5 Model Compounds.

The SF_5 starting material for the preparation of the polynitro SF_5 model compounds was pentafluorothioacetyl chloride.[12] This material was hydrolyzed to pentafluorothioacetic acid[12] ($SF_5CH_2CO_2H$) which was condensed with polynitroalcohols such as 2,2-dinitropropanol, 3-fluoro-3,3-dinitropropanol and

3,3,3-trinitropropanol (similar to the method of Witucki and Frankel[1], see EXPERIMENTAL section). It was hoped that the resulting esters (compounds 2-4 in TABLE 2) would melt appreciably higher than ester 1 but 2 - 4 had low melting points which made them unattractive as candidates for further evaluation.

TABLE 2

Polynitroaliphatic Esters of Pentafluorothioacetic Acid



$F_5SCH_2\overset{\overset{O}{\|}}{C}-OR$

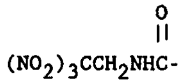
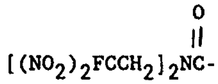
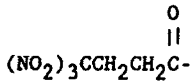
Compound	R	Melting Point, °C
2	$-CH_2C(NO_2)_2CH_3$	22
3	$-CH_2CH_2CF(NO_2)_2$	28
4	$-CH_2CH_2C(NO_2)_3$	32

In a search for higher melting SF_5 explosives, the starting pentafluorothioacetyl chloride was first reduced to pentafluorothioethanol[13] ($F_5SCH_2CH_2OH$) which was then treated with a variety of energetic intermediates including 2,2,2-trinitroethyl isocyanate,[14] N,N-bis(2-fluoro-2,2-dinitroethyl)carbamyl chloride,[15] 4,4,4-trinitrobutyric acid and tris(2-fluoro-2,2-dinitroethyl)chloroorthoformate.[16,17] The products (compounds 5 - 8) had sufficiently high melting points to be attractive candidates for this study (see TABLE 3).

TABLE 3

SF_5 Explosives from Pentafluorothioethanol

$ROCH_2CH_2SF_5$

Compound	R	Melting Point, °C	Density (g/cc)
5	 $(NO_2)_3CCH_2NH\overset{\overset{O}{\|}}{C}-$	81	1.82^a
6	 $[(NO_2)_2FCCH_2]_2N\overset{\overset{O}{\|}}{C}-$	61	-
7	 $(NO_2)_3CCH_2CH_2\overset{\overset{O}{\|}}{C}-$	45	-
8	$[(NO_2)_2FCCH_2O]_3C-$	96	1.81^a

[a] By gas pycnometer; Dr. Michael Chaykovsky, NSWC

Polynitro SF_5 Model Compound Chosen for Further Evaluation: Model Compound with Best Overall Properties.

The best polynitro SF_5 model compound, based mainly on melting point and ease of synthesis, was compound 8, tris(2-fluoro-2,2-dinitroethyl)-pentafluorothioethyl orthocarbonate. Compound 8 has a high melting point (96°C) and was synthesized in good yield from tris(2-fluoro-2,2-dinitroethyl)chloroorthoformate which is readily prepared [via the intermediate tris(fluorodinitroethoxy)methyl trichloromethyl disulfide] starting from fluorodinitroethanol and commercially available thiophosgene and trichloromethanesulfenyl chloride (see equation below and references 16 and 17).

$$\mathrm{FC(NO_2)_2CH_2OH + Cl_2C{=}S + Cl_3CSCl} \xrightarrow[\mathrm{CH_2Cl_2/H_2O}]{\mathrm{NaOH}}$$

$$\underset{65\%}{\mathrm{[FC(NO_2)_2CH_2O]_3CSSCCl_3}} \xrightarrow{\mathrm{Cl_2}} \underset{95\%}{\mathrm{[FC(NO_2)_2CH_2O]_3CCl}}$$

$$\xrightarrow{\mathrm{SF_5CH_2CH_2OH}} \underset{\underline{8},\ 74\%}{\mathrm{[FC(NO_2)_2CH_2O]_3COCH_2CH_2SF_5}}$$

Approximately 75 grams of compound 8 was prepared to provide sufficient material for further evaluation. The properties of 8 (including impact sensitivity and thermal stability) are shown in TABLE 4 and are compared with those of tris(2-fluoro-2,2-dinitroethyl)(2-nitroethyl)orthocarbonate (compound 9) and tetrakis(2-fluoro-2,2-dinitroethyl)orthocarbonate (compound 10). As expected, 8 has good thermal stability, but the most striking property of 8 is its appreciably lowered impact sensitivity relative to 9 and 10. This large reduction in impact sensitivity is a strong indication that the SF_5 group is effective in reducing the impact sensitivity of nitro explosives.

Heat and Products of Detonation for the Selected Polynitro SF_5 Model Compound (Compound 8).

The calorimetric determination of the heat and products of detonation for 8 was done at LLNL using a monel calorimeter bomb with a gold confining cylinder.[18,19] For the detonation

TABLE 4

Properties of Orthocarbonates

$[(NO_2)_2FCCH_2O]_3COCH_2R$

Compound	R	H_{50}% (cm)	Density (g/cc)	Thermal Stab.	mp °C
<u>8</u>	$-CH_2SF_5$	61; RDX-17[b] 91; RDX-28[c]	1.81[e]	0.04-0.05[g]	96
<u>9</u>	$-CH_2NO_2$[a]	41; RDX-28[b]	-	-	89
<u>10</u>	$-CF(NO_2)_2$	26; RDX-24[d]	1.80[f]	-	136

[a] Prepared as in reference 17
[b] Determined at NSWC
[c] Determined at LLNL; HMX-32, TNT-148
[d] Determined at NSWC[20]
[e] By gas pycnometer, Dr. Michael Chaykovsky, NSWC
[f] X-ray crystal density[21]
[g] Determined at LLNL; total gas from 0.25g after 22h at 120°C; HMX:<0.01, RDX:0.02-0.025, TNT: 0.01-0.012

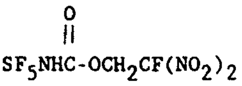
calorimetry experiments, compound <u>8</u> was pressed into two 26 gram charges using a pressure of 230 MPa (34,000 psi) under a vacuum of less than 0.5mm Hg at a temperature of 45°C to give average densities for the charges of 1.801 and 1.807 g/cc (99.5 and 99.8% of theoretical maximum density). The charges were initiated with a PETN booster and the heat of detonation was measured to be 1085 ± 25 cal/g.

The detonation calorimetry experiments showed that the only fluorine containing detonation product was HF and no CF_4, SF_4, SF_6, etc. were detected. This was a desirable result since the conversion of S-F to HF in the detonation is an exothermic process (compare respective bond energies of 79 and 135 Kcal/mole). Suprisingly, the main sulfur species (about 70%) recovered after the detonation was carbonyl sulfide (COS) and no significant amounts of SO_2, SO_3, or products derived therefrom were found. This is an important result since it indicates that incorporation of sulfur will not reduce the limited amount of oxygen available for hydrocarbon combustion. In fact, with the formation of COS, sulfur is not consuming oxygen in the detonation process but is behaving as an oxidant. Hydrogen sulfide (H_2S) was identified as the other major sulfur detonation product, a product in which sulfur also behaves as an oxidant.

Additional SF_5 Explosives.

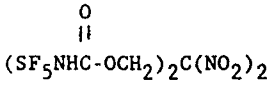
The evaluation of model compound 8 gave sufficiently encouraging results that additional energetic materials containing the SF_5 group have been and are currently being prepared. These materials include products from pentafluorosulfanyl isocyanate ($SF_5N{=}C{=}O$) and pentafluorosulfanyldichloroimine ($SF_5N{=}CCl_2$). Synthetic procedures for these products will be published in a subsequent paper.

The products from the SF_5 isocyanate included a number of carbamates and dicarbamates (such as 11, 12, and 13) (for the structure of 13, see TABLE 5). Representative SF_5



$$SF_5NH\overset{O}{\overset{\|}{C}}\text{-}OCH_2CF(NO_2)_2$$

11



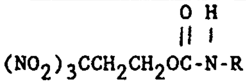
$$(SF_5NH\overset{O}{\overset{\|}{C}}\text{-}OCH_2)_2C(NO_2)_2$$

12

carbamates/dicarbamates exhibited high crystal densities [2.04(-40°C) and 1.99g/cc, respectively, for 11 and 12].[22] TABLE 5, which compares the impact sensitivity of the SF_5 carbamate 13 with that of a very similar non-SF_5 explosive 14, shows the greatly reduced impact sensitivity (higher impact number) for the SF_5 explosive. These additional results support

TABLE 5

Properties of Trinitropropyl Carbamates



$$(NO_2)_3CCH_2CH_2O\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{\overset{|}{N}}\text{-}R$$

Compound	R	H_{50}% (cm)	mp °C	Density (g/cc)
13	SF_5	117[b]	67	1.96[c]
14[a]	H	44[b]	82	1.74[d]

[a] Prepared by treating trinitropropyl chloroformate (from triphosgene[23] and 3,3,3-trinitropropanol) with ammonia
[b] RDX-28; determined at NSWC
[c] Calculated; see references 21 and 24
[d] Calculated; see reference 21

those from the model compound <u>8</u>, i.e., the SF_5 group will provide increased density and reduced sensitivity for nitro explosives.

We do not have a completely satisfactory explanation for the ability of the SF_5 group to decrease the sensitivity of nitro explosives. Possibilities include SF_5 acting as a radical trap to inhibit reaction or SF_5 desensitizing by a process in which impact energy is absorbed prior to breaking of the trigger linkage ($C-NO_2$ being a more probable trigger linkage than $C-SF_5$). A mechanism that may partially account for less sensitization by SF_5 relative to NO_2 involves the effect of free SF_5 and NO_2 on the explosive surrounding hot spots formed during sensitivity testing. This mechanism was based on a concept developed by J. M. McBride and co-workers[25] who studied the mechanical stress created by CO_2 molecules (generated by photo decomposition of a diacyl peroxide) which are left in a cavity too small to hold them. Using this concept, one can predict which functionality, NO_2 or SF_5, will generate the lower mechanical stress in a solid by comparing the relative volume requirement of bound versus free NO_2 with that of bound versus free SF_5. Assuming, for example, that bond breaking of both $C-NO_2$ and $C-SF_5$ will occur in hot spots during sensitivity testing, then the functionality (NO_2 or SF_5) that has the larger volume increase from the bound to the free state should create the greater stress on adjacent molecules and tend to produce an increase in sensitivity. The volume requirements of bound and free NO_2 and SF_5, determined by molecular modeling, are shown in FIGURE 1. (The MVOLUME command in the SYBYL molecular modeling software by Tripos Associates was used to obtain the plots and relative volumes shown; units are in cubic Angstroms.) In moving from bound NO_2 to free NO_2, there is a slight opening of the O-N-O angle which accounts for the small, initial increase in volume. To determine the volume requirements of a disordered NO_2 molecule, the volume which would be swept out if an NO_2 molecule moved with a screw motion was considered.[25] The results indicate that a free nitro group would need an almost 50% increase in spatial requirements over a bound nitro group. On the other hand, the geometry of a free SF_5 group does not differ significantly from that of a bound SF_5 group, and the disordered SF_5 group can best be approximated by an SF_6 molecule. As is shown, this results in less than a 20% increase in spatial requirements for a bound versus free SF_5 group.

SUMMARY AND CONCLUSIONS

Several polynitro SF_5 model compounds were prepared and one was selected for in-depth physical evaluation. The SF_5 compound exhibited high density and good thermal stability but most significantly showed greatly reduced impact sensitivity relative to very similar compounds that contain no SF_5 group. Detonation calorimetry for the model compound showed that the only fluorine containing detonation product was HF, a desirable result since conversion of S-F to HF in the detonation is exothermic (comparison of bond energies). The main sulfur species among the detonation products was COS, another beneficial result since sulfur did not consume any oxygen needed for hydrocarbon combustion. A number of energetic SF_5 carbamates and dicarbamates were prepared and representatives from this group were found to have high crystal densities (ranging from 1.90 to 2.04g/cc). These initial results support the hypothesis that the SF_5 group can provide nitro explosives with improved properties (increased density, decreased sensitivity, good thermal stability) and produce energy in the detonation.

Also during the course of this investigation, it was observed that the SF_5 group exhibits a strong tendency to lower the melting points of nitro explosives. Therefore the SF_5 group should also prove advantageous for the preparation of low melting energetic plasticizers, an area that is currently being explored.

EXPERIMENTAL

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. ^1H NMR spectra were determined on a Varian EM-390 spectrometer with TMS as the internal standard and IR spectra were obtained with a Perkin-Elmer Model 283 spectrometer. Melting points were recorded on a Thomas Hoover apparatus and are uncorrected. Impact sensitivities were determined on an ERL machine with type 12 tools and a 2.50kg weight.[26]

Pentafluorothioethanol[13]

Pentafluorothioacetyl chloride[12] (24ml, 41.4g) in 120ml of dry ether (distilled from lithium aluminum hydride) was added drop-wise to a mixture of 9.2g of lithium aluminum hydride and 200ml of dry ether stirred in a water bath at 15-25°C. The mixture was stirred at reflux temperature for 1 h before it was cooled in an ice bath and water (12ml) was slowly added drop wise (the mixture became very thick). After the mixture was stirred at room temperature for 15 min, it was again cooled in ice and a cold solution of 18ml of conc. sulfuric acid in 120ml of water was added. After standing overnight, essentially all solid material had dissolved. The ether layer was separated and the aqueous phase was extracted with 3 X 60ml of ether. The ether extracts were combined, dried over magnesium sulfate and most of the ether was removed by distillation through a vigreaux column (water bath temperature reached 70°C before distillation was stopped). Methylene chloride (100ml) was added and then removed through a vigreaux column. This was repeated with 100ml of methylene chloride and then the liquid residue was pulled under vacuum (water aspirator) for a short time to give 32.1g (92%) of pentafluoro- thioethanol. The product was combined with 110ml of dry 1,2-dichloroethane and the solution was dried over 50g of 3A molecular sieves for 72 h before the sieves were removed by filtration and washed with 3 X 50ml of dry dichloroethane. The filtrate (280ml) was then stored over 10g of 3A molecular sieves for at least 24 h before use.

N-(2,2,2-Trinitroethyl)-pentafluorothioethyl carbamate (5).

A solution of 1.2g (0.0058 mole) of 2,2,2-trinitroethyl isocyanate[14], 1.0g (0.0058 mole) of pentafluorothioethanol and 10mg of iron (III) 2,4-pentanedionate in 8ml of 1,2-dichloroethane was heated at 80°C for 1 h. The cooled solution was decanted from a small amount of dark insoluble material before the volatiles were removed to give an oil which was chromatographed on silical gel 40 (methylene chloride as eluent) to give 1.93g (88%) of product, mp 76-79°C. Crystallization from methylene chloride-hexanes gave 1.60g (73%), mp 81-82°C; ^1H NMR ($CDCl_3$): 3.95 (m, 2H), 4.63 (t, 2H), 4.93 (d, 2H), 5.6 (broad, 1H). IR (KBr): 3460, 3320 (NH), 1725 (C=O), 1610 (NO_2), 900-800 (SF_5) cm^{-1}. Anal. Calcd for $C_5H_7F_5N_4O_8S$: C, 15.88; H, 1.86; F, 25.12; N, 14.81; S, 8.48. Found: C, 15.92; H, 1.86; F, 25.06; N, 14.58; S, 8.80.

N,N-Bis(2-fluoro-2,2-dinitroethyl)-pentafluorothioethyl carbamate (6).

To a solution of 0.70g (0.002 mole) of N,N-bis(2-fluoro-2,2-dinitroethyl) carbamyl chloride[15] and 0.45g (0.0026 mole) of pentafluorothioethanol in 3ml of dry methylene chloride stirred in an ice bath was added 0.2ml of pyridine. After 3 h at room temperature 4ml of 10% hydrochloric acid was added and the methylene chloride layer was separated and dried over sodium sulfate. Removal of the volatiles gave an oil which was chromatographed on silica gel 60 (methylene chloride as eluent) to give 0.45g (46%) of essentially pure product. Crystallization from chloroform-hexanes gave crystals, mp 61-62°C; ^1H NMR ($CDCl_3$): 3.90 (m, 2H), 4.60 (t, 2H), 4.82 (d, 4H); IR (KBr): 1745 (C=O), 1620 (NO_2), 900-800 (SF_5).

Anal. Calcd for $C_7H_8F_7N_5O_{10}S$: C, 17.26; H, 1.66; F, 27.30; N, 14.37; S, 6.58. Found: C, 17.30; H, 1.63; F, 27.82; N, 14.25; S, 6.57.

Pentafluorothioethyl 4,4,4-Trinitrobutyrate (7).

A mixture of 0.55g (0.0025 mole) of 4,4,4-trinitrobutyric acid, 0.47g (0.0027 mole) of pentafluorothioethanol and 0.3ml of conc. sulfuric acid in 9ml of 1,2-dichloroethane was stirred at reflux temperature for 2 h in a flask with a reverse Dean Stark trap attached. The cooled reaction mixture was decanted from the insoluble sulfuric acid before the volatiles were removed to give a dark oil which was chromatographed on silica gel 40 using methylene chloride as eluent. The product was 0.81g (86%) of solid, mp 44-46°C. Crystallization from chloroform-hexanes raised the melting point to 45-46°C; ^1H NMR ($CDCl_3$): 2.83 (t,2H), 3.47 (t, 2H), 3.97 (m, 2H), 4.64 (t, 2H).

Anal. Calcd for $C_6H_8F_5N_3SO_8$: C, 19.10; H, 2.14; F, 25.18; N, 11.14; S, 8.50. Found: C, 19.19; H, 2.10; F, 24.82; N, 11.05; S, 8.48.

Tris(2-fluoro-2,2-dinitroethyl)-pentafluorothioethyl orthocarbonate (8).

Dry chlorine gas was passed for 2 h into a solution of 81.0g (0.124 mole) of tris(2-fluoro-2,2-dinitroethoxy)methyl trichloromethyl disulfide[16] in 300ml of dry 1,2-dichloroethane at 60-65°C. The solution was allowed to stand at ambient temperature overnight before the volatiles were removed with a stream-of nitrogen and heating at 60-65°C. The cooled residue was stirred with 300ml of dry hexanes to give tris(fluorodinitroethyl)chloroorthoformate[16,17] as an insoluble white solid. The hexanes solution was decanted from the solid which was washed with hexanes and then dissolved in 150ml of dry 1,2-dichloroethane. A solution (195ml) containing 22.3g (0.129 mole) of pentafluorothioethanol in 1,2-dichloroethane was added and the reaction solution was heated for 8 h at reflux temperature. The volatiles were removed to give 74.2g of residue which was dissolved in 150ml of warm chloroform. The hot solution was treated with charcoal, filtered and the filter pad was washed with 3 X 30ml of hot chloroform. Hexanes (100ml) was slowly added followed by cooling to -20°C to give 58.8g (74%) of crystals, mp 95-97°C. Recrystallization from chloroform-hexanes raised the melting point to 96-97°C; ^{1}H NMR ($CDCl_3$): 3.7 to 4.2 (broad m, 4H), 4.76 (d, 6H); IR (KBr): 1615 (NO_2), 880-800 (SF_5) cm^{-1}.

Anal. Calcd for $C_9H_{10}F_8N_6O_{16}S$: C, 16.83; H, 1.57; F, 23.66; N, 13.08; S, 4.99. Found: C, 16.89; H, 1.60; F, 23.11; N, 12.11; S, 5.14.

Polynitroaliphatic Esters of Pentafluorothioacetic Acid.

(a) 3,3,3-Trinitropropyl Pentafluorothioacetate (4).

A mixture of 0.57g (0.003 mole) of pentafluorothioacetic acid,[12] 1.2g (0.006 mole) of 3,3,3-trinitropropanol and 0.3ml of conc. sulfuric acid in 10ml of 1,2-dichloroethane was stirred at reflux temperature for 24 h in a flask with a reverse Dean Stark trap attached. The reaction mixture was cooled and the organic layer was decanted from the insoluble sulfuric acid. After the removal of volatiles from the organic layer, the residue (oil) was chromatographed on silica gel 40 using methylene chloride as eluent to give 0.99g (89%) of product, mp 32°C; ^{1}H NMR ($CDCl_3$): 3.52 (broad t, 2H), 4.35 (quintet, 2H), 4.70 (t, 2H); IR (film): 1870 (C=O), 1605 (NO_2), 920-800 (SF_5).

Anal. Calcd for $C_5H_6F_5N_3O_8S$: C, 16.54; H, 1.66; F, 26.16; N, 11.56; S, 8.83. Found: C, 16.44; H, 1.67; F, 26.01; N, 11.19; S, 8.84.

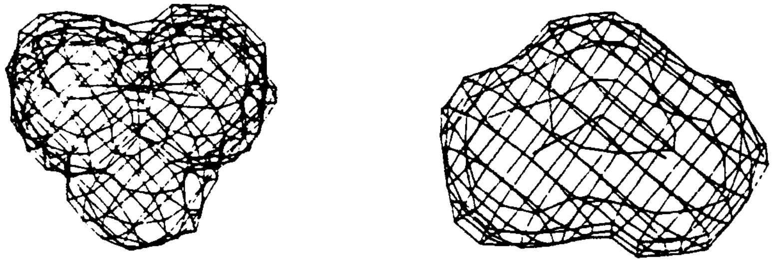
(b) 2,2-Dinitropropyl Pentafluorothioacetate (2) and 3-Fluoro-3,3-dinitropropyl Pentafluorothioacetate (3).

These esters were prepared in similar fashion to the trinitropropyl ester described above. The dinitropropyl ester (95% yield) has mp 22°C; ^{1}H NMR ($CDCl_3$): 2.27 (s, 3H), 4.40 (quintet, 2H), 5.10 (s, 2H); IR (film): 1775 (C=O), 1580 (NO_2) 920-800 (SF_5).

Anal. Calcd for $C_5H_7F_5N_2O_6S$: C, 18.87; H, 2.22; F, 29.86; N, 8.80; S, 10.08. Found: C, 18.90; H, 2.28; F, 29.74; N, 8.75; S, 10.03.

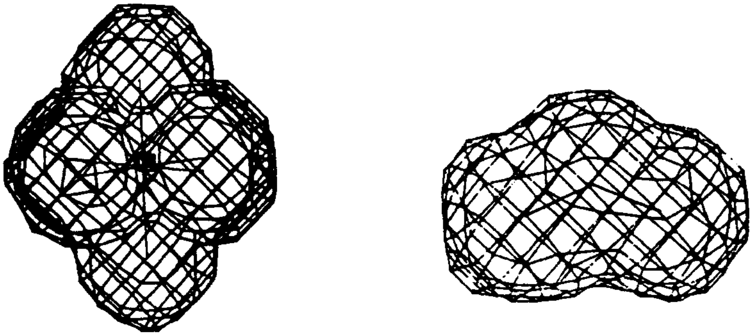
The fluorodinitropropyl ester (83% yield) has mp 28°C; ^{1}H NMR ($CDCl_3$): 3.17, 3.37 (d of t, 2H), 4.30 (quintet, 2H), 4.55 (t, 2H); IR (film): 1770 (C=O), 1605 (NO_2), 920-800 (SF_5).

Anal. Calcd for $C_5H_6F_6N_2O_6S$: C, 17.86; H, 1.80; F, 33.91; N, 8.33; S, 9.53. Found: C, 17.85; H, 1.92; F, 34.12; N, 8.32; S, 9.45.



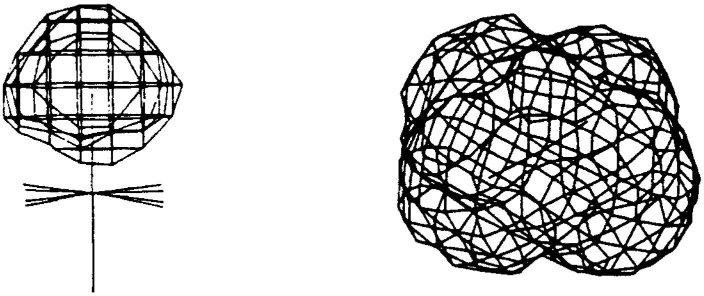
SF_5 VOLUME 48.4

$\cdot NO_2$ BOUND VOLUME 28.9



SF_6 VOLUME 57.4

NO_2 FREE VOLUME 29.4



SF_6-SF_5 VOLUME 9.0

FREE NO_2 WITH DISORDER VOLUME 42.6

FIGURE 1

Molecular Modeling Results (units are in cubic Angstroms)

ACKNOWLEDGEMENTS

Gratitude is extended to Dr. H. G. Adolph of NSWC for suggesting this study which was supported by the NSWC Independent Research Program. J. S. T. acknowledges Tripos Associates, Inc., St. Louis, Missouri, for a grant of the SYBYL Molecular Modeling Software.

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