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Organic Difluoramine Derivatives

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Abstract This article reviews recent developments in synthesis and characterizations of organic difluoramine (NF_2) derivatives since the 1980s. Specific classes of chemical compounds are covered: cyclic difluoramino-nitramines, especially *gem*-bis(difluoramino)-substituted analogs of conventional nitramines; products from the relatively new transformation of electrophilic difluoramination; other classes of difluoramines such as polymers, plasticizers, and compounds not otherwise categorized. Also covered are aspects of other recently developed synthetic methodology to prepare compounds in this general class, as well as purely theoretical treatments of the chemistry and properties of this class.

Keywords Difluoramine · Difluoroamine · Difluoramination · HNFX · Nitramines

Abbreviations

BNMO	3,3-Bis(nitratomethyl)oxetane
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

HNFX	3,3,7,7-Tetrakis(difluoramino)octahydro-1,5-dinitro-1,5-diazocine
NMMO	3-Methyl-3-(nitratomethyl)oxetane
PETN	Pentaerythrityl tetranitrate
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RNFX	5,5-Bis(difluoramino)hexahydro-1,3-dinitropyrimidine
TNFX	3,3-Bis(difluoramino)octahydro-1,5,7,7-tetranitro-1,5-diazocine

1
Introduction

This review will emphasize recent developments in synthesis and characterizations of organic difluoramine (NF_2) derivatives[1]. Organic monofluoramines have been recently reviewed [1–3], as many of them tend to be suitable as electrophilic fluorinating reagents. Early [4–7] and recent [8] reviews of inorganic N–F derivatives have appeared.

Interest in organic difluoramines has been predominantly due to their potential as energetic materials in rocket propellant and explosives formulations. This potential derives from the intrinsically high energy of the difluoramino (NF_2) group relative to other substituents of oxidizing capability in energetic ingredients, such as nitro (NO_2). While this difference in energy content is not conspicuously apparent in thermodynamic properties such as the heats (enthalpies) of formation, which tend to be more negative than those of analogous nitro derivatives [9], the energetics of processes of interest (e.g., combustion) manifest this difference distinctly, as will be seen in discussions of these properties for certain compounds of interest. Thus, quantitative measures of realistic chemical processes (such as specific impulse of rocket propellant combustion) offer a more valid comparison of the energetics of difluoramino derivatives.

An attractive feature of fluorinated oxidizers is that their combination with metal fuel ingredients (e.g., aluminum or boron) offers a propellant performance advantage of producing more moles of more-volatile, lower-molecular-weight combustion products, such as BOF (O=B–F) rather than simple oxides (B_2O_3) produced by solely oxygenated oxidizers [10, 11]. Difluoramino derivatives should also offer a kinetically more available form of fluorine (to achieve higher combustion or explosion efficiency) than the "stabler" fluoroalkyl (C–F) derivatives that have been employed in energetic formulations.

The difluoramino (NF_2) substituent is also more dense than NO_2, contributing favorably to explosive performance and to the propellant property density×(specific impulse). According to Ammon's linear vol-

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[1] This review will use the colloquial American English term "difluoramino" rather than the (admittedly more systematic) equivalent "difluoroamino", which is more commonly used in non-English publications and English translations of non-English (especially Russian) publications.

ume additivity method [12], NF_2 has a substituent density of 2.303 g cm^{-3} (52.0035 amu/37.504 Å^3) vs. an NO_2 density of 2.166 g cm^{-3} (46.005 amu/ 35.265 Å^3).

2
Historical Development

Although an organic difluoramine derivative (CF_3NF_2 by-product formed by direct fluorination of silver cyanide) had been reported as early as 1936 [13], the impetus for the major development of this class of compound was the recognition by the US Advanced Research Projects Agency and Department of Defense that various N–F compounds, especially organic difluoramines, offered the prospect of being superior propellant oxidizers, for reasons alluded to above. Thus, Project Principia was carried out over the period 1958–1965 to explore the possibilities offered by these materials [14]. While research projects funded by this program ended in 1964–1965, open-literature publications of their results appeared for several years afterward. Hundreds of organic difluoramines (even hundreds with the *gem*-bis(difluoramino) linkage, $C(NF_2)_2$) were prepared under the aegis of Project Principia and of foreign efforts along the same lines. Several good reviews [15–25] over subsequent years have described the early organic difluoramine chemistry of this era.

Project Principia failed to produce a difluoramine-based oxidizer candidate sufficiently superior to replace nitro derivatives that were the technological standards. Almost all difluoramine derivatives at that time had inadequate stability, insensitivity, or physical properties to serve as such replacements. Organic difluoramine research languished for a couple of decades afterward, though results were published throughout the 1970s and 1980s by a few researchers, especially Fokin and coworkers at the Nesmeyanov Institute of Heteroorganic Compounds (Moscow).

3
A New Hope

A resurgence in interest in organic difluoramines occurred in the USA in the late 1980s, based on support by the Office of Naval Research [26], with additional support soon received from the Ballistic Missile Defense Organization (manager of the Strategic Defense Initiative program). Efforts were made to pursue a specific new class of compounds proposed by Baum and Archibald of Fluorochem [27]: cyclic difluoramino-nitramines that were analogs of conventional nitramines (e.g., HMX and RDX) but with *gem*-bis(difluoramino) groupings replacing some of the nitramine groups. Also in the late 1980s, Zheng et al. (Xi'an Modern Chemistry Institute, China) alluded, in a conference proceeding, to preparing at least one member of this class [28]: "For example, the difluoramination of cyclic derivatives of 1,3-diaminoacetone (the substituents on the nitrogen atoms were $-NO_2$... etc.) is easier to be carried out than that of the chain derivatives." However, no specific example was described, and subsequent journal reports [29,30] of other chemistry from this conference proceeding made no mention of cyclic derivatives.

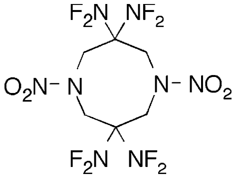
This section will review a variety of experimental results arising from this renaissance period in difluoramine chemistry.

3.1
Cyclic Difluoramino-nitramines

Although nitramines containing (difluoramino)alkyl substituents had been prepared as early as 1963 and published by 1972 [31,32], they were *vic*-bis(difluoramino)-substituted primary nitramines and *N*-alkyl-*N*-(difluoraminomethyl)nitramines with insufficient stability and difluoramine content to constitute attractive candidates for formulations. In contrast, the newly proposed *gem*-bis(difluoramino)-substituted cyclic nitramines would have high difluoramine content and should exhibit high densities compared to the analogous conventional nitramines. The favorable effect of cyclic (or even cage) structures in imparting desirable higher density and better oxygen balance was better appreciated by this time. It would also be expected that difluoramine derivatives with a nitramine component would exhibit better physical properties (e.g., melting point) than the earlier simple (difluoramino)alkanes. However, cyclic nitramines with β,β-bis(difluoramino) substituents relative to nitramine components posed a likely synthetic challenge: conventional methodology for preparation of *gem*-bis(difluoramino)alkanes required strongly acidic conditions (such as anhydrous sulfuric acid, fuming sulfuric acid, difluorosulfamic acid, or fluorosulfonic acid) with which most nitramines are incompatible. Alternatively, conventional nitrolyzably protected heterocyclic nitrogens tended not to survive such difluoramination conditions either. So, finding methodology to efficiently prepare this new class of organic difluoramine would be a daunting task.

3.1.1
HNFX

On the basis of estimations (personal communications from Baroody E of the Naval Ordnance Station, Indian Head, MD; Ammon HL of the University of Maryland, College Park; and Adolph HG, Koppes WM, and Lawrence GW of the Naval Surface Warfare Center, Silver Spring, MD, cited in [33]) of physical and performance properties of several *gem*-bis(difluoramino)-substituted



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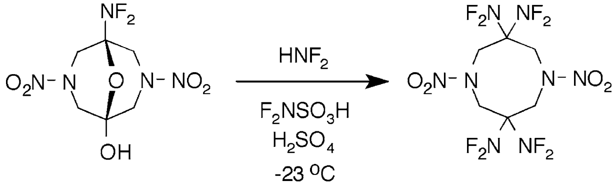
analogs of known cyclic nitramines, 3,3,7,7-tetrakis(difluoramino)octahydro-1,5-dinitro-1,5-diazocine (HNFX, **1**) was seriously pursued early on as the most attractive candidate member of this class. (The acronym HNFX [26] signifies the HMX analog of the class of NF_2-modified cyclic nitramine explosives.)

Synthesis

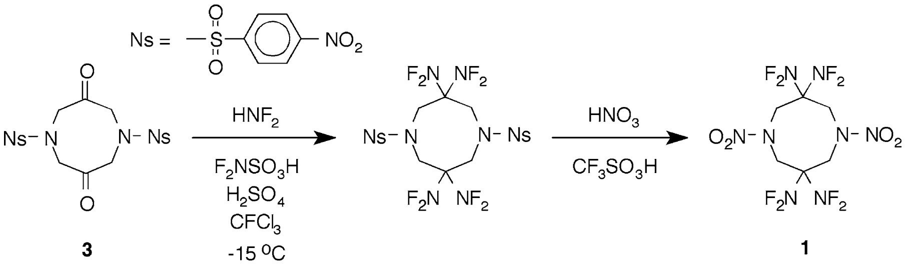
In the first synthesis of HNFX, the use of a nitramine reactant, 5-(difluoramino)-3,7-dinitro-9-oxa-3,7-diazabicyclo[3.3.1]nonan-1-ol (**2**), in a typical difluoramination reaction (difluoramine–difluorosulfamic acid–sulfuric acid) produced HNFX in only ~ 1% yield [34] (Scheme 1).



2 **1**

Scheme 1 The first preparation of HNFX (**1**)

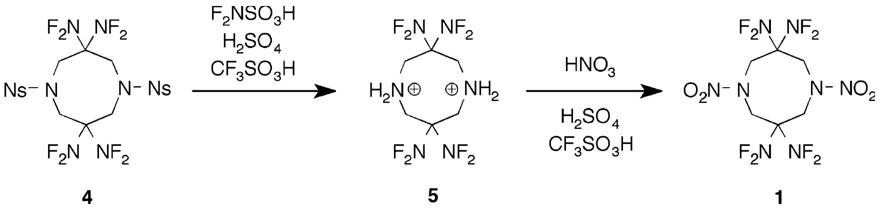
Therefore, the *N*-nitro component was preferably incorporated after difluoramination to produce *gem*-bis(difluoramino)alkyl components. A dilemma encountered in the preparation of a β,β-bis(difluoramino)-substituted heterocycle, such as a 3,3,7,7-tetrakis(difluoramino)octahydro-1,5-diazocine, is that the nitrogen in most aminoacetone derivatives would be more basic than the ketone carbonyl (and oxygen in hemiaminal intermediates). This would deactivate difluoramination via difluoramino-carbocations unless the nitrogen is protected with a sufficiently electronegative protecting group to favorably affect this basicity. The dilemma was resolved by employment of a strong-acid-stable N-protecting group, 4-nitrobenzenesulfonyl, allowing acceptably efficient difluoramination of the ketone reactant tetrahydro-1,5-bis(4-nitrobenzenesulfonyl)-1,5-diazocine-3,7(2*H*,6*H*)-dione (**3**) while keeping the *N*-nosyl group intact [35] (Scheme 2). Also, trichlorofluoromethane ($CFCl_3$) was utilized as an inert cosolvent for difluoramine in order to alleviate the known hazards of condensed-phase neat HNF_2. The next dilemma



Scheme 2 An improved preparation of HNFX (**1**): *p*-nosyl N-protection during difluoramination plus nitrolysis with protonitronium ion

encountered in this approach, however, was the known reluctance of more-electronegatively substituted amides and of sterically hindered amides to undergo direct nitrolysis. The *N*-nosyl protecting group could be directly nitrolyzed by use of the protonitronium (NO_2H^{2+}) reagent formed from a nitronium source in the presence of a superacid, such as the system nitric acid–trifluoromethanesulfonic acid [36].

Although this transformation worked well enough in small reactions, it proved inefficient upon scale-up. A superior, scalable one-pot process (Scheme 3) from diazocinedione to HNFX was developed more recently [37]. Here, efficient protolytic N-denosylation is effected by trifluoromethanesulfonic acid added to the crude 3,3,7,7-tetrakis(difluoramino)octahydro-1,5-bis(4-nitrobenzenesulfonyl)-1,5-diazocine intermediate (**4**), still contained in the acid system used for difluoramination after expulsion of volatiles such as excess difluoramine and trichlorofluoromethane. The denosylated intermediate, a 3,3,7,7-tetrakis(difluoramino)octahydro-1,5-diazocinium salt (**5**), is straightforwardly nitrated to HNFX by added nitric acid.



Scheme 3 Scalable preparation of HNFX (**1**): protolytic N-denosylation plus simple nitration

Chapman et al. [36] had suggested that solvents with less ozone-depleting potential than $CFCl_3$ could be used, and a preliminary demonstration of difluoramination with dichloromethane solvent was described. Adolph and Stern more recently chose *n*-pentane as an example of an alternative cosolvent (with $CFCl_3$) for this purpose [38].

Structure

X-ray crystallographic analysis of HNFX recrystallized from a variety of solvent systems showed an interesting, unpredicted feature (Fig. 1): channels, with a threefold axis of symmetry surrounded by HNFX molecules, passing through each unit cell [36]. Analysis sometimes showed the presence of disordered mass due to recrystallization solvent(s), though solvent-free crystals can be prepared by driving out solvent (e.g., by heating under vacuum).

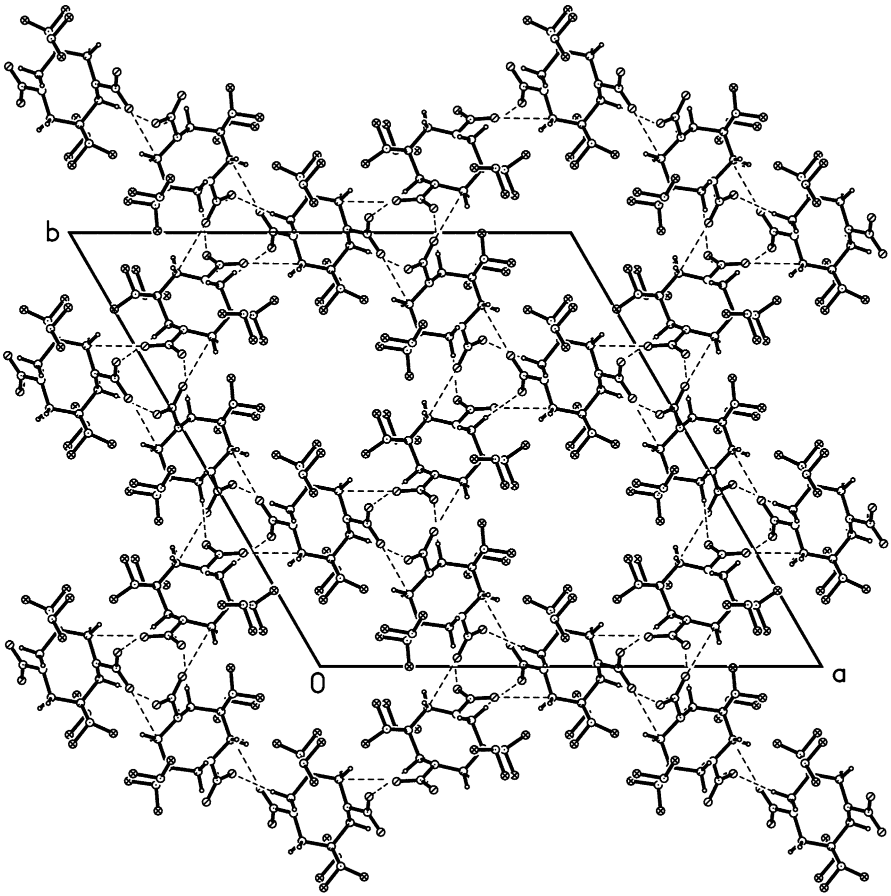


Fig. 1 Crystal packing of HNFX in the trigonal crystal form; empty channels occur along threefold axes

The Manifest Density of HNFX

The crystal density of the initial form is 1.807 $\mathrm{g\,cm^{-3}}$ (21 °C), assuming a vacuum (i.e., zero mass) in the channels. This contrasts significantly with a density of 2.027 g cm^{-3} recently predicted by Ammon [39] from its possible crystal packings. However, cyclic nitramines, especially those incorporating eight-membered rings, are well known to exhibit polymorphism [40, 41]: HMX has four known polymorphs of different densities. The phenomenon of solvent inclusion observed in HNFX crystals is also qualitatively similar to that found in the first polymorph of hexanitrohexaazaisowurtzitane (α-CL-20) [42], which is the lowest-density form. With the promise of preparing a higher-density polymorph of HNFX, which would dramatically improve its attractiveness as a munitions ingredient, several technical approaches have been undertaken to effect such a phase transition. Peiris monitored HNFX for phase transitions during compression in a diamond anvil cell at pressures up to 5 GPa but observed none [43]. Nicol and coworkers subjected HNFX to pressures up to 30 GPa in a diamond anvil cell and studied it by synchrotron radiation X-ray diffraction and Raman and infrared spectroscopy at ambient temperature, also without observing evidence of a polymorphic transition [44]. More recently, a combined experimental and modeling study of the vibrational spectra of solid HNFX was reported [45]. Kalyon and coworkers have performed a systematic study of recrystallizations of HNFX with several different solvent systems [46], similarly without evidence of a new polymorph, though they independently computationally corroborate the feasible existence of a higher-density form [47]. While these failures to achieve formation of a new polymorph of HNFX might indicate that its manifest density is that observed in the crystals prepared to date, they may instead reflect the recognized poor understanding, in general, of how to predict and prepare new stable polymorphs [48].

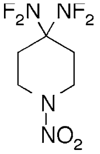
Hazard Properties

Sensitivity measurements on HNFX (the "polymorph" tentatively called α-HNFX) show it to be comparable to CL-20 and PETN on impact but more sensitive by friction and electrostatic discharge [49]. Impact sensitivity (Explosives Research Laboratory impact tester, modified Type 12 tooling, 2.5-kg weight): HNFX h_{50} = 8 cm; CL-20 $\sim$ 8 cm; PETN = 10–13 cm; RDX = 16–17 cm. Friction sensitivity (Allegany Ballistics Laboratory test, per MIL-STD-1751, threshold initiation value): HNFX fired at 72 lbf; PETN low-fires ranged 159–316 lbf. Electrostatic sensitivity: HNFX fired at 0.05 J; PETN showed 10/10 no-fires at 0.25 J. DSC (2 °C min^{-1} per ASTM E537) onset/peak: 221/231 °C.

However, it is also well known that sensitivities of the polymorphs of another eight-membered-ring nitramine, HMX, correlate inversely with density [50–52]: the lowest-density δ form exhibits the highest sensitivity. If this correlation transfers to HNFX, a higher-density "β-HNFX" would exhibit lower sensitivity than "α-HNFX".

3.1.2
4,4-Bis(difluoramino)-1-nitropiperidine

Although HNFX was expected to be the most attractive target difluoramino-nitramine in terms of performance, other examples of the class were desired in order to characterize the behavior of the mixed functionalities present in the compounds. For this reason, a synthetically more straightforward example was prepared [53]: 4,4-bis(difluoramino)-1-nitropiperidine (**6**). As an N-protected γ-aminoketone, the starting material, 1-acetyl-4-piperidinone, would have fewer complications in undergoing difluoramination than β-aminoketones used for more-energy-dense heterocycles. The acetyl N-protecting group would also undergo nitrolysis more readily than *N*-nosyl-protected precursors, such as for HNFX.



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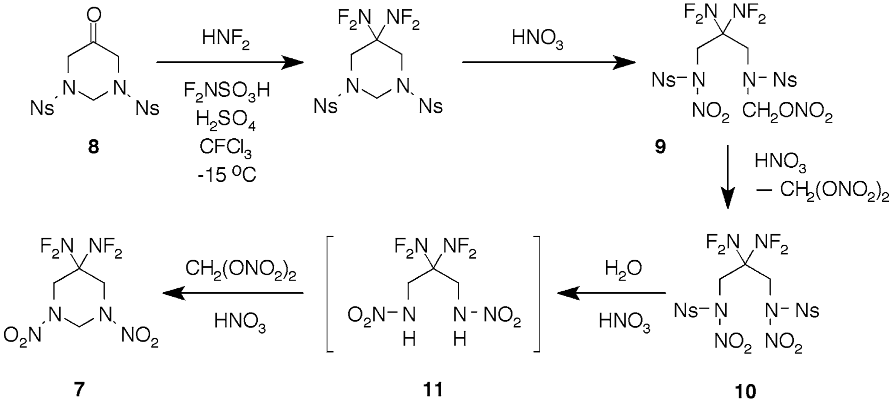
Mass spectral fragmentation pathways of several cyclic nitro and difluoramino compounds, including HNFX and 4,4-bis(difluoramino)-1-nitropiperidine, were studied by Smith and coworkers [53], and their thermal decomposition behavior was reported by Oxley et al. [54]. Kuo and Young studied the burning behavior of formulated propellants (including boronized and aluminized compositions) containing 4,4-bis(difluoramino)-1-nitropiperidine in comparison to simple nitro derivatives 1,4-dinitropiperazine and 1,4,4-trinitropiperidine [55]. They determined that a non-metallized propellant based on 4,4-bis(difluoramino)-1-nitropiperidine offered an enhancement of specific impulse by 7.5% over that of a formulation based on 1,4-dinitropiperazine. The difluoramine-containing propellants had burning rates significantly higher than those of the nitramines. However, they exhibited a drastic and uncontrollable increase in burning rate at an initial temperature of 50 °C. This was believed to be caused by melting of the 4,4-bis(difluoramino)-1-nitropiperidine at 40 $\sim$ 50 °C in the formulations (even though the pure ingredient melts at 71–72 °C), producing a burn rate as high as 508 cm s^{-1}.

3.1.3
RNFX

Another attractive example of the class of difluoramino-nitramines was pursued by Chapman and Nguyen [56]: RNFX, 5,5-bis(difluoramino)hexahydro-

1,3-dinitropyrimidine (**7**). (RNFX is an RDX analog in the series of NF_2-modified cyclic nitramine explosives.) A key step of the synthesis (Scheme 4) was mechanistically similar to that of HNFX: tetrahydro-1,3-bis(4-nitrobenzenesulfonyl)pyrimidin-5(4*H*)-one (**8**) served as an *N*-nosyl-protected reactant for difluoramination of the carbonyl group. However, subsequent conversion to a heterocyclic nitramine product differed significantly from the route used to prepare HNFX. Rather than nitrolytic or protolytic denosylation of the hexahydropyrimidine intermediate with protonitronium ion or superacid, the hexahydropyrimidine ring was intentionally cleaved at the methylene bridge by treatment with $\sim$ 98% nitric acid. The resulting initial product, 2,2-bis(difluoramino)-*N*-(nitratomethyl)-*N*′-nitro-*N*,*N*′-bis(4-nitrobenzenesulfonyl)-1,3-propanediamine (**9**), underwent further nitrolysis to 2,2-bis(difluoramino)-*N*,*N*′-dinitro-*N*,*N*′-bis(4-nitrobenzenesulfonyl)-1,3-propanediamine (**10**), which was adventitiously N-denosylated by water contained in the nitric acid, forming 2,2-bis(difluoramino)-*N*,*N*′-dinitro-1,3-propanediamine (**11**). This did not accumulate but combined spontaneously with the formaldehyde equivalent generated in the nitrolysis, methylene dinitrate, which recyclized the primary nitramine termini to form RNFX.

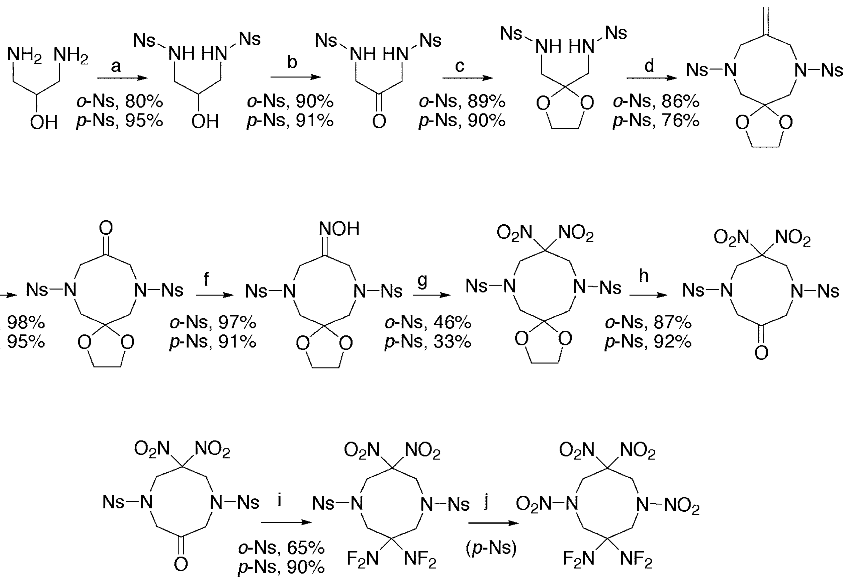


Scheme 4 The first preparation of RNFX (**7**)

Nucleophilic N-desulfonation of *N*-nitrosulfonamides is a well documented transformation [57–60], and N-denosylation of the 2,2-bis(difluoramino)-*N*,*N*′-dinitro-*N*,*N*′-bis(4-nitrobenzenesulfonyl)-1,3-propanediamine intermediate (**10**) was relatively facile, employing only the minor water content of the nitric acid medium. Beyond definitive identification of its preparation, properties of RNFX have not been experimentally well elucidated.

3.1.4
TNFX

Another early conceptual target member of this class was one in which one each of two nitramine groups of HMX was replaced by a *gem*-bis(difluoramino) grouping and a *gem*-dinitro grouping. This would provide a product of better oxygen balance than HNFX but still some NF_2 content. The introduction of asymmetric components into a 1,5-diazocine substrate suitable for the incorporation of three different energetic functionalities was a formidable challenge, which was undertaken by Axenrod et al. [61]; the successful synthetic sequence is shown below (Scheme 5). The ultimate nitrolysis step proved inordinately difficult because of steric and electronic deactivating effects of $C(NF_2)_2$ *and* $C(NO_2)_2$. Thus, the reaction required not only a superacid (trifluoromethanesulfonic acid) as a medium for nitric acid in order to generate protonitronium reagent, but also the addition of a strong Lewis acid, antimony pentafluoride, in order to increase the superacid strength to generate a higher concentration of NO_2H^{2+}. Upon its successful preparation, the new product (**12**) was named TNFX (a tetranitro derivative in the series of NF_2-modified cyclic nitramine explosives).



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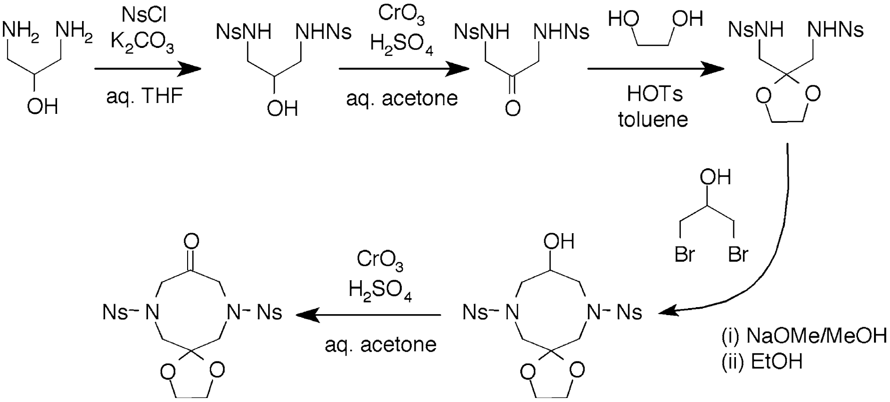
Scheme 5 The first preparation of TNFX (**12**). Reagents and conditions: *a* *o*- or *p*-nitrobenzenesulfonyl chloride, THF-H_2O, K_2CO_3, r.t.; *b* CrO_3, H_2SO_4, acetone, r.t.; *c* ethylene glycol, *p*-TsOH, toluene; *d* $CH_2{=}C(CH_2Br)_2$, K_2CO_3, acetone, reflux; *e*(i) O_3, CH_2Cl_2, - 78 °C, *e*(ii) Me_2S; *f* $NH_2OH{\cdot}HCl$, NaOAc, EtOH, reflux; *g* HNO_3, NH_4NO_3, urea; *h* conc. H_2SO_4, r.t.; *i* HNF_2-F_2NSO_3H-H_2SO_4-$CFCl_3$, - 15 °C; *j* HNO_3-CF_3SO_3H-SbF_5

Yoon and coworkers have explored alternative preparations (Scheme 6) of the asymmetric precursors to TNFX [62].



Scheme 6 An alternative preparation of precursors to TNFX or HNFX

TNFX proved structurally interesting in forming two crystallographically distinct polymorphs [63] upon crystallization from its first preparation (as HNFX was hoped to do): a low-density trigonal form of $\rho = 1.712\ \mathrm{g\,cm^{-3}}$ and a high-density orthorhombic form of $\rho = 1.904\ \mathrm{g\,cm^{-3}}$. Thus, the low-density trigonal form of HNFX ($\rho = 1.807\ \mathrm{g\,cm^{-3}}$) has an experimentally observed density enhancement of $0.095\ \mathrm{g\,cm^{-3}}$ imparted by replacement of $C(NO_2)_2$ in TNFX with $C(NF_2)_2$ in HNFX. A similar enhancement in a previously unobserved orthorhombic form of HNFX would provide an experimental density of $\rho = 1.999\ \mathrm{g\,cm^{-3}}$, coincidentally identical to the (still attractive) value initially estimated for HNFX by Ammon [26].

Beyond synthetic and structural elucidation, properties of TNFX have not been experimentally well characterized.

3.1.5
Properties and Applications

Solid-state heats of formation of some cyclic difluoramino-nitramines have been computationally estimated by Politzer and Lane [9]: HNFX, $-67\ \mathrm{kcal\,mol^{-1}}$; TNFX, $-39\ \mathrm{kcal\,mol^{-1}}$; RNFX, $-21\ \mathrm{kcal\,mol^{-1}}$. Application of these values to rocket engine specific impulse (I_{sp}) calculations (performed with a code such as the Air Force Specific Impulse Program [64]) allows ranking of the cyclic difluoramino-nitramines (as monopropellants) relative to state-of-the-art nitramines: β-HMX < ε-CL-20 < TNFX < RNFX < HNFX. The I_{sp} of CL-20 has been reported by Hong et al. as 272.6 s [65, 66]. An early estimate of the I_{sp} of RNFX was reported by Politzer et al. as being 108% of that of HMX, which is 265.1 s [67].

As reports of preparations of this new class of energetic material started appearing, their potential in ordnance applications started receiving notice overseas. Feng reviewed recent examples of renewed interest in organic difluoramine derivatives in Western research [68, 69], including early reports on the pursuit of HNFX. Tan reported the new preparation of HNFX [36] to the Xi'an Modern Chemistry Research Institute [70]; and Li et al. cited Tan's report in an outlook on the prospects of this and other classes of ingredients in advanced solid propellants [71, 72]. This new class of ingredient has received interest in Korea as well [73].

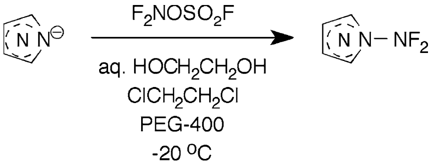
3.2
Electrophilic Difluoramination and Its Products

In the 1990s, researchers throughout the Russian Academy of Sciences reported syntheses and characterizations of a variety of compounds derived from a new transformation, electrophilic difluoramination, particularly of some compounds derived from difluoramination of various nitroalkyl reactants. Examples of such new products were first described by Pepekin and coworkers in terms of thermodynamic properties [74, 75] and physical properties [76, 77], which will be mentioned below.

3.2.1
Syntheses

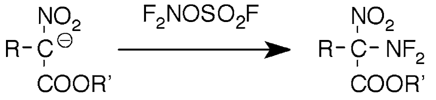
Synthetic routes involving the new transformation started appearing in 1996. Shevelev and coworkers [78] prepared a variety of *N*-(difluoramino)azoles (Scheme 7) by reactions of electronegatively substituted azole anions with *N*,*N*-difluorohydroxylamine-*O*-sulfonyl fluoride ("*O*-fluorosulfonyl-*N*,*N*-difluorohydroxylamine"), F_2NOSO_2F, preferably in water–ethylene glycol–dichloroethane mixtures with a phase transfer catalyst such as polyethylene glycol (PEG-400). If the pK_a of an azole was < 5, there was no interference by formation of *N*-fluorosulfonylazoles. They later offered computational predictions of molecular and crystal parameters and of detonation and combustion parameters of five examples of this class of compound [79].

Fokin et al. used *N*,*N*-difluorohydroxylamine-*O*-sulfonyl fluoride for electrophilic difluoramination of anions of α,α-dinitroalkyl derivatives, such as



Scheme 7 Electrophilic difluoramination of azole (pyrazole, imidazole, triazole) anion [78]

1,1-dinitroethane and dinitroacetonitrile. Sodium dinitroacetonitrile underwent difluoramination in 70.8% yield, but the other compounds formed in 18.8–29.3% yields at the time of this report [80, 81]. However, yields of dinitroacetate esters were later improved to 50–52%, and other α-mononitro derivatives were prepared in 67–91% yields [82, 83] (Scheme 8).



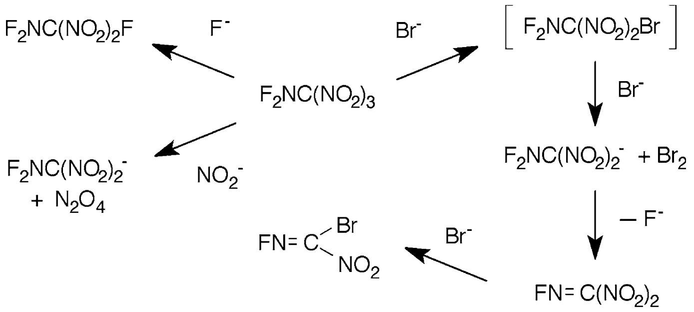
R	R'
NO_2	Me; Et
COOMe	Me
COOEt	Et
CN	Me; Et

Scheme 8 Electrophilic difluoramination of nitroalkyl anion [82, 83]

The chemistry of (difluoramino)dinitroacetonitrile was further explored as well [84, 85]: it underwent common transformations such as hydrolysis to (difluoramino)dinitroacetamide; reaction with HCl in anhydrous methanol to form the *O*-methyl imidate hydrochloride; trimerization to 2,4,6-tris[(difluoramino)dinitromethyl]-1,3,5-triazine; and reaction with azides (NaN_3, HN_3) to make 5-[(difluoramino)dinitromethyl]tetrazoles.

Electrophilic difluoramination of certain (especially tertiary) alkoxide salts and *N*-hydroxyimide salts with F_2NOSO_2F produced new difluoraminoxy derivatives [86, 87].

Khisamutdinov et al. showed that the difluoramino group in various (difluoramino)dinitromethane derivatives could be displaced by azide anion to make azidodinitromethyl derivatives [88, 89]. In contrast, a *nitro* group in (difluoramino)trinitromethane was displaced by nucleophiles such as fluoride and nitrite [90, 91]. The nitrite by-product keeps yields low by competitive reaction with the starting material, resulting in (difluoramino)dinitromethane anion side product. With bromide nucleophile, the course of reaction was unexpectedly complex, as the initial bromo(difluoramino)dinitromethane un-



Scheme 9 Nucleophilic displacement reactions in (difluoramino)trinitromethane

derwent further reactions (bromide additions and fluoride elimination) to produce bromo(*N*-fluoro)nitromethanimine (Scheme 9).

3.2.2
Thermochemical and Other Properties

Pepekin's first report [74, 75] of products in this class gave experimental values of thermodynamic properties such as heats of formation. Also prior to the synthetic methodology descriptions [80, 81], Litvinov et al. [76, 77] reported various physical properties (melting point and/or boiling point, density) of several members of this class, including a particularly dense and energetic one: bis[2-(difluoramino)-2,2-dinitroethyl]nitramine, $[NF_2C(NO_2)_2CH_2]_2N{-}NO_2$ (**13**). This compound had an attractive density of 2.045 g cm^{-3}, a melting point of 103 °C, and thermal stability better than bis(2,2,2-trinitroethyl)nitramine. However, the authors made an assessment of these members of this new class: "Nevertheless, it should be noted that the considered compounds exhibit a rather high sensitivity to the action of external factors, and thus have no practical application" [76, 77]. Indeed, Shchetinin [92, 93] later reported that bis[2-(difluoramino)-2,2-dinitroethyl]nitramine (**13**) had a sensitivity comparable to the primary explosive lead azide: the critical pressure of explosion excitation measured by the disintegrating shell method was $\bar{p}_{cr}^{DS} = 0.42 \pm 0.02$ for $[NF_2C(NO_2)_2CH_2]_2N{-}NO_2$ (**13**) compared to $\bar{p}_{cr}^{DS} = 0.38 \pm 0.03$ for lead azide; $\bar{p}_{cr}^{DS} = 0.93 \pm 0.03$ for PETN; and $\bar{p}_{cr}^{DS} = 1.15 \pm 0.03$ for RDX.

Nazin and coworkers measured thermal decomposition of α-(difluoramino)polynitroalkanes and concluded that (difluoramino)dinitroalkanes differ little in their stability from their nitro analogs, trinitroalkanes [94, 95]. Bis[2-(difluoramino)-2,2-dinitroethyl]nitramine (**13**) was not one of the examples in this study, however.

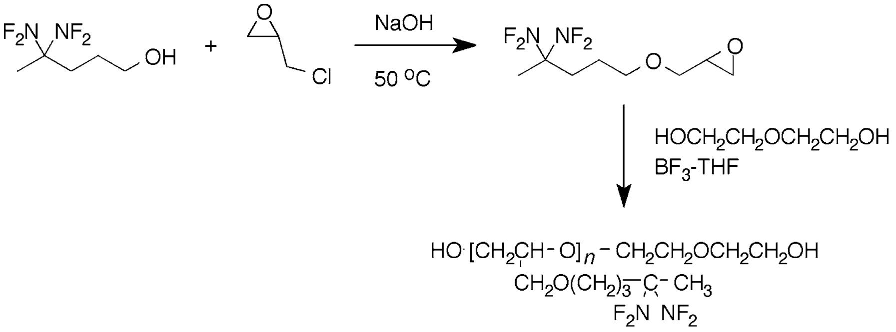
Pepekin [96] measured and reported experimental detonation parameters and the metal acceleration ability of bis[2-(difluoramino)-2,2-dinitroethyl]-nitramine (**13**), as well as compositions of it with HMX and with aluminum, and compared them to these parameters for HMX as well as formulations of bis(2,2,2-trinitroethyl)nitramine. The highest metal acceleration ability was offered by a 60 : 40 composition of **13** with HMX, which performed at 110.8% of HMX. Pure **13** also exhibited a higher detonation velocity than HMX. Literature involving this class of compound has mostly subsided in recent years, though there is another report by Pepekin and Gubin [97, 98] that **13** exhibits propellant performance that is 105.2% of that of HMX, measured by the "M-40 technique" (acceleration of steel plates 40 mm in diameter and 4 mm thick accelerated from the end of a cylindrical 40 × 40 mm charge placed in a thick-walled steel shell). Hexanitrobenzene is reported as having a performance 106% of that of HMX.

3.3
Other Organic Difluoramines

The compounds mentioned in this subsection are examples of specific classes not otherwise reviewed above, and specifically examples that have a structural feature not commonly encountered in the conventional chemistry of difluoramines or compounds that show prospective new applicability.

3.3.1
Polymers

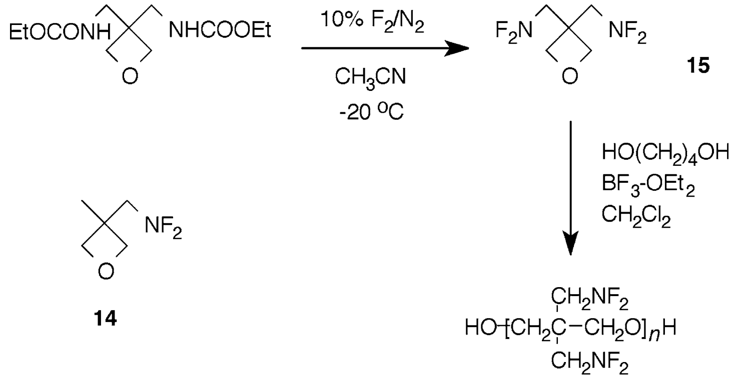
Although its difluoramination chemistry is straightforward, a relatively recent preparation of an NF_2-substituted polymer (a binder ingredient candidate) was reported by Jiang et al. (Hubei Redstar Chemical Institute, China) [99]. 4,4-Bis(difluoramino)pentyl glycidyl ether polymer was prepared by reaction of 4,4-bis(difluoramino)pentanol with epichlorohydrin followed by homopolymerization of the resulting oxirane ether monomer (Scheme 10) or copolymerization with THF.



Scheme 10 Preparations of a *gem*-bis(difluoramino)-substituted monomer and polymer [99]

Archibald, Manser, and coworkers developed a series of analogs of nitratoalkyl polymers (e.g., poly-NMMO and poly-BNMO). 3-(Difluoraminomethyl)-3-methyloxetane (**14**) and 3,3-bis(difluoraminomethyl)oxetane (**15**) [100] monomers were prepared by direct fluorination of corresponding carbamate ester derivatives [101, 102]. The monomers were polymerized (Scheme 11) to form homopolymers and copolymers with load-bearing polyether backbones as well as energetic NF_2 groups.

Solomun et al. [103] have demonstrated that it is feasible to produce large concentrations of NF_2 constituency embedded in a polyamide matrix by brief exposure to elemental fluorine (1 mbar of 1–10% F_2 in N_2) of bulk and thin-film samples of polycaprolactam (PA6) and polylauryllactam (PA12). The

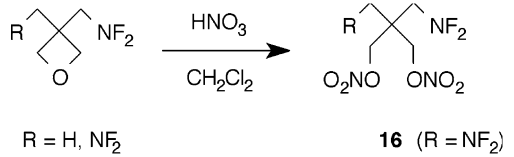


Scheme 11 Preparations of a difluoramino-substituted oxetane monomer and polymer

resulting fluorinated films were characterized by reflection–absorption FTIR, X-ray photoelectron, and NMR spectroscopies. The process utilizes the same transformation that small-molecule amides undergo in producing (difluoramino)alkanes by direct fluorination [104].

3.3.2
Plasticizers

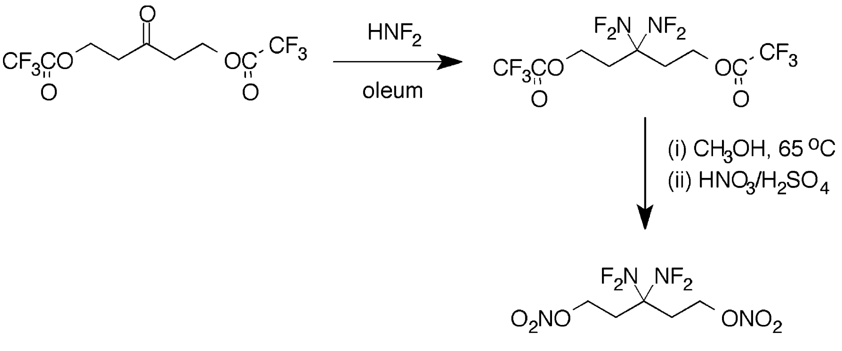
Archibald and Manser prepared NF_2-substituted analogs of pentaerythrityl esters (such as PETN). Specifically, 3-(difluoraminomethyl)-3-methyloxetane (**14**) and 3,3-bis(difluoraminomethyl)oxetane (**15**) [101] were subjected to ring-opening nitration by nitric acid (Scheme 12), giving corresponding 1,3-propanediyl dinitrate esters in quantitative yield [105, 106]. As neopentyl difluoramines, the products had superior stability compared to many other mono(difluoramino)alkyl-substituted compounds. 2,2-Bis(difluoraminomethyl)-1,3-propanediyl dinitrate (**16**) showed a melting point of 58 °C and DSC onset/peak of 177/188 °C.



Scheme 12 Preparations of difluoramino-substituted nitrate plasticizers

Rice and Russell (US Naval Research Laboratory) conducted a high-pressure study of the thermal interaction between elemental boron and Aerojet's 2,2-bis(difluoraminomethyl)-1,3-propanediyl dinitrate (**16**), as well as with PETN [107]. The mixture compressed in a cubic zirconia anvil cell was heated by absorption of a single laser pulse (Nd : YAG frequency-doubled laser at 532 nm), followed by recooling of the sample. Products observed at 1.7 GPa and 50 K included O=B–F, identified by infrared absorptions.

3,3-Bis(difluoramino)-1,5-dinitratopentane (**17**), as a potentially useful plasticizer, was prepared by Adolph and Trivedi [108] by conventional difluoramination of 1,5-bis(trifluoroacetoxy)-3-pentanone followed by transesterification with methanol, and then nitration with mixed acid (Scheme 13).



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Scheme 13 Preparation of a *gem*-bis(difluoramino)-substituted nitrate plasticizer [108]

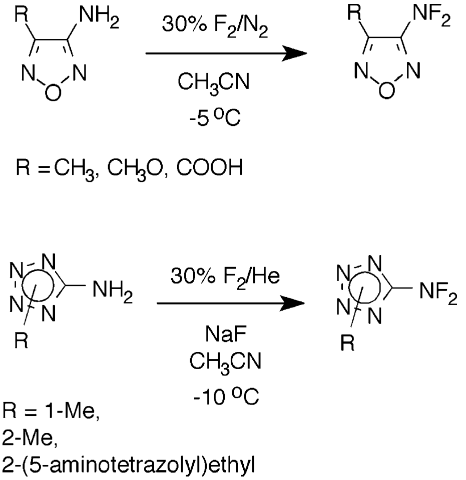
3.3.3
Miscellaneous Organic Derivatives

Synthesis

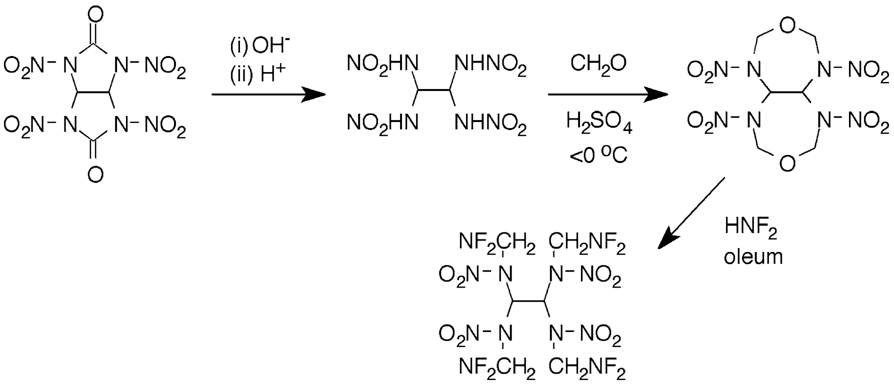
Fokin et al. directly fluorinated several aminofurazans (Scheme 14) to prepare 3-(difluoramino)furazans [109, 110]. Similarly, certain *N*-alkyl-5-aminotetrazoles were amenable to direct fluorination to 5-(difluoramino)tetrazole derivatives [111, 112]. NF$_2$-containing 1,2,4-oxadiazoles were prepared by Shreeve and coworkers by reactions of sodium 5-[(difluoraminomethyl)difluoromethyl]tetrazolate with oxalyl chloride [113].

1,1,2,2-Tetrakis[*N*-(difluoraminomethyl)nitramino]ethane (**18**) was first reported by Zheng et al. in a 1985 conference [114], and its chemistry (Scheme 15) was described further in later publications [28–30].

An interesting example of a unique product of difluoramination of a heterocyclic imide carbonyl group appeared in the context of a report by Gilardi and coworkers of structural features among a group of *gem*-bis(difluoramino)-substituted organics [115]: 1-{3-[5,5-bis(difluoramino)-2-oxopyrrolidinyl]-2-oxopropyl}pyrrolidine-2,5-dione (**19**). Imide carbonyls are usually not subject to difluoramination under typical reaction conditions.



Scheme 14 Direct fluorination of various aminoazoles to (difluoramino)azoles



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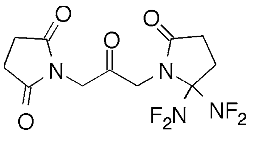
Scheme 15 Preparation of 1,1,2,2-tetrakis[*N*-(difluoraminomethyl)nitramino]ethane (**18**)



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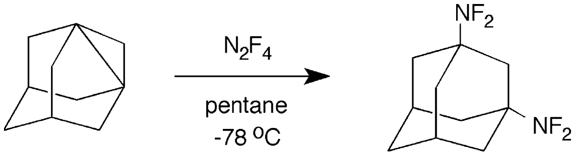
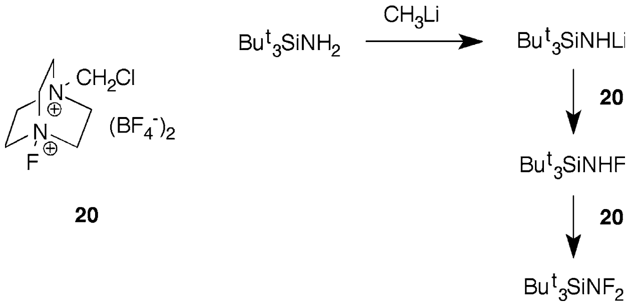
Other examples of typical reaction products, *N*-[*gem*-bis(difluoramino)-alkyl]imides, from ketone-substituted imides are provided in the same paper as well as in an earlier work by Fokin et al. [116, 117].

Many examples of addition of tetrafluorohydrazine (N_2F_4) to unsaturated organics had been discovered in the course of early work on difluoramines [20, 21]. A new example (Scheme 16) of this general transformation was the addition of N_2F_4 to 1,3-dehydroadamantane to prepare 1,3-bis(difluoramino)adamantane [118].



Scheme 16 Addition of tetrafluorohydrazine to 1,3-dehydroadamantane [118]

Though more accurately an organic silazane than a simple "organic difluoramine", the first stable trialkyl(difluoramino)silane was prepared by Shreeve, Williams, and coworkers by two stepwise fluorinations (Scheme 17) of tris(*tert*-butyl)silazane by Selectfluor (**20**) fluorinating agent [119].



Scheme 17 Preparation of tris(*tert*-butyl)(difluoramino)silane using Selectfluor (**20**)

Thermochemistry

Thermochemical characterizations of several organic difluoramines prepared during the Project Principia era were reported throughout the 1960s and 1970s and will not be reviewed here. Studies of the specific class of products of electrophilic difluoramination were reviewed above (Sect. 3.2.2).

More recently, two significant papers by Fokin, Grebennikov, Manelis, and Nazin [120–123] reported kinetic studies of thermal decomposition of a good number of organic difluoramine derivatives. The structures were chosen in order to ascertain inductive and steric effects on thermal decomposition, as well as effects of conjugation within the reactant and the presence of an α-hydrogen (relative to NF_2). The authors report that internal alkyl-substituted difluoramines (i.e., those lacking α-hydrogen) are more stable than analogous nitro compounds, owing to higher activation energies and somewhat smaller preexponential factors. The presence of α-hydrogen (e.g., in benzyldifluoramine) fundamentally changes the decomposition rate, and decomposition probably occurs by cleavage of HF. Otherwise, the decomposition rate does not depend on electronic effects of substituents but is decreased by steric shielding of the NF_2 group. (These results were also recently reviewed by Manelis et al. [124].) One of the specific systems studied, 2,2-bis(difluoramino)propane, was recently reinvestigated by Lin and coworkers [125]. In agreement with Fokin et al. [120, 121], it was concluded that the primary fragmentation process in this system, similarly to other internal *gem*-bis(difluoramino)alkanes, is homolytic cleavage of a $C–NF_2$ bond.

Pepekin's study of the thermodynamic properties of difluoramino and nitro compounds [74, 75] included many organic difluoramines besides the products of electrophilic difluoramination cited above. Properties reported include heats of combustion, formation, and atomization, Clausius–Clapeyron equation parameters, and the enthalpies and entropies of evaporation and sublimation. This collection of properties allowed estimation of group additivity parameters for general calculations of thermodynamic properties of organic difluoramines, which were compared to those of corresponding nitro groups.

Organic difluoramines were among the many classes of high-energy compounds analyzed by Nazin et al. in assessing the influence of molecular structure on their thermal stability [126, 127]. The sites of primary breakdown were discussed, as was the mutual influence of different functional groups.

Several difluoramines (along with nitro compounds) were also among the collection of energetic materials in a study by Matveev, Nazin, and coworkers [128, 129] of polyfunctional compounds with several of the same type of reactive substituent, to determine the stepwise character of successive thermal degradation steps. It was found that the degradation of most of the studied classes occurred stepwise via long-lived intermediate products.

4

New Synthetic Methodology

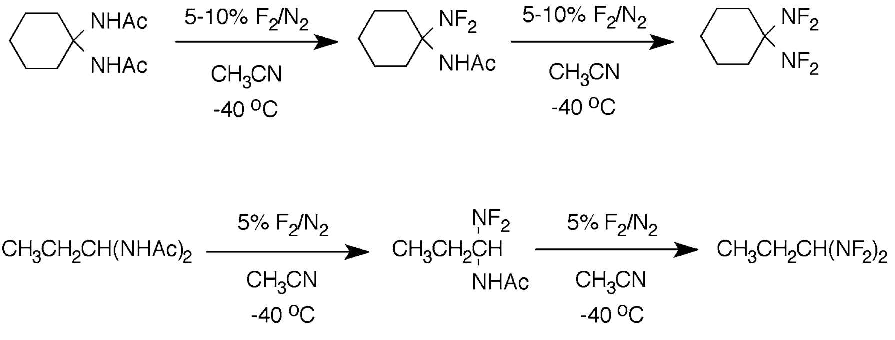
The technique of electrophilic difluoramination [80, 81], reviewed above, has produced the greatest variety of new products in the class of organic difluoramines. Otherwise, most recent results have employed the conventional methodology that was devised in the era of Project Principia, as reviewed elsewhere [16–25]. Process improvements in conventional difluoramination of ketones by HNF_2 [35, 37] have made the transformation more scalable, particularly by employing an inert cosolvent to alleviate hazards of difluoramine, but employ the same fundamental chemical reactions as in the 1960s. However, the recognition of a requisite nitrogen-protection strategy made the transformation applicable to heterocycles with proximate nitrogens.

The feasibility of isolating relatively stable salts of difluorosulfamic acid and their utility in performing difluoraminations of model ketones was demonstrated by Chapman et al. [130, 131], offering the prospect of alleviating many of the problems inherent in the use of hazardous difluoramine (HNF_2) in conventional difluoraminations. Sodium difluorosulfamate was prepared by direct fluorination of aqueous sodium sulfamate; it could be isolated by separation from sodium fluoride by-product and water after neutralization; and it could be safely stored cold. Difluoramination of 1,3-dibromoacetone by sodium difluorosulfamate in sulfuric acid (1% SO_3) produced 1,3-dibromo-2,2-bis(difluoramino)propane in 38% crude yield, comparable to conventional difluoramination. Later, Christe and coworkers [132] better characterized sodium difluorosulfamate (Raman and IR spectra) and other difluorosulfamate salts (X-ray crystallography).

A direct fluorination of nucleophilic primary (as well as secondary) amines with Selectfluor fluorinating agent (**20**), rather than elemental fluorine, has been reported by Singh and Shreeve [133], making small-scale preparations of (non-geminal) organic difluoramines more convenient.

The utility of trityldifluoramine (Ph_3CNF_2), a known source of difluoramine via acidic hydrolysis [134], for effecting in-situ difluoramination of ketones [22, 23, 135, 136] has been recently rediscovered [137]. The latter system invokes the mechanism of difluoramine alkylation by carbenium ions generated in strong acids, as traditionally employed in conventional difluoraminations of ketones with added difluoramine [138, 139].

A fundamentally new preparation of internal and terminal *gem*-bis(difluoramino)alkanes was demonstrated by Chapman et al. [140] via the direct fluorination of the corresponding *gem*-bisacetamides, with 1,1-bisacetamidocyclohexane and 1,1-bisacetamidopropane used as examples, leading to 1,1-bis(difluoramino)cyclohexane and 1,1-bis(difluoramino)propane, respectively (Scheme 18). 1,1-Bis(difluoramino)cyclohexane behaved less than ideally as a model system: its yield by conventional difluoramination is atypically



Scheme 18 Preparations of *gem*-bis(difluoramino)alkanes via direct fluorination of *gem*-bisacetamides [140]

low (31%) for ketone difluoramination, and its yield by the new transformation maximized at about 10%. 1,1-Bis(difluoramino)propane's yield (~ 40%) was more typical of conventional difluoraminations.

5
Theoretical Treatments

An early report on computational estimation of the thermodynamic properties of (difluoramino)alkanes, outside of the context of the American and Russian research programs, was by İnel (Boğaziçi University, Turkey), who estimated heats of formation, entropies, and bond dissociation energies of several simple difluoramines [141, 142], derived from published experimental data on perfluorinated amines and thermochemical relationships.

Heats of formation of known and hypothetical difluoramino (and nitro) compounds were estimated by Leroy, Bourasseau, and coworkers [143], initially by a semiempirical computational procedure (of Pople et al.). Calculation was based on the concept of isodesmic reactions, which conserves, as far as possible, the number and nature of chemical bonds. A reaction energy change, calculated at the SCF level, approximates the experimental heat of reaction by incorporating experimental heats of formation of reference compounds. The new compounds had been studied at ab initio level using a 6-31G basis set for geometry optimization and total energy determination. These authors also developed group additivity parameters for calculating heats of formation of new energetic compounds (nitro and difluoramino) by Benson's method [144].

The most significant contributions to computational studies of organic difluoramines, which have also directed synthetic research efforts, have been by Politzer and coworkers. (Difluoramino)aromatics were among the first systems studied by calculations of average local ionization energies [145] and electrostatic potentials [146] for predicting chemical reactivity and substituent effects. Politzer et al. also developed the application of density functional theory (DFT) and electrostatic potentials to estimation of thermodynamic properties (especially dissociation energies and solid-state heats of formation) of many new hypothetical NF_2-containing structures [147–150], including predictions of thermochemical processes undergone by difluoramine derivatives [151]. This approach led to early estimations [9, 26] of important thermodynamic properties of the difluoramino-nitramines that were being synthetically pursued. Politzer's computational methodology has been presented in recent overviews [152, 153].

Thermochemical properties of difluoramino-substituted cage hydrocarbons, specifically, poly(difluoramino)cubanes [154] and poly(difluoramino)-adamantanes [155], have been estimated by Ju et al. in order to compare results from a variety of computational methods: density functional theory, Hartree–Fock, and MP2 methods (6-31G* and 6-311G** basis sets), as well as semiempirical MO methods MNDO, AM1, and PM3 for the former chemical system. The semiempirical methods did not produce accurate and reliable results for heats of formation. Interactions between difluoramino substituents were determined. Ju and coworkers also calculated (using DFT and semiempirical methods) heats of formation of a variety of difluoramino pentaerythrityl derivatives [156], including some that had been considered by Archibald and Manser [106] as prospective plasticizers, for example, a tetrakis(difluoramino) analog of PETN, $C(CH_2NF_2)_4$, as a theoretical structure of interest.

References

1. Furin GG, Fainzilberg AA (1999) Russ Chem Rev 68:653
2. Taylor SD, Kotoris CC, Hum G (1999) Tetrahedron 55:12431
3. Li Y (2001) Huaxue Shiji [Chemical Reagents] 23:143
4. Colburn CB (1965) Endeavour 24:138
5. Fokin AV, Kosyrev YuM (1966) Russ Chem Rev 35:791
6. Freeman JP (1967) Inorg Chim Acta Rev 1:65
7. Ruff JK (1967) Chem Rev 67:665
8. Klapötke TM (2006) J Fluorine Chem 127:679
9. Politzer P, Lane P (1997) Adv Mol Struct Res 3:269
10. Brown RC, Kolb CE, Yetter RA, Dryer FL, Rabitz H (1995) Combust Flame 101:221
11. Yetter RA, Dryer FL, Rabitz H, Brown RC, Kolb CE (1998) Combust Flame 112:387
12. Ammon HL (2001) Struct Chem 12:205
13. Ruff O, Giese M (1936) Ber Dtsch Chem Ges B 69B:598
14. Davenas A (2003) J Propul Power 19:1108
15. Holzmann RT (ed) (1966) Advanced propellant chemistry. American Chemical Society, Washington, DC
16. Fokin AV, Kosyrev YuM (1970) Zh Vses Ova im D I Mendeleeva 15:81
17. Fokin AV, Kosyrev YuM (1970) Mendeleev Chem J 15:109
18. Baum K (1971) Intra-Sci Chem Rep 5:69
19. Fokin AV, Studnev YuN, Kuznetsova LD (1976) Reakts Metody Issled Org Soedin 24:7
20. Fokin AV, Studnev YuN (1982) Izv Akad Nauk SSSR Ser Khim 1812
21. Fokin AV, Studnev YuN (1982) Bull Acad Sci USSR Div Chem Sci 31:1609
22. Fokin AV, Kosyrev YuM, Shevchenko VI (1982) Izv Akad Nauk SSSR Ser Khim 1831
23. Fokin AV, Kosyrev YuM, Shevchenko VI (1982) Bull Acad Sci USSR Div Chem Sci 31:1626
24. Urbański T (1984) Chemistry and technology of explosives, vol 4, chap 9. Pergamon, Oxford
25. Hanefeld W (1990) *N*,*N*-Dihalogen-amine. In: Klamann D (ed) Methoden der organischen chemie (Houben-Weyl), vol E16a, organische Stickstoff-Verbindungen I, Part 2. Georg Thieme, Stuttgart, p 893
26. Miller RS (1996) Mater Res Soc Symp Proc 418:3
27. Chapman RD, Archibald TG, Baum K (1989) Research in energetic compounds. Report ONR-7-1 (interim). Fluorochem, Azusa, CA; NTIS accession number

ADA214106, available from http://www.ntis.gov/help/ordermethods.asp, last visited: 23 April 2007

28. Zheng Y, Huang T, Zhang M, Wang X (1987) A study on the syntheses and detonation properties of difluoroamino compounds. In: Ding J (ed) Proceedings of the international symposium on pyrotechnics and explosives. China Academic, Beijing, p 234
29. Zheng Y, Zhou J, Zhou D, Zhang M (1988) Binggong Xuebao [Acta Armamentarii] 59
30. Zheng Y, Zhou J, Zhou D, Zhang M (1988) Chem Abstr 109:189782
31. Sayles DC (1972) US Patent 3 636 154
32. Tyler WE, Lovett JR (1972) US Patent 3 687 954
33. Baum K, Trivedi NJ, Lovato JM, Iyer VK (1993) Novel approaches to the synthesis of fluorodinitromethane and fluorodinitroethanol. Report NRO-1-1 (final). Fluorochem, Azusa, CA; available at http://stinet.dtic.mil/cgi-bin/GetTRDoc?AD=A269158&Location=U2&doc=GetTRDoc.pdf, last visited: 26 April 2007
34. Fluorochem (1991) Research in energetic compounds. Report ONR-7-1 (final) to the Office of Naval Research (Arlington, VA) on Contract N00014-88-C-0536. Fluorochem, Azusa, CA. Described in: Baum K, Trivedi NJ, Lovato JM, Iyer VK (1993) Novel approaches to the synthesis of fluorodinitromethane and fluorodinitroethanol. Report NRO-1-1 (final). Fluorochem, Azusa, CA; NTIS accession no. ADA269158, available at http://stinet.dtic.mil/cgi-bin/GetTRDoc?AD=A269158, last visited: 26 April 2007
35. Chapman RD, Welker MF, Kreutzberger CB (1998) J Org Chem 63:1566
36. Chapman RD, Gilardi RD, Welker MF, Kreutzberger CB (1999) J Org Chem 64:960
37. Chapman RD, Groshens TJ (2004) US Patent Application 11/ 010 059
38. Adolph HG, Stern AG (2006) US Patent 7 145 003
39. Ammon HL, Holden JR, Du Z (2002) Structure and density predictions for energetic materials. In: Energetic materials design MURI kick-off meeting [extended abstracts]. Aberdeen Proving Ground, MD. http://www.chem.missouri.edu/Thompson/MURI02/extended/Ammon_MURI_extended_abstract_4.pdf, last visited: 20 April 2007
40. Oyumi Y, Brill TB, Rheingold AL (1986) J Phys Chem 90:2526
41. Achuthan CP, Jose CI (1990) Propellants Explos Pyrotech 15:271
42. Ryzhkov LR, McBride JM (1997) J Am Chem Soc 119:4826
43. Peiris SM (2002) Experimental and computational studies of molecular and lattice symmetries of energetic materials at high pressure. DTIC, available at http://stinet.dtic.mil/str/quick-tr.html, last visited: 23 April 2007
44. Gobin C, Orwig J, Nicol M (2006) American Physical Society March Meeting, Baltimore, MD, abstract Q1.150. http://meetings.aps.org/link/BAPS.2006.MAR.Q1.150, last visited: 20 April 2007
45. Nicol M, Gobin C, Kim E (2007) American Physical Society March Meeting, Denver, CO, abstract V23.6. http://meetings.aps.org/link/BAPS.2007.MAR.V23.6, last visited: 20 April 2007
46. Degirmenbasi N, Peralta-Inga Z, Olgun U, Gocmez H, Kalyon DM (2006) J Energ Mater 24:103
47. Peralta-Inga Z, Degirmenbasi N, Olgun U, Gocmez H, Kalyon DM (2006) J Energ Mater 24:69
48. Chew JW, Black SN, Chow PS, Tan RBH, Carpenter KJ (2007) Cryst Eng Comm 9:128
49. HNFX Rev. 1.3 (2005) Material safety data sheet (MSDS). Naval Air Weapons Station, China Lake, CA

50. Cady HH, Smith LC (1962) Studies on the polymorphs of HMX. Report LAMS-2652. Los Alamos Scientific Laboratory, Los Alamos, NM
51. Licht HH (1971) In: Hansson J (ed) Proceedings of symposium on chemical problems connected with the stability of explosives. Sektionen för Detonik och Förbränning, Sundbyberg, Sweden, p 168
52. McCrone WC (2001) Microscope 49:47
53. Zhang J, Oxley J, Smith J, Bedford C, Chapman R (2000) J Mass Spec 35:841
54. Oxley JC, Smith JL, Zhang J, Bedford C (2001) J Phys Chem A 105:579
55. Kuo KK, Young G (2002) Proc Combust Inst 29:2947
56. Chapman RD, Nguyen BV (2001) US Patent 6 310 204
57. Emmons WD, Freeman JP (1955) J Am Chem Soc 77:6061
58. Luk'yanov OA, Ternikova TV (1983) Izv Akad Nauk SSSR Ser Khim 667
59. Luk'yanov OA, Ternikova TV (1983) Bull Acad Sci USSR Div Chem Sci 32:605
60. Garcia J, González J, Segura R, Urpí F, Vilarrasa J (1984) J Org Chem 49:3322
61. Axenrod T, Guan X-P, Sun J, Qi L, Chapman RD, Gilardi RD (2001) Tetrahedron Lett 42:2621
62. Park Y-D, Cho S-D, Kim J-J, Kim H-K, Kweon D-H, Lee S-G, Yoon Y-J (2006) J Heterocycl Chem 43:519
63. Gilardi R (2004) Polytypical polymorphs occurring in an energetic material. In: Virtual course on polymorphism: diversity amidst similarity, International School of Crystallography – 35th course, Erice, Sicily, Italy; http://erice2004.docking.org/vcourse/polymorph/15tue/1830-Gilardi/Gilardi.ppt, last visited: 20 April 2007
64. Dunn BP (2001) Rocket engine specific impulse program. http://dunnspace.com/isp.htm, last visited: 20 April 2007
65. Hong W-L, Tian D-Y, Liu J-H, Wang F (2001) Guti Huojian Jishu [J Solid Rocket Technol] 24:41
66. Hong W-L, Tian D-Y, Liu J-H, Wang F (2001) Chem Abstr 135:275005
67. Politzer P, Murray JS, Grice ME, Sjoberg P (1991) Computer-aided design of monopropellants. In: Olah GA, Squire DR (eds) Chemistry of energetic materials, chap 4. Academic, San Diego, CA
68. Feng Z (2000) Huaxue Jinzhan [Prog Chem] 12:171
69. Feng Z (2000) Chem Abstr 134:88422
70. Tan G-H (2000) 火炸药科技动态 2 [Trends in Explosives]
71. Li S-W, Zhao F-Q, Yuan C, Luo Y, Gao Y (2002) Guti Huojian Jishu [J Solid Rocket Technol] 25:36
72. Li S-W, Zhao F-Q, Yuan C, Luo Y, Gao Y (2002) Chem Abstr 138:6183
73. Kim YG (2004) BK21 Program in Chemical Engineering, Seoul National University, Newsletter 5(1):22, http://web.archive.org/web/20041112214526/http://bk21-chem-eng.snu.ac.kr /news/newsletter/2004_spring/5-1.pdf, last visited: 23 April 2007
74. Pepekin VI (1994) Khim Fiz 13:42
75. Pepekin VI (1994) Chem Phys Rep 13:67
76. Litvinov BV, Fainzil'berg AA, Pepekin VI, Smirnov SP, Loboiko BG, Shevelev SA, Nazin GM (1994) Dokl Akad Nauk 336:67
77. Litvinov BV, Fainzil'berg AA, Pepekin VI, Smirnov SP, Loboiko BG, Shevelev SA, Nazin GM (1994) Dokl Chem 336:86
78. Dalinger IL, Vinogradov VM, Shevelev SA, Kuz'min VS (1996) Mendeleev Commun 6:13
79. Dalinger IL, Vinogradov VM, Shevelev SA, Kuz'min VS, Arnautova EA, Pivina TS (1998) Propellants Explos Pyrotech 23:212

80. Fokin AV, Studnev YuN, Kuznetsova LD (1996) Dokl Akad Nauk 346:358
81. Fokin AV, Studnev YuN, Kuznetsova LD (1996) Dokl Chem 346:22
82. Fokin AV, Studnev YuN, Rapkin AI, Kuznetsova LD (1996) Izv Akad Nauk Ser Khim 2689
83. Fokin AV, Studnev YuN, Rapkin AI, Kuznetsova LD (1996) Russ Chem Bull 45:2547
84. Fokin AV, Studnev YuN, Kuznetsova LD (1996) Izv Akad Nauk Ser Khim 2056
85. Fokin AV, Studnev YuN, Kuznetsova LD (1996) Russ Chem Bull 45:1952
86. Fokin AV, Studnev YuN, Stolyarov VP, Valiev RSh (1999) Izv Akad Nauk Ser Khim 130
87. Fokin AV, Studnev YuN, Stolyarov VP, Valiev RSh (1999) Russ Chem Bull 48:131
88. Khisamutdinov GKh, Slovetsky VI, Golub YuM, Shevelev SA, Fainzil'berg AA (1997) Izv Akad Nauk Ser Khim 338
89. Khisamutdinov GKh, Slovetsky VI, Golub YuM, Shevelev SA, Fainzil'berg AA (1997) Russ Chem Bull 46:324
90. Khisamutdinov GKh, Shevelev SA (2001) Izv Akad Nauk Ser Khim 706
91. Khisamutdinov GKh, Shevelev SA (2001) Russ Chem Bull 50:736
92. Shchetinin VG (1999) Fiz Goreniya Vzryva 35:116
93. Shchetinin VG (1999) Combust Explos Shock Waves (Engl Transl) 35:570
94. Grebennikov VN, Nazin GM, Manelis GB (1995) Izv Akad Nauk Ser Khim 649
95. Grebennikov VN, Nazin GM, Manelis GB (1995) Russ Chem Bull 44:628
96. Pepekin V (1996) Development of high-efficiency energetic explosives. 27th international annual conference of ICT, 25–28 June 1996, Karlsruhe, Germany,
97. Pepekin VI, Gubin SA (2007) Fiz Goreniya Vzryva 43:99
98. Pepekin VI, Gubin SA (2007) Combust Explos Shock Waves (Engl Transl) 43:84
99. Jiang Z, Xu G, Chen Y (1990) 21st International Annual Conference of ICT, Karlsruhe, Germany
100. Gilardi R, Evans RN, Manser GE (2003) Acta Crystallogr Sect E Struct Rep Online E59:o2032
101. Archibald TG, Manser GE, Immoos JE (1993) US Patent 5 272 249
102. Archibald TG, Manser GE, Immoos JE (1995) US Patent 5 420 311
103. Solomun T, Schimanski A, Sturm H, Illenberger E (2005) Macromolecules 38:4231
104. Grakauskas V, Baum K (1970) J Org Chem 35:1545
105. Archibald TG, Manser GE (1994) PCT Patent WO 94/05 643
106. Archibald TG, Manser GE (1998) US Patent 5 789 617
107. Rice JK, Russell TP (1996) Mater Res Soc Symp Proc 418:373
108. Adolph HG, Trivedi NJ (2001) US Patent 6 325 876
109. Fokin AV, Tselinskii IV, Mel'nikova SF, Vergizov SN, Studnev YuN, Stolyarov VP, Il'in SS (1986) Izv Akad Nauk SSSR Ser Khim 2086
110. Fokin AV, Tselinskii IV, Mel'nikova SF, Vergizov SN, Studnev YuN, Stolyarov VP, Il'in SS (1986) Bull Acad Sci USSR Div Chem Sci 35:1901
111. Fokin AV, Studnev YuN, Stolyarov VP, Mel'nikov AA (2000) Izv Akad Nauk Ser Khim 950
112. Fokin AV, Studnev YuN, Stolyarov VP, Mel'nikov AA (2000) Russ Chem Bull 49:949
113. John EO, Kirchmeier RL, Shreeve JM (1990) J Fluorine Chem 47:333
114. Zheng YY, Zhou JZ, Huang TJ, Zhou DL, Zhang MN (1985) J Fluorine Chem 29:216
115. Butcher RJ, Gilardi R, Baum K, Trivedi NJ (2002) Thermochim Acta 384:219
116. Fokin AV, Voronkov AN, Timofeenko IA (1978) Izv Akad Nauk SSSR Ser Khim 2644
117. Fokin AV, Voronkov AN, Timofeenko IA (1978) Bull Acad Sci USSR Div Chem Sci 27:2366

118. Prakash GKS, Bae C, Kroll M, Olah GA (2002) J Fluorine Chem 117:103
119. Majumder U, Armantrout JR, Williams RV, Shreeve JM (2002) J Org Chem 67:8435
120. Fokin AV, Grebennikov VN, Manelis GB, Nazin GM (1993) Dokl Akad Nauk 332:735
121. Fokin AV, Grebennikov VN, Manelis GB, Nazin GM (1993) Dokl Chem 332:247
122. Grebennikov VN, Manelis GB, Nazin GM, Fokin AV (1994) Izv Akad Nauk Ser Khim 336
123. Grebennikov VN, Manelis GB, Nazin GM, Fokin AV (1994) Russ Chem Bull 43:315
124. Manelis GB, Nazin GM, Rubtsov YuI, Strunin VA (2003) Thermal decomposition and combustion of explosives and propellants. Taylor & Francis, London, chap 7
125. Park J, Chakraborty D, Jamindar S, Xia WS, Lin MC, Bedford C (2002) Thermochim Acta 384:101
126. Nazin GM, Prokudin VG, Manelis GB (2000) Izv Akad Nauk Ser Khim 231
127. Nazin GM, Prokudin VG, Manelis GB (2000) Russ Chem Bull 49:234
128. Dubikhin VV, Karnauh GE, Lagodzinskaya GV, Matveev VG, Nazin GM, Prokudin GV (2003) 34th International Annual Conference of ICT, 24–27 June 2003, Karlsruhe, Germany
129. Matveev VG, Nazin GM (2003) Kinet Catal 44:735
130. Chapman RD, Kreutzberger CB, Welker MF (1995) Difluoramino energetic materials. JANNAF novel ingredients for liquid and solid propellants specialist session, 4 April 1995, Pasadena, CA; http://stinet.dtic.mil/cgi-bin/GetTRDoc?AD=A451187, last visited: 20 April 2007
131. Chapman RD, Yee RY, Gilardi RD, Pinkerton AA (1996) Chemistry of difluoramine derivatives. 15th annual working group institute on synthesis of high energy density materials, 12–13 June 1996,Picatinny Arsenal, NJ; http://stinet.dtic.mil/cgi-bin/GetTRDoc?AD=A451459, last visited: 20 April 2007
132. Haiges R, Wagner R, Boatz JA, Yousufuddin M, Etzkorn M, Prakash GKS, Christe KO, Chapman RD, Welker MF, Kreutzberger CB (2006) Angew Chem Int Ed Engl 45:5179
133. Singh RP, Shreeve JM (2001) Chem Commun, p 1196
134. Graham WH, Parker CO (1963) J Org Chem 28:850
135. Fokin AV, Kosyrev YuM, Shevchenko VI, Potarina TM (1971) USSR Patent 299 505
136. Fokin AV, Kosyrev YuM, Shevchenko VI, Potarina TM (1971) Chem Abstr 75:76265
137. Prakash GKS, Etzkorn M, Olah GA, Christe KO, Schneider S, Vij A (2002) Chem Commun, p 1712
138. Fokin AV, Kosyrev YuM, Makarov VA, Novoselov NP (1969) Dokl Akad Nauk SSSR 186:112
139. Fokin AV, Kosyrev YuM, Makarov VA, Novoselov NP (1969) Proc Acad Sci USSR Chem Sect 186:350
140. Chapman RD, Davis MC, Gilardi R (2003) Synth Commun 33:4173
141. Inel Y (1976) Bogazici Univ Derg Temel Bilimler Kim 4/5:9
142. Inel Y (1977) Chem Abstr 92:170261
143. Leroy G, Sana M, Wilante C, Peeters D, Bourasseau S (1989) J Mol Struct: THEOCHEM 187:251
144. Sana M, Leroy G, Wilante C, Peeters D, Bourasseau S (1991) J Energ Mater 9:137
145. Sjoberg P, Murray JS, Brinck T, Politzer P (1990) Can J Chem 68:1440
146. Haeberlein M, Murray JS, Brinck T, Politzer P (1992) Can J Chem 70:2209
147. Politzer P, Lane P, Grice ME, Concha MC, Redfern PC (1995) J Mol Struct: THEOCHEM 338:249
148. Politzer P, Lane P, Sjoberg P, Grice ME, Shechter H (1995) Struct Chem 6:217

149. Politzer P, Murray JS, Grice ME (1996) Mater Res Soc Symp Proc 418:55
150. Politzer P, Lane P (1996) J Mol Struct: THEOCHEM 388:51
151. Politzer P, Lane P, Grice ME (1996) J Mol Struct: THEOCHEM 365:89
152. Politzer P, Murray JS, Seminario JM, Lane P, Grice ME, Concha MC (2001) J Mol Struct: THEOCHEM 573:1
153. Politzer P, Lane P, Concha MC (2003) Computational approaches to heats of formation. In: Politzer P, Murray JS (eds) Energetic materials, part 1. Decomposition, crystal and molecular properties, chap 9. Elsevier, Amsterdam
154. Ju X-H, Li Y-M, Xiao H-M (2005) J Phys Chem A 109:934
155. Ju X-H, Ji G-F, Xiao H-M (2006) Chem Phys 326:395
156. Fan X-W, Ju X-H, Xiao H-M, Qiu L (2006) J Mol Struct: THEOCHEM 801:55