



Energetic materials containing fluorine. Design, synthesis and testing of furazan-containing energetic materials bearing a pentafluorosulfanyl group

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ABSTRACT

The advantageous impact of a pentafluorosulfanyl substituent on the properties of furazan-containing energetic materials was demonstrated by the synthesis and study of the energetic properties of ten new compounds. The thermal stability of these compounds was evaluated by DSC and TGA, whereas densities, heats of formation, pressures of detonation and speeds of detonation were obtained computationally. On the basis of these data, it was concluded that the combination of the SF₅ substituent with the furazan ring led to materials of higher density and predicted detonation properties than other known furazans or SF₅-containing materials. In addition, the synthetic studies provided insight regarding the electron-withdrawing nature of the furazan ring, in particular its effect on the basicity and nucleophilic reactivity of amino furazans.

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1. Introduction

Energetic materials can be considered compounds or mixtures of compounds that constitute a source of massive controllable energy. Interest in the design of new materials with higher energy content, better performance, lower cost, less sensitivity to impact and with less danger to synthesize and process has allowed this research area to remain active. Also, continued concerns related to the potential use of chemical and biological weapons (CW/BW) has necessitated the development of new mechanisms of defense [1].

The synthesis of new high energy materials has been focused on use of heterocyclic compounds with high nitrogen content such as tetrazines, furazans, triazoles and tetrazoles due to the relatively positive heats of formation (ΔH_f°) of these compounds [2]. Recently, the introduction of fluorine into such compounds has resulted in a boost in their performance, mainly due to the increase in their density and their thermal and chemical stability.

By definition, an energetic material is a compound or a mixture of compounds that, after an initiation process, undergoes very rapid self-propagating decomposition, producing gases at tremendous pressure and with the evolution of a lot of heat. Temperatures ideally can reach up to 6000 K and the pressure up to 40 GP [2].

The performance of an energetic material is mainly evaluated on the basis of the type of products that are formed, the energy that

is released, the pressure and speed of detonation, and the thermal and chemical stability of the material. The carbon–oxygen balance (OB) and the density are directly related to a compound's performance. According to the semi-empirical equations developed by Kamlet and Jacobs, the square of the density is directly proportional to the performance of the compound (Eqs. (1)–(3)) [3].

$$P_{(CJ)} = 15.58\rho^2\phi \quad (1)$$

$$D = A\phi^{1/2}(1 + B\rho) \quad (2)$$

$$\phi = NM^{1/2}Q^{1/2} \quad (3)$$

P is the detonation pressure (GPa), D is the speed of detonation (m/s), A and B are constants, N is the number of moles of gaseous products of detonation per gram of explosive, M the average molecular weight of the gases, Q is the heat of detonation in calories per gram of explosive and ρ is density. The higher the density is, the better the performance will be. Although the increase of oxygen balance results in a more sensitive material, it also increases the performance due to the “complete” oxidation of all carbons and hydrogens. Most energetic materials, however, are “oxygen-deficient” [4].

In evaluating new energetic materials, they are generally compared to three of the most important known energetic materials: cyclotrimethylenetrinitramine (RDX), cyclotetramethylene-tetranitramine (HMX) and trinitrotoluene (TNT).

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Table 1
Performance data of three common energetic materials.

	d (g/cm ³) ^a	P (Gpa) ^b	vD (m/s) ^c
RDX	1.81	33.8	8750
HMX	1.91	39.3	9100
TNT	1.65	20.0	6900

^a Density.

^b Detonation pressure.

^c Velocity of detonation.

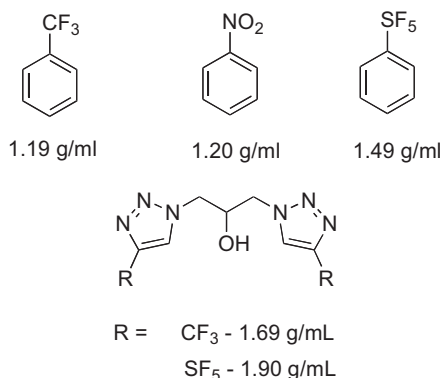


Fig. 1. Higher density of SF₅ compounds.

The performances of these three materials are given in Table 1 [1]. The development of new energetic materials with better performance than RDX, HMX or TNT constitutes an important area of current active research.

In order to achieve better performance than RDX or HMX, new energetic materials have often incorporated fluorine into the system [1,3,4], and during recent decades there has been increased interest regarding the use of the SF₅ group in energetic materials [4–9]. Incorporation of the SF₅ group gives rise to compounds of higher density (Fig. 1), and the high fluorine content along with the presence of hydrogen leads to the formation of hydrogen fluoride (HF) upon detonation, generating a large amount of energy. The S–F Bond Dissociation Energy (BDE) is 79 kcal/mol, while the BDE of H–F is 136 kcal/mol [5,6,8,9].

The possibility of a higher density, larger energy release, and better thermal and chemical stability without increasing the sensitivity make the SF₅ group attractive in the synthesis of high energy materials (HEM).

Fig. 2 provides an example of a polynitro-SF₅ energetic material, which upon detonation produces HF as the only product containing fluorine, while the presence of sulfur (S) leads into the

formation of COS, inhibiting the formation of COF₂, which is considered a waste of fluorine [9].

1.1. Furazan-containing energetic materials

1,2,5-Oxadiazoles (commonly known as furazans) have been included in several publications as great building blocks for the generation of insensitive High Performance Energetic Materials (HEM) [4,10–19]. The aromaticity present in the ring increases the thermal stability, while the planarity increases the density. That combined with their positive heat of formation (ΔH_f°) makes furazans an excellent building block for the generation of HEM [10].

Since the first synthesis of 3,4-diaminofurazan **1** by Coburn in 1968 [20], a vast number of furazan derivatives with good densities and energetic properties have been prepared.

Studies on the thermal decomposition of amino furazan derivatives at different temperatures have shown that the major products are CO, CO₂, H₂O, HCN, N₂ (when the azo or hydrazine moieties are present) and NO₂ (when present as a nitro group in the molecule). Minor products include HCNO, NH₃, HNO₃ and N₂O. The same studies indicate that most aminofurazans have a higher thermal stability than HMX or RDX [19,21,22].

Alternatively, the high nitrogen content and positive ΔH_f° of tetrazole also makes this heterocycle an excellent building block for the synthesis of HEM. Although tetrazole has a positive ΔH_f° , it exhibits good thermal stability [23–25]. Theoretical and experimental studies have shown that the thermal decomposition of 5-aminotetrazole goes through two different retro [3+2] mechanisms with relatively close activation energies. The first mechanism and most favorable generates NH₂CN and HN₃, while the second one produces CH₃N₃ and N₂. However, when the amino group of the aminotetrazole has been functionalized, the second mechanism is the most favorable [23–27].

A combination of tetrazole and furazan rings has been previously reported [28], and recently Shreeve et al. reported furazan tetrazolate-based salts as highly insensitive energetic materials [29].

A number of SF₅-containing energetic materials with predicted performance close to those for HMX, RDX and TNT, and having the benefit of lesser or no impact sensitivity, have been previously synthesized [5,30]. Fig. 3 shows five such SF₅-containing energetic materials that have densities ~ 1.85 g/cm³, and which have predicted pressures and velocities of detonation of approximately 17.8–20.5 GPa and 6900–7100 m/s, respectively.

Despite all the potential benefits provided by the SF₅ moiety, the number of SF₅-containing energetic materials has been limited by the few available sources of the aliphatic SF₅ group. SF₅Br and SF₅Cl are the main ultimate building blocks for preparation of aliphatic SF₅ compounds, and the chemistry of these two species is limited to free radical chemistry. For this reason, the synthesis of

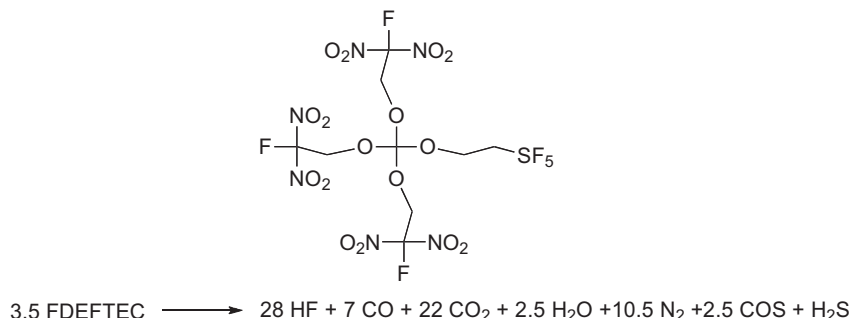


Fig. 2. Polynitro-SF₅ energetic material.

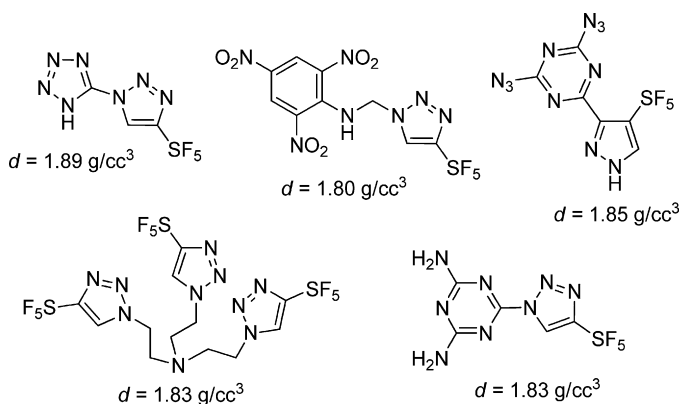


Fig. 3. Examples of SF₅-containing energetic materials.

organic SF₅ building blocks that would allow the “easy” incorporation of this group into HEM remains a significant challenge.

In the current paper we will be reporting the synthesis of several SF₅-building blocks and evaluation of their potential utility in the synthesis of some new high-density SF₅-furazan-based energetic materials with relatively low hydrogen content, and which therefore have the potential to release “free fluorine” upon detonation. The thermal and chemical stability of these new energetic materials will be evaluated and insight provided by Cheetah calculations regarding their possible energetic performance.

2. Results and discussion

2.1. Synthesis of SF₅-furazan-based energetic materials

The synthesis of aminofurazans generally starts with the synthesis of aminoglyoximes, followed by dehydration under basic

conditions. Scheme 1 shows the synthetic pathway that was utilized in this work for the synthesis of some common aminofurazan building blocks [10,14–17].

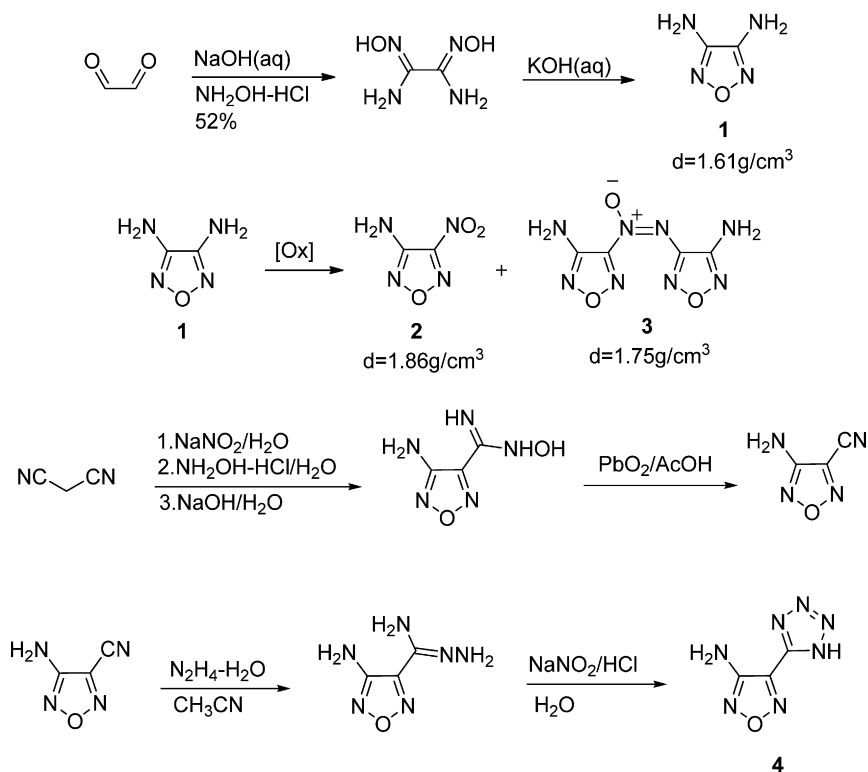
The furazan ring possesses an electron withdrawing ability that makes the amino group(s) in aminofurazans a challenge to derivatize [31,32]. Nevertheless most of the productive synthetic chemistry involving aminofurazans involves nucleophilic attack and condensation reactions of the amino groups or oxidative reactions of the amino groups. Ring opening reactions are also common, but of course such reactions destroy the energetic properties of the material [31].

2.2. The SF₅-acetyl building block

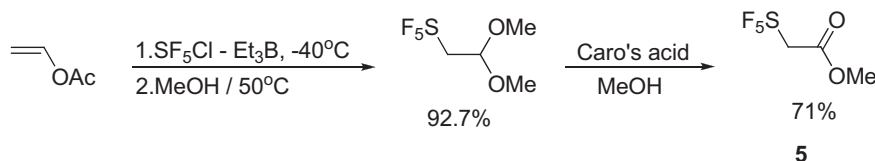
In order to achieve an efficient and in principle “easy” incorporation of the SF₅ group into aminofurazans, methyl 2-pentafluorosulfanylacetate **5** was chosen as a potentially useful SF₅-containing building block, and it was prepared by the method that was developed in our lab in 2006 (Scheme 2) [33].

3,4-Diaminofurazan **1** was chosen as our initial starting furazan substrate, and it was used to establish conditions for preparation of SF₅-acetamidofurazan derivatives. Various reaction conditions were attempted, including refluxing the two reactants in toluene or methanol, and using methoxide or NaH to promote the substitution, but all attempts proved unsuccessful in obtaining the desired product from ester **5** (Scheme 3).

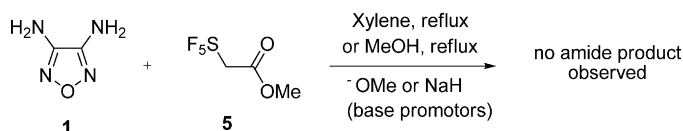
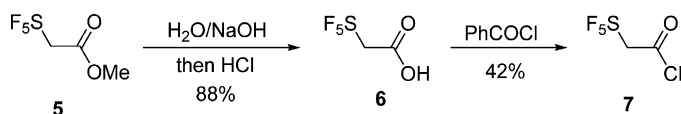
Aminofurazan **1** was therefore, in practice, insufficiently nucleophilic to replace the methoxy group of **5**. Known pK_a values of various substituted aminofurazans, which are given in Table 2 [32], are consistent with this conclusion. Protonated diaminofurazan **1** is only slightly less acidic than protonated methanol (CH₃OH₂⁺) (pK_a's of –1.94 and –2.2, respectively), which means that the amino groups of **1** are only slightly more electron donating than the oxygen of methanol. A SciFinder search revealed that the more basic/nucleophilic *p*-nitroaniline (pK_a ~ +1) is also not



Scheme 1. Synthesis of common furazan building blocks.



Scheme 2. Synthesis of methyl 2-pentafluorosulfanylacetate 5.

Scheme 3. Attempted reactions between diaminofurazan 1 and SF₅-ester 5.

Scheme 4. Synthesis of pentafluorosulfanylacetyl chloride (7).

converted to its acetamide derivative by reaction with esters, but requires the more reactive acetyl chloride or acetic anhydride.

Indeed, most previous amide-forming reactions with **1** have required acyl chlorides as acylating agents [34]. Thus **5** was converted via the carboxylic acid (**6**), into its respective acid chloride, pentafluorosulfanylacetyl chloride (**7**), the latter step of Scheme 4 using methodology virtually identical to that reported by Sitzmann for the preparation of SF₅CF₂COCl [35]. In contrast to attempts to use SOCl₂ or oxalyl chloride in this preparation, the use of benzoyl chloride allowed easy isolation of almost pure **7** via its distillation from the reaction mixture into an ice-cooled trap.

Pentafluorosulfanylacetyl chloride **7** proved sufficiently reactive with diaminofurazan **1** to allow formation of a mixture of the mono- and bis-amide products, **8** and **9**, as shown in Scheme 5. Nevertheless, the low yield for preparation of acyl chloride **7** encouraged us to seek a more efficient method for this conversion.

The reaction between amines and *N*-acylbenzotriazoles has been widely used for the synthesis of amides [36], with the reaction often providing better yields and cleaner reactions than could be obtained from the reactions of amines and acyl chlorides. Acylbenzotriazole **10** was readily prepared, in higher yield than the acid chloride, but unfortunately its reaction with diaminofurazan **1** (Scheme 6) proved not nearly as efficient as that of the acid chloride, so there was no overall advantage to using the acylbenzotriazole method.

Ultimately, the process that proved most efficient for preparation of both the mono- and the bis-amide from acid **6** was its direct condensation with the diaminofurazan in the presence of a carbodiimide [37]. Various carbodiimides were tried, with the best results being obtained with 1-ethyl-3-(3-dimethylaminopropyl)

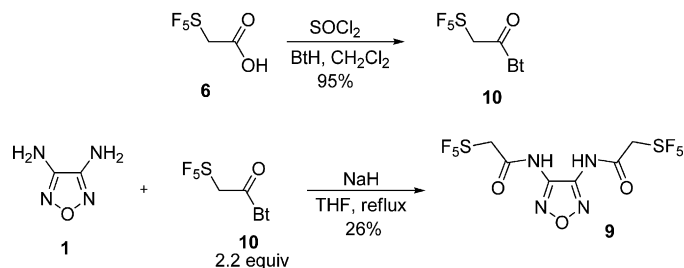
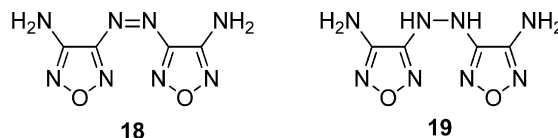
Scheme 6. Synthesis and use of the benzotriazole derivative of SF₅-acetic acid.

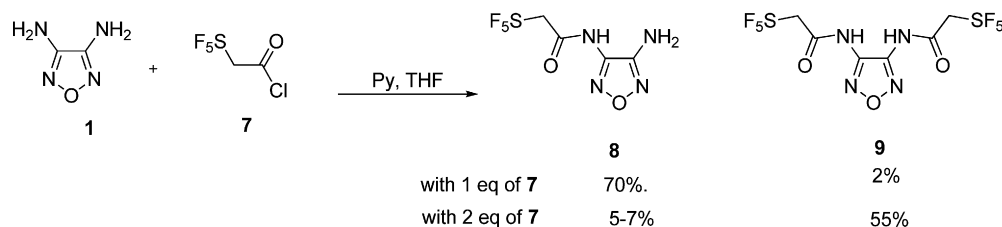
Fig. 4. Other synthesized, but unreactive aminofurazans.

carbodiimide (EDC). As can be seen from the second sequence given in Scheme 7, both the mono- or the bis-amide were able to be obtained relatively free of the other by control of the reaction stoichiometry.

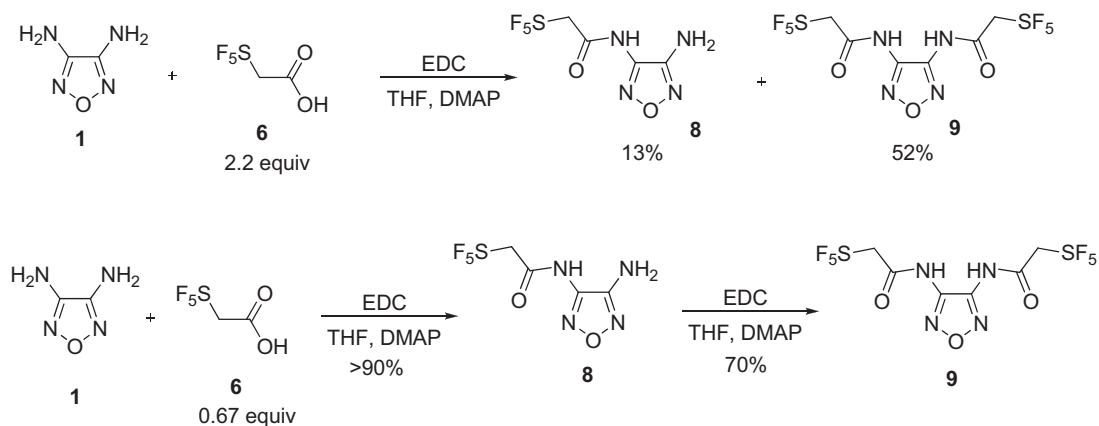
This carbodiimide methodology was then used to prepare four additional pentafluorosulfanylacetamide HEMs using three aminofurazans and aminotetrazole (Scheme 8).

Product **14** was contaminated by 5% of the isomeric product with the amide derived from the other amino group. Neither **12** nor **14** could be converted to their bis-acetamides. Two other aminofurazans that we had prepared, 3-amino-4-nitrofurazan (**2**) and azoxy-bis-aminofurazan (**3**) were not sufficiently reactive to form SF₅-acetamides under these conditions. The former was not surprising considering its reported pK_a value of -4.46 (Table 2). Two other aminofurazans compounds, the azo and hydrazino-bis-aminofurazans, **18** and **19**, which had been prepared from azoxy precursor **3** by literature methods [16], were also unreactive under the EDC reaction conditions (Fig. 4).

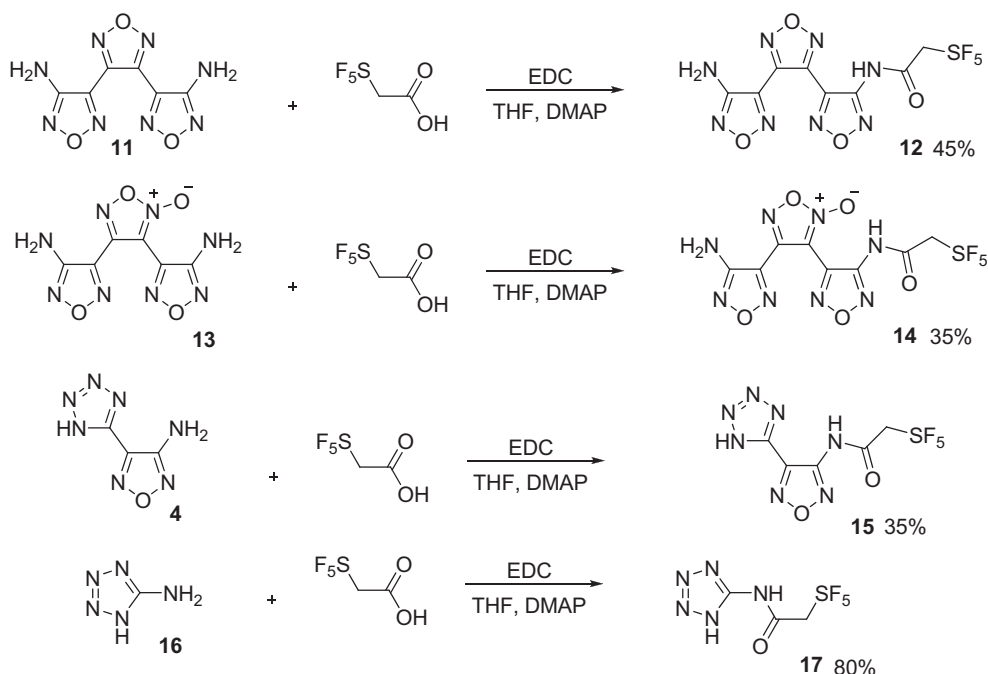
During the process of making new SF₅-energetic materials, it was noted that the synthesis of 4-(1*H*-tetrazol-5-yl)-3-amine-*N*-(2,4,6-trinitrophenyl)furazan (**20**) had not been reported. Due to the high energy that the three rings present on this compound, it was expected that this material should have good energetic properties. Therefore **20** was prepared as shown in Scheme 9.



Scheme 5. First synthesis of pentafluorosulfanylacetamidofurazans.



Scheme 7. Synthesis of mono and bis-amides from SF₅-acetic acid using EDC.



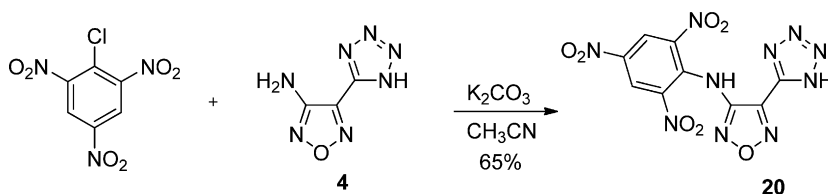
Scheme 8. Reaction between various amines and SF₅-acetic acid in the presence of EDC.

2.3. The pentafluorosulfanyl isocyanate building block

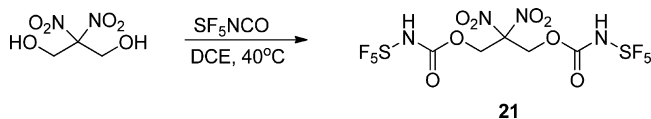
The high reactivity of SF₅-N=C=O toward several nucleophiles has been already carefully studied [38,39], including its addition to polynitro alcohols to yield the respective carbamates [7,40].

Scheme 10 shows the synthesis of bis-SF₅-carbamate **21**, which was previously prepared by Sitzmann [40], and which will be used as a “baseline” material in evaluating our new compounds.

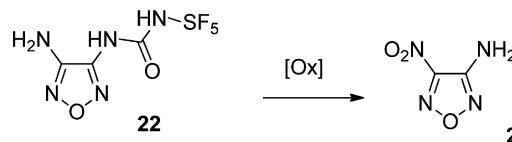
The high reactivity of SF₅NCO toward nucleophiles makes it potentially a great building block. However, it is this same high reactivity that limits the possible solvents in which it can be used. A solvent screen carried out with SF₅NCO indicated that it reacts with acetone rapidly and slowly with THF and acetonitrile. Although the isocyanate is unreactive with solvents such as dichloromethane and 1,2-dichloroethane, unfortunately most of the furazan substrates had virtually no solubility in these non-polar solvents.



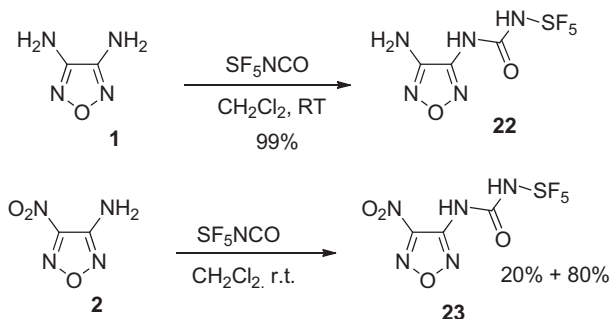
Scheme 9. 4-(1H-tetrazol-5-yl)-3-amine-N-(2,4,6-trinitrophenyl)furazan (**20**).



Scheme 10. Synthesis of a *bis*-SF₅-carbamate energetic material.



Scheme 13. Attempted oxidation of amino urea **22**.



Scheme 11. Reactions of SF₅NCO with aminofurazans **1** and **2**.

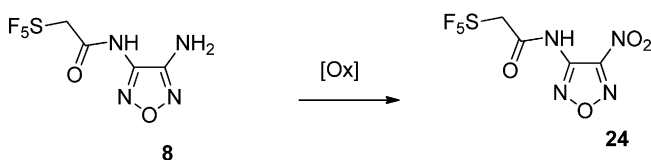
Due to this solvent limitation, only two urethane compounds were able to be prepared via the reaction of SF₅NCO with furazan derivatives, with the latter one (**23**) only able to be obtained as a mixture with starting furazan. Obviously, this was very disappointing. Any attempt to react the remaining NH₂ group of **22** with a second equivalent of SF₅NCO was prevented by the insolubility of **22** (Scheme 11).

2.4. Attempts to carry out *N*-nitration of acetamides

Although all of the newly synthesized SF₅-furazan-based materials should themselves have energetic properties, an increase in C/O balance through incorporation of nitro groups should improve their energetic performance. However, using *bis*-acetamide **9** as test substrate, all attempts to accomplish *N*-nitration of acetamides failed. Three mild nitration conditions were used: (1) H₂SO₄ (98%)–HNO₃ (70%), (2) NH₄NO₃–CF₃CO₃H–HNO₃ (70%) cat., and (3) NO₂BF₄–CH₃CN or THF. In all of these cases, starting materials were recovered. Stronger conditions for nitration were attempted: (1) HNO₃ (>99%), (2) NO₂NO₃–HNO₃ (>99%), (3) TFAA–HNO₃ (>99%), and (4) NO₂BF₄–NaH or Py–THF. However, under these conditions, the starting materials were either partially or completely destroyed.

Another approach to adding additional oxygen to the synthesized SF₅-furazan materials could be through the oxidation of residual amino groups to nitro groups. Indeed, the oxidation of mono acetamide **8** was successful using three different methods: (1) H₂O₂ (50%)–H₂SO₄ (98%)–Na₂WO₄ in 50% yield; (2) HOF·CH₃CN [41,42] in 65% yield; (3) H₂O₂ (50%)–H₂SO₄ (98%) in 30% yield (Scheme 12).

The oxidation of SF₅-urea-amino-furazan **22** was attempted using these same three methods, plus a fourth method using Ph₃PCH₂Ph⁺H₂SO₅[−]–CH₃CN. In all cases, the amino group had been oxidized, but the urea had proved unstable to the



Scheme 12. Oxidation of amino group of **8**.

reactions conditions, and the product was amino nitro furazan **2** (Scheme 13).

All synthesized materials exhibited good thermal and chemical stability, with the exception of 3-*N*-pentafluorosulfanylacetamide-4-(1*H*-tetrazol-5-yl)-furazan **15**, which was stable in the solid state, but decomposed rapidly in solution. This is probably due to the enhancement of the electron-withdrawing ability of the furazan by the presence of the highly electron-withdrawing tetrazole group, which makes the carbonyl group of **15** more electron deficient and thus more susceptible to nucleophilic attack.

2.5. Reactivity of aminofurazans

There is little significant information related to the reactivity of aminofurazans other than the few reported p*K*_a values of some derivatives (Table 2). In order to have a better understanding of the lack of reactivity of other aminofurazan derivatives that were prepared and used in this project, the ground states of some of these materials were calculated at B3LYP/6–31+G(d,p) level using Gaussian 03 Rev. E.01 [43], and the calculated C–NH₂ bond lengths were correlated with the p*K*_a values reported by Tselinskii (Table 2) [32].

The equation derived from the plot of was found to be $y = 71.67x - 101.11$, with a correlation coefficient of $R^2 = 0.9914$. This correlation coefficient indicates that there is strong correlation between these two parameters. Using the equation from the plot in Table 3 and the calculated C–NH₂ bond distances from the ground states of some aminofurazans used in this project, the p*K*_a values (NH₃⁺) were estimated in order to understand and establish an order of reactivity (Table 4). Combining our observed experimental results with the calculated p*K*_a values, it can be

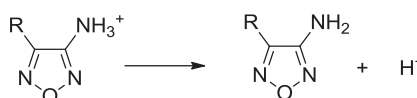
Table 2

p*K*_a values of some aminofurazan derivatives.

R	p <i>K</i> _a
NH ₂	−1.94
CH ₃	−2.15
OCH ₃	−2.51
N ₃	−2.88
NO ₂	−4.46

Table 3

Furazan p*K*_a vs. C–NH₂ bond distance.



R	p <i>K</i> _a	C–NH ₂ (Å)
NH ₂	−1.94	1.38516
CH ₃	−2.15	1.38093
OCH ₃	−2.51	1.37397
N ₃	−2.88	1.36974
NO ₂	−4.46	1.34938

Table 4
Calculated pK_a values using the plot from Table 3.

R	C–NH ₂ (Å)	pK_a
1	1.38516	–1.94 ^a
2	1.34938	–4.46 ^a
3^b	1.35792 ^c	–3.77 ^c
	1.35014 ^d	–4.33 ^d
4	1.35872	–3.73
11	1.3625	–3.45
13^b	1.36186 ^c	–3.50 ^c
	1.36957 ^d	–2.95 ^d
18	1.35046	–4.31
	1.37266	–2.71 (NH ₂)
19^b	1.39755	–0.94 (NH)

^a Exp. value Ref. [32].

^b Unsymmetrical amino groups, two values are calculated.

^c NH₂ group far from the =N–O[–] moiety.

^d NH₂ group closer from the =N–O[–] moiety.

seen that for any furazan–NH₃⁺ that has a pK_a greater or equal to –3.72, that amino furazan will form a SF₅–acetamide in the EDC reaction. This is the case for the 3-amino-4-(tetrazo-5-yl-furazan) (**4**), which gives a product that is not stable in solution. The high electron-withdrawing ability of the tetrazole added to that innate in the furazan ring pushes the amino group to the limit of its nucleophilic reactivity. The azoxy-bis-aminofurazan **3** did not yield any product, and it has calculated pK_a values of –3.77 and –4.33 for its unsymmetrical amino groups. There is a possibility that a product is formed, but that it is unstable under the reaction conditions. Interestingly, hydrazino-bis-aminofurazan **19** has calculated pK_a values for its two types of nitrogens of greater than –3.72 (–2.71 and –0.93) but did not give products using either the SF₅–acetyl chloride or the SF₅–acetic acid–EDC method. Based on the calculated C–N distances (Table 4), the NH from the hydrazine

moiety should be more reactive than the –NH₂ group, but if it reacts with the SF₅–acetyl building block, the product must be unstable, perhaps due to the adjacent NH group.

2.6. Properties of the synthesized SF₅–furazan-based energetic materials

For the convenience of the reader, Fig. 5 summarizes the ten new energetic materials that were prepared within this project. These materials were characterized by three methods: shock sensitivity, thermal stability, and performance as determined by Cheetah calculations.

The impact sensitivity was evaluated qualitatively by placing 5–10 mg of sample in a flat polished area, and hitting the sample with a flat-head hammer. With the exception of compound **20**, all of the synthesized materials exhibited no sensitivity to impact under the conditions of this test. Compound **20** showed partial decomposition. By comparison, when nitroguanidine was tested in the identical manner, detonation occurred. Although there is a more technical procedure to evaluate the impact sensitivity, this particular test serves to exemplify the intrinsic ability of the SF₅ group to reduce the impact sensitivity of high energy materials.

In order to evaluate the thermal stability of the new materials, thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were utilized for all compounds in Fig. 5 using a TA instrument SDT Q600, TGA/DSC combo instrument, which uses a ventilated system (open-pan). An example of a DSC/TGA thermogram is shown in Fig. 6, with all other DSC/TGA thermograms being given in Supporting information. Detailed information for the thermograms is presented in Table 5.

Fig. 6 shows in green the loss of weight vs. the temperature. Compound **28** has a 5% weight loss at 243.73 °C which indicates high thermal stability. At 293 °C it has lost almost 80% of its weight and remains the same even at temperature up to 1000 °C. This indicates that there is a remaining mass that did not convert into

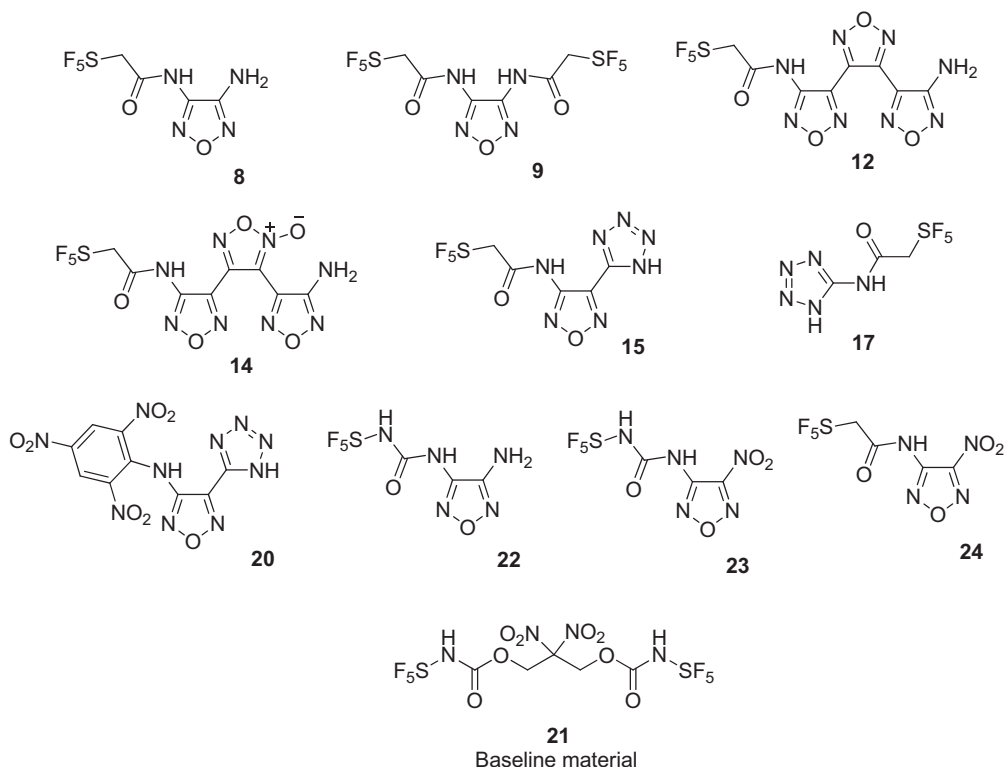


Fig. 5. New energetic materials prepared in this work.

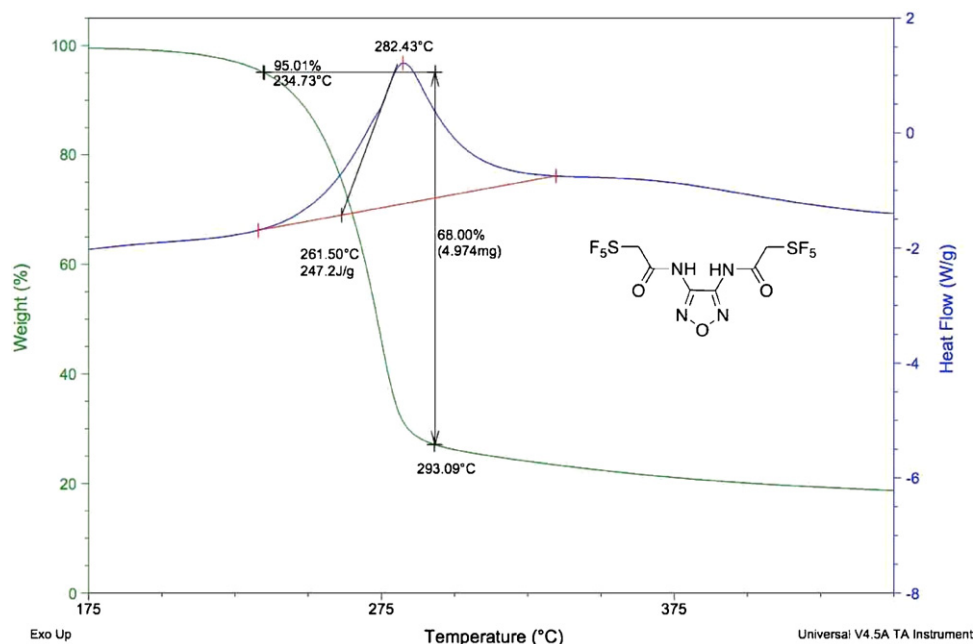


Fig. 6. DSC/TGA thermogram of compound 9.

gas. This is probably due to the lack of oxygen in the molecule. This problem is usually addressed in the final explosive material by mixing the desired compound with some oxidizers, which is essentially a material that will provide “oxygen” during the combustion process. The blue line shows the heat flow with an exotherm (energy release) at the maximum point of 282.43 °C with an energy release of 247.2 J/g, indicating that this and the other derivatives are promising as energetic materials.

Compound **21** was taken as a baseline material. This compound has been previously synthesized [40], and it exhibited good thermal stability. When compared to **21**, all of our new energetic materials exhibited from good (>100 °C) to excellent (>200 °C) thermal stability. Between compounds **8** and **9**, there is a 65 °C difference in the starting decomposition temperature, where the *bis*-acetamide **9** is more stable than the mono-acetamide **8**. This is a good indication that the addition of an SF₅-acetyl group increases the thermal stability of the energetic materials. Another example of this behavior is seen in compound **15**. Even though its starting decomposition temperature is the second lowest value (100.45 °C), its starting material, the 3-amino-4-(tetrazol-5-yl)furazan, starts to decompose at 45.76 °C. However there were exceptions to this

trend, since diaminofurazan (**1**) starts to decompose at 200 °C, whereas its mono-SF₅-acetamide (**8**) begins decomposition at 169.01 °C.

Compound **20** exhibits three stages of decomposition. This is characteristic of compounds that contain the tetrazole group. The retro-1,3-dipolar cycloaddition at the tetrazole group releases nitrogen at the first stage followed by a subsequent unknown decomposition process.

Our baseline material exhibited an endotherm at 160.56 °C, even though it was expected to exhibit an exotherm instead. The open-pan system used for this thermogram might not capture the energy liberated when gases are released rapidly. Four other materials also exhibited endotherms, whereas the other six energetic materials exhibited exotherms. The exotherms ranged up as high as −1758 J/g.

In addition to considering its impact sensitivity and thermal stability, the most important way to evaluate these materials is through their density (*d*), detonation pressure (*P*) and velocity of detonation (*vD*). The heats of formation (HOF) and densities were calculated by using the group additive method,[44,45] while the pressure and velocity of detonation, *P* and *vD* respectively, were calculated using Cheetah software (6.0) at the Lawrence Livermore National Laboratory (Table 6).

It is essential to remember that the density is one of the most important properties according to the semi-empirical equations suggested by Kamlet and Jacobs [3,46]. Only two compounds, **12** and **17**, did not converge in the calculations when using the Cheetah software. Because the way SF₅ affects energetic materials upon detonation is still not fully understood, it is not certain why these two molecules did not converge during the calculations.

All of the synthesized materials have from good to excellent densities, and when compared with the baseline material all but three have a greater density, and one of those does not contain the furazan group (**17**), while another does not contain an SF₅ group (**20**). This is consistent with the fact that a combination of these two groups has good potential to enhance the properties of energetic materials. In spite of having a positive HOF, compound **20** does not have the SF₅ group, which results in a relatively low density and thus relatively poor performance.

Table 5
Thermogram data of the synthesized energetic materials.

Compound	TGA temp. of decomp. (°C)	DSC (°C, J/g)
8	169.01–245.95	149.79, endo, 76.38 225.32, endo, 67.15
9	234.73–293.09	282.43, exo, −247.20
24	172.06–233.88	[161.98, 232.31], endo, 412.10
12	134.10–410.88	286.85, exo, −1023
14	214.81–382.10	[268.60, 325.27], exo, −1758
15	100.45–191.88	175.55, exo, −215.7
17	155.45–300.00	198.23, exo, −340.9
22	149.61–200.05	[159.28, 196.09], endo, 241.2
23	099.66–161.50	[114.46, 146.71], endo, 2481.0
20	141.00–201.46 267.78–300.00 732.75–971.64	172.58, endo, 55.52 294.32, exo, −708.4 895.99, endo, 2529
21	158.22–204.29	160.56, endo, 128.4

Table 6
Calculated performance data of the synthesized energetic materials.^a

Compound	<i>d</i> (g/cm ³)	HOF (kcal/mol)	<i>P</i> ^b (Gpa)	<i>v</i> D ^c (m/s)
8	2.01	−239.05	20.22	6741
9	2.05	−533.70	–	–
24	2.02	−251.56	29.48	7234
12	2.01	−109.65	26.12	7368
14	2.03	−109.17	28.62	7430
15	1.81	−169.13	17.85	7002
17	1.96	−174.52	–	–
22	2.11	−196.85	27.16	8049
23	2.10	−209.36	30.67	6862
20	1.54	147.35	18.25	6788
21	1.99	−623.00	23.73	6263

^a Calculated using Cheetah software v6.

^b Calculated detonation pressure.

^c Calculated velocity of detonation.

Pressure and speed of detonation for most of our materials are better than TNT, but below RDX and HMX. When compared to the chosen baseline material (**21**), most of the compounds exhibit better performance, which indicates once more that SF₅ and furazan groups combine to give good energetic properties. The SF₅-containing furazan compounds reported in the current paper exhibited lower heats of formation, but higher densities than the earlier-prepared SF₅-containing 1,2-diazoles and 1,2,3-triazoles reported by Shreeve [5,30]. When our materials are compared to these diazole and triazole materials, they performed considerably better with respect to pressure and velocity of detonation, as determined by Cheetah calculations.

3. Conclusions

The goal of this work was to combine the beneficial high density and resulting high energy properties of the furazan ring with those of the pentafluorosulfonyl (SF₅) group to make new high energy materials. To that end, ten new potentially high energy materials have been synthesized and characterized, all having higher density and predicted detonation properties than other known furazans or SF₅-containing materials. As a result of this work, insights were also gained regarding the fundamental chemistry of furazans, as well as the chemistry of SF₅-containing building blocks. Aminofurazans are inherently of low basicity and thus of low nucleophilicity, which makes functionalization of aminofurazans very challenging. On the other hand, because of the electron withdrawing power of the SF₅ group, those derivatives of aminofurazans that could be prepared were relatively unstable and susceptible to destruction by nucleophilic attack, a fact that, combined with the low nucleophilicity of the aminofurazans, made them particularly challenging to prepare.

Nevertheless, examination of the high energy properties of the ten derivatives that were able to be prepared indicates that there is significant potential and future promise for the creation of new and excellent furazan-based, SF₅-containing high energy materials, if these synthetic challenges can be overcome.

4. Experimental

4.1. General

All ¹H NMR (300 MHz), ¹⁹F NMR (282 MHz) and ¹³C NMR (75 MHz) spectra were recorded in CDCl₃, acetone-d₆ or DMSO-d₆ on a VXR 300 spectrophotometer. Chemical shifts were referenced with TMS, CDCl₃ and CFCl₃ (0 for ¹H, 77.23 for ¹³C and 0 for ¹⁹F). High-resolution mass spectra (HRMS) were obtained using a Finnegan 4500 gas chromatograph/mass spectrometer using

chemical ionization (CI). Thermal analyses were taken using a TA instrument SDT Q600, TGA/DSC combo instrument.

The SF₅NCO was provided by Dr. Joseph Mannion of National Naval Laboratories at Indian Head, whereas SF₅Cl was donated by Air Products for this project.

4.2. General method for the syntheses of pentafluorosulfonylacetamide-furazans

To a solution of aminofurazan (7.2 mmol, 1.5 equiv.) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) (9.6 mmol, 2.0 equiv.) in anhydrous THF (30 mL), was added pentafluorosulfonylacetamide (**6**) (4.8 mmol, 1 equiv.) in anhydrous THF (15 mL), dropwise with stirring using a pressure equalizing dropping funnel. After the addition of the acid, which took about 10 min, 4-dimethylaminopyridine (DMAP) (0.48 mmol, 0.1 equiv.) was added, and the stirring was continued for 16 h. The reaction mixture was then treated with 50 mL of water, extracted with ethyl acetate (3 × 30 mL), and the organic layer dried over Na₂SO₄, filtered, and the solvent removed under reduced pressure. The resulting solid (or oil) was purified by column chromatography (silica gel, 4:1 CH₂Cl₂:ethyl acetate).

4.2.1. 3-Amino-4-N-(2-pentafluorosulfonylacetamide)-1,2,5-oxadiazole (**8**)

White solid, 90% yield; mp (DSC) = 133.5 °C; ¹H NMR (DMSO-d₆), δ 4.79 (q, *J* = 9.0 Hz, 2H, CH₂), 6.00 (b, 2H, NH₂), 11.32 (b, 1H, NH); ¹⁹F NMR (DMSO-d₆), δ_A 83.60 (m, 1F), δ_B 71.30 (d, *J*_{AB} = 149 Hz, 4F); ¹³C NMR (DMSO-d₆), δ 72.2 (m, CH₂), 144.0 (s, C–NH), 156.2 (s, C–NH₂), 160.0 (m, CO); HRMS (M–H, calc): 266.9981, found: 266.9992.

4.2.2. 3,4-N,N'-bis-(2-pentafluorosulfonylacetamide)-1,2,5-oxadiazole (**9**)

White solid 70% yield; mp (DSC, decomp.) = 234.7 °C; ¹H NMR (DMSO-d₆), δ 4.82 (q, *J* = 9.0 Hz, 4H, CH₂), 11.42 (br, 2H, NH); ¹⁹F NMR (DMSO-d₆), δ_A 83.57 (m, 1F), δ_B 71.49 (d, *J*_{AB} = 149 Hz, 4F); ¹³C NMR (DMSO-d₆), δ 71.8 (m, CH₂), 146.4 (s, C–NH), 160.0 (m, CO); HRMS (M+H, calc): 436.9794, found: 436.9796.

4.2.3. 4-Amino-4''-N-(2-pentafluorosulfonylacetamide)-[3,3':4',3'']-Ter-[1,2,5]-oxadiazole (**12**)

Light yellow solid, 45% yield; mp (DSC) = 133.3 °C; ¹H NMR (DMSO-d₆), δ 4.72 (q, *J* = 9.0 Hz, 2H, CH₂), 6.66 (br, 2H, NH₂), 12.44 (br, 1H, NH); ¹⁹F NMR (DMSO-d₆), δ_A 83.53 (m, 1F), δ_B 71.53 (d, *J*_{AB} = 149 Hz, 4F); HRMS (M+H, calc): 405.0153, found: 405.0161.

4.2.4. 4-Amino-4''-N-(2-pentafluorosulfonylacetamide)-2'-oxy-[3,3':4',3'']-Ter-[1,2,5]-oxadiazole (**14**)

Light yellow solid, 35% yield; mp (DSC) = 125.2 °C; ¹H NMR (DMSO-d₆), δ 4.73 (q, *J* = 9.0 Hz, 2H, CH₂), 6.67 (br, 2H, NH₂), 12.43 (br, 1H, NH); ¹⁹F NMR (DMSO-d₆), δ_A 83.51 (m, 1F), δ_B 71.46 (d, *J*_{AB} = 147 Hz, 4F); HRMS (M–H, calc): 418.9951, found: 418.9966.

4.2.5. 3-N-(2-pentafluorosulfonylacetamide)-4-(1H-tetrazo-5-yl)-1,2,5-oxadiazole (**15**)

Light yellow solid, 35% yield; mp (DSC, decomp.) = 100.5 °C; ¹H NMR (DMSO-d₆), δ 4.62 (q, *J* = 9.0 Hz, 2H, CH₂), 11.03 (br, 1H, NH); ¹⁹F NMR (DMSO-d₆), δ_A 82.32 (m, 1F), δ_B 71.16 (d, *J*_{AB} = 149 Hz, 4F); HRMS (M–H, calc): 319.9995, found: 320.0001.

4.2.6. 5-N-(2-pentafluorosulfonylacetamide)-1H-tetrazole (**17**)

White Solid, 80% yield; mp (DSC, decomp.) = 155.5 °C; ¹H NMR (DMSO-d₆), δ 4.89 (q, *J* = 9.0 Hz, 2H–CH₂), 12.75 (br, 1H, NH); ¹⁹F NMR (DMSO-d₆), δ_A 84.00 (m, 1F), δ_B 71.51 (d, *J*_{AB} = 149 Hz, 4F); ¹³C NMR (DMSO-d₆), δ 72.0 (m, CH₂), 149.5 (s, =C–NH), 159.8 (m, CO); HRMS (M–H, calc): 251.9984, found: 251.9982.

4.3. Synthesis of 3-N-(2-pentafluorosulfonylacetamide)-4-nitro-1,2,5-oxadiazole (24)

To a solution of 50% H₂O₂ (1.6 g) and concentrated sulfuric acid (1.1 g) at 0 °C, was added 160 mg of Na₂WO₄·H₂O and 30 mg of 3-amino-4-(pentafluorosulfonylmethyl)furazan (**8**) in one portion. The mixture was stirred until the starting material disappears on the TLC (~16 h, 4:1 CH₂Cl₂:ethyl acetate). The mixture was then treated with 5 mL of water and extracted with ethyl acetate. The solvent was removed under reduced pressure and the resulting oil purified by column chromatography (silica gel, 4:1 CH₂Cl₂:ethyl acetate): light yellow solid, 50% yield. mp (DSC, decomp.) = 172.1 °C. ¹H NMR (DMSO-d₆, ppm), δ 5.11 (q, J = 9.0 Hz, 2H, CH₂), 11.87 (br, 1H, NH); ¹⁹F NMR (DMSO-d₆, ppm), δ_A 83.90 (m, 1F), δ_B 71.97 (d, J_{AB} = 149 Hz, 4F); ¹³C NMR (DMSO-d₆, ppm), δ 71.6 (m, CH₂), 144.7 (s, C–NH), 158.2 (s, C–NO₂), 160.0 (m, CO). HRMS (M+H, calc): 298.9873, found: 266.9902.

4.4. General method for the syntheses of pentafluorosulfonylurea-furazans

To 30 ml of anhydrous CH₂Cl₂ in a glass heavy wall pressure vessel, closed with a septum at –40 °C, 7.8 mmol of pentafluorosulfonyl isocyanate was bubbled. Then, the septum was removed and quickly 7.8 mmol of aminofurazan were added, after which the septum was replaced by a sealed cap. The cold bath was removed and the reaction mixture was stirred for 24 h. After that the vessel was opened and the solvent evaporated under reduced pressure.

4.4.1. 3-Amino-4-N-(3-pentafluorosulfonylurea)-1,2,5-oxadiazole (22)

White solid, 99% yield; mp (DSC, decomp.) = 149.61 °C; ¹H NMR (acetone-d₆), δ 10.55 (br, 1H, NH–SF₅), 8.83 (br, 1H, NH–CO), 5.57 (br, 2H, NH₂); ¹⁹F NMR (acetone-d₆), δ_A 77.44 (m, 1F), δ_B 72.40 (d, J_{AB} = 149 Hz, 4F); ¹³C NMR (acetone-d₆), δ 145.0 (s, C–NH₂), 148.7 (s, C–NH), 153.0 (m, CO); HRMS (M–H, calc): 267.9933, found: 267.9941.

4.4.2. 3-N-(3-pentafluorosulfonylurea)-4-nitro-1,2,5-oxadiazole (23)

Yellow Solid, 20% NMR yield; mp (DSC, decomp.) = 99.7 °C; ¹H NMR (acetone-d₆), δ 11.18 (br, 1H, NH–SF₅), 9.19 (br, 1H, NH–CO); ¹⁹F NMR (acetone-d₆), δ_A 76.78 (m, 1F), δ_B 72.13 (d, J_{AB} = 155 Hz, 4F); HRMS (M–H, calc): 297.9575, found: 297.9678.

4.5. Synthesis of 3-amino-N-(2,4,6-trinitrophenyl)-4-(1H-tetrazol-5-yl)-furazan (20)

To a solution of 3-amino-4-(1H-tetrazol-5-yl)-furazan (**4**) (153 mg, 1 mmol) and K₂CO₃ (2 mmol, 2 equiv.) in acetonitrile (10 ml), was added picryl chloride in one portion (371 mg, 1.5 mmol, 1.5 equiv.). The reaction mixture was stirred overnight, and the precipitate was filtered and washed with acetonitrile. The solid was recrystallized from acetonitrile: yellow solid, 65% yield; mp (DSC, decomp.) = 141.2 °C. ¹H NMR (acetone-d₆), δ 8.56 (s, 2H, =CH), 6.53 (b, 1H, NH); HRMS (calc): 387.0157, found: 387.0155.

4.6. Synthesis of 1-(1H-benzotriazolyl)-2-pentafluorosulfonylurethane (10)

To a solution of SF₅-acetic acid (**6**) (50 mg, 0.27 mmol) in CH₂Cl₂ (1 mL) was added dropwise a mixture of SOCl₂ (22 μL, 0.29 mmol, 1.1 equiv.) and 1H-benzotriazole (96 mg, 3 equiv.) in CH₂Cl₂ (1.5 mL). The mixture was stirred for 4 h at RT, the white precipitate was filtered off, and the organic solution evaporated under reduced pressure. The resulting oil was purified by flash column chromatography (silica gel, CH₂Cl₂), collecting 73.3 mg of

product (95% yield): ¹H NMR (CDCl₃), δ 5.43 (q, J = 7.2 Hz, 2H), 8.31 (d, J = 8.2 Hz, 1H), 8.19 (d, J = 8.2 Hz, 1H), 7.75 (t, J = 8.4 Hz, 1H), 7.61 (t, J = 8.4 Hz, 1H); ¹⁹F NMR (CDCl₃), δ_A 78.01 (m, 1F), δ_B 72.84 (d, J_{AB} = 151 Hz, 4F); HRMS (calc M–H⁺): 288.0230, found: 288.0243.

4.7. Computational methods

The quantum chemical calculations were performed with a hybrid basis set at MP2/6–31+G(d,p)-LANL2DZ level of theory. The effective core potential (ECP) of iodide was included in the calculations in order to minimize the time in the optimization. DMSO was used as a solvent in all calculations using the Polarizable Continuum Model (PCM). The transition states were characterized by one and only one negative frequency and the Intrinsic Reaction Coordinate (IRC) connecting both the starting material and the product. All the calculations were performed using Gaussian 03 Rev. E01 Software package [43].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2012.03.010.

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