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# Selective Synthesis of Bis(3-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-4,4′-azo- and -azoxyfurazan Derivatives

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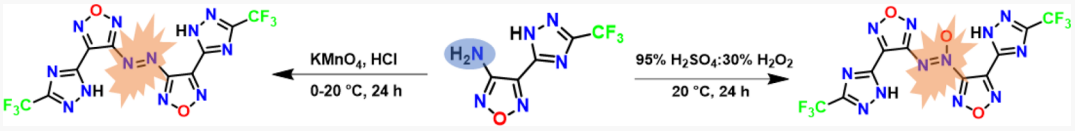


**ABSTRACT:** In this paper, we report the synthesis of two new derivatives, bis(3-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-4,4′-azo- and -azoxyfurazans by selective oxidation of 4-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-1,2,5-oxadiazol-3-amine. Ammonium salts of these derivatives were prepared, and all of them were fully characterized by multinuclear NMR, FTIR spectroscopy, elemental analysis, differential scanning calorimetry (DSC), and single-crystal X-ray diffraction. All of the new compounds have high measured crystal densities, and the energetic properties have been investigated.



Azo and azoxy-bridged compounds are the core scaffolds of numerous biologically active molecules and exhibit innumerable applications in biological chemistry and materials science due to the presence of the N═N and N═N−O moieties.[1] Generally, azoxy compounds are relatively thermally stable compared to their azo equivalents due to the release of $N_2O$ or $N_2$ upon decomposition or pyrolysis.[2] These derivatives can be synthesized using selective oxidation of their corresponding primary amines. Conventional approaches for the preparation of azo-bridged heteroaromatic compounds are by selective oxidation of amines with $(NH_4)_2S_2O_8$, $Na_2S_2O_8$, $KMnO_4$, DBI, AcOBr, DCI, TCICA, SDIC, NaClO, etc., while azoxy-bridged heterocycle derivatives are obtained by using oxidizing reagents such as Oxone or mixed acids with hydrogen peroxide or *m*-chloroperoxybenzoic acid (mCPBA) and other peroxy acids.[3] Similarly, reported by the selective reduction of nitroaromatic compounds to the corresponding azo or azoxy derivatives under the influence of metal catalysts, the majority of these methods are limited to only nonheterocyclic aromatic compounds.[4]

In the field of energetic materials, azo and azoxy moieties are a primary source for improving properties such as density, heat of formation, and oxygen balance, which enhance detonation performance.[5] Five-membered heterocycles, including pentazole, tetrazole, triazole, pyrazole, and furazans, constitute a promising class of high-density energetic materials. These are high nitrogen heteroaromatic compounds which generally possess high density, good thermostability, and large positive heats of formation. Heterocyclic rings with amine substituents utilized for the construction of highly thermostable, good oxygen balanced derivatives of azo- and azoxy-bridged energetic materials have been reported. Further functionalization of these derivatives by the formation of energetic salts or by the introduction of more energetic groups (e.g., $-NO_2$, $NHNO_2$, and $C(NO_2)_3$, etc.) and their detonation properties have been exhaustively investigated, showing them to be less stable and highly sensitive energetic materials.[6−8] As a result, for the development of stable and insensitive energetic materials, fluorinated explosives have attracted attention. In general, addition of fluorine atoms to the corresponding energetic materials (for, e.g., difluoroamino ($-NF_2$), fluorodinitromethyl ($-CF(NO_2)_2$)) increases the oxidizing properties and include high density, thermostability, and lower sensitivity.[9]

Fluorine compounds often find interesting applications as energetic materials as well as in medicinal chemistry, bioorganic chemistry, and agrochemicals.[10] Due to their unique nature, small size, and high electronegativity, fluorine atoms play a major role in influencing the physical, chemical, and biological properties of the corresponding organic compounds. Increasing the number of fluorine atoms in energetic materials provides better detonation performance along with high density, oxygen balance, and stability.[11] On many occasions, trifluoromethyl-based heterocyclic compounds, especially nitrogen-rich heterocycles, are found in many bioactive molecules.[12] They are found in many applications in materials science; e.g., trifluoromethyl 1,2,4-triazole derivatives are frequently encountered as ligands in the construction of metal organic frameworks (MOF) or metal coordination polymers for applications in gas and energy storage devices.[13]

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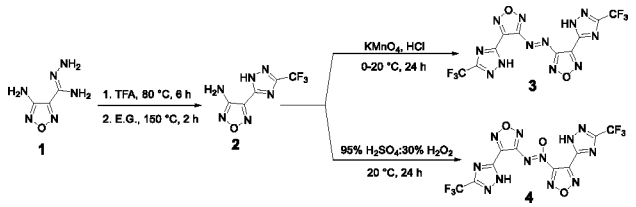
In keeping with our interest in design and synthesis of new heterocycles, we have developed a simple synthetic route for the construction of bis(3-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-4,4′-azo- and -azoxyfurazan derivatives, **3** and **4**, in good yields. Ammonium salts of **3** and **4** have been prepared and all of the new compounds were fully characterized by multinuclear NMR, FTIR and elemental analysis. The new structures **3**−**6** were confirmed by single-crystal X-ray diffraction analyses. Thermostabilities and physicochemical properties have been investigated and compared to TNT.

As given in Scheme 1, the initial precursor, 4-amino-1,2,5-oxadiazole-3-carbohydrazonamide, **1**, was prepared from

**Scheme 1. Synthesis of 1,2-Bis(4-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-1,2,5-oxadiazol-3-yl)diazene, 3, and 4,4′-(1-($\lambda^1$-Oxidanyl)-1$\lambda^4$-diazene-1,2-diyl)bis(3-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-1,2,5-oxadiazole, 4**

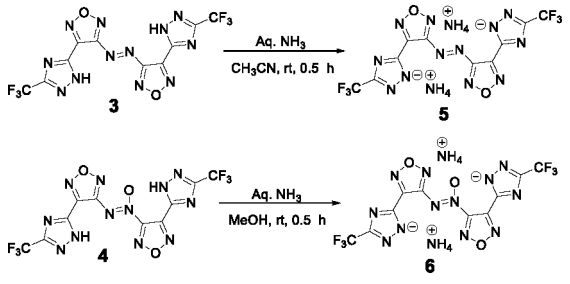



malononitrile using a literature procedure.[14] Treatment of compound **1** with excess trifluoroacetic acid (TFA) at 65 °C followed by reflux in ethylene glycol at 150 °C gave the cyclized product, 4-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-1,2,5-oxadiazol-3-amine, **2**, in 78% yield. Oxidation of **2** in a mixture of $KMnO_4$ and dilute hydrochloric acid (6 M) gives bis(3-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-4,4′-azofurazan, **3**, in 83% yield. On the other hand, the oxidation of compound **2** in a mixture of 95% $H_2SO_4$ and 30% $H_2O_2$ (1:2 ratio) gave the azoxy-bridged compound of bis(3-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-4,4′- azoxy furazan, **4**, in 73% yield.

The neutral compounds, **3** and **4**, were used as precursors to ammonium salts, **5** and **6**, respectively. Compound **3** was dissolved in acetonitrile, neutralized with aqueous ammonia (28%), and stirred at room temperature for 0.5 h. A yellow precipitate **5** was formed and collected by filtration. Similarly, compound **4** was neutralized with aqueous ammonia in methanol at room temperature to give the colorless solid ammonium salt, **6**, in 93% yield (Scheme 2).

All of the new compounds were fully characterized by FTIR, multinuclear NMR ($^1$H, $^{13}$C and $^{19}$F) spectroscopy, and elemental analysis (Supporting Information). In the $^1$H NMR spectrum of **2**, the $NH_2$ proton signal is found at $\delta$ 6.45 ppm.

**Scheme 2. Synthesis of Ammonium Salts 5 and 6**




In the neutral azo- and azoxy-bridged compounds **3** and **4**, one broad signal shift for the triazole N−H was found at $\delta$ 14.81 and 6.47 ppm, respectively. The $^{13}$C NMR spectra of compounds **2**−**6** have two different quartet signals with expected coupling constants ($^1J^{13}_{C-}{}^{19}_{F}$), and ($^2J^{13}_{C-}{}^{19}_{F}$) corresponding to $CF_3$ and its attached triazole carbon. The $^{19}$F NMR spectrum of **2** and azo compounds have one signal and azoxy derivatives have two signals with equal intensity, which support the unsymmetrical structure of the azoxy moiety. In addition, the $^{19}$F chemical shifts of neutral and ammonium salts have significant differences (Table 1).

**Table 1. $^{13}$C, and $^{19}$F NMR Chemical Shifts of Compounds 3−6**

| nuclei | assignment | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|
| $^{13}$C | N<u>C</u>N$_{furazan}$ | 161.8 | 158.4 | 162.3 | 156.7 |
| | N<u>C</u>N$_{furazan}$ | | 155.3 | | 153.4 |
| | C$_{triazole}$ | 152.9q | 152.7dq | 154.3q | 154.2dq |
| | C$_{triazole}$ | 143.8 | 145.9 | 149.0 | 149.3 |
| | C$_{triazole}$ | | 143.8 | | 147.5 |
| | C<u>C</u>N$_{furazan}$ | 141.3 | 143.0 | 146.0 | 145.2 |
| | C<u>C</u>N$_{furazan}$ | | 141.1 | | 144.0 |
| | $CF_3$ | 119.0q | 118.9dq | 121.7q | 121.6dq |
| $^{19}$F | | −64.11 | −64.13 | −61.28 | −61.11 |
| | | | −64.26 | | −61.21 |

The $^{15}$N NMR spectra were recorded for compounds **3**, **4**, and **6** in DMSO-$d_6$ (Figure 1). To control the proton exchange

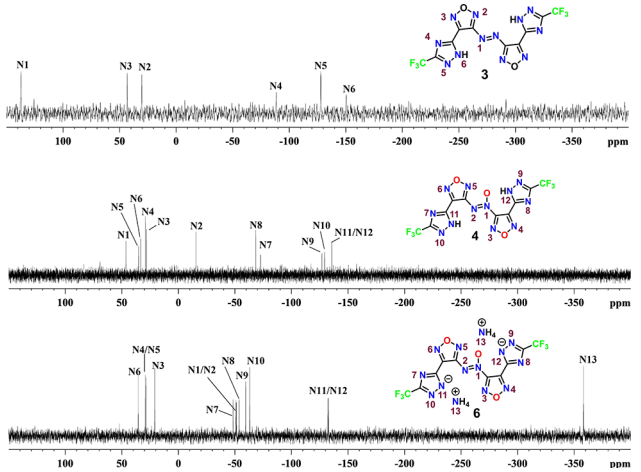



**Figure 1.** $^{15}$N NMR spectra of **3**, **4**, and **6**.

on triazole rings, one drop of $D_2O$ was added for compounds **3** and **4**. In the $^{15}$N NMR spectra of **3**, there are six signals: the azo nitrogen atom signal was observed at $\delta$ = 137.2 (N1) followed by furazan ring nitrogen signals at $\delta$ = 43.2 (N3), $\delta$ = 30.4 (N2) and the triazole ring nitrogen signals at $\delta$ = −88.4 (N4), $\delta$ = −127.8 (N5) and $\delta$ = −150.3 (N6). In compound **4**, there are 12 signals: the azoxy nitrogen atom with the oxygen atom is downfield at $\delta$ 46.29 (N1) compared to $\delta$ −15.60 (N2), followed by four furazan ring nitrogen signals at $\delta$ = 35.29 (N5), 33.26 (N6), 29.13 (N4), and 28.09 (N3) and six triazole ring nitrogen signals at $\delta$ = −68.42 (N8), −72.70 (N7), −126.85 (N9), −129.18 (N10), and −135.70 (N11/N12). In the ammonium salt, **6**, one signal was found at $\delta$ −358.02 (N13) for the ammonium cation ($NH_4^+$), and 12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nitrogen signals were found and compared to the neutral compound, **4**.

The crystal structures of compounds **3**–**6** were obtained. The crystallographic data and structure determination details, including bond lengths and bond angles, are available in the Supporting Information. Red prism crystals of **3** and yellow needle crystals of **5** were obtained by slow evaporation of DMSO/water and EtOH/water solutions at room temperature, respectively. Both compounds have cosolvents in their crystal structures with crystal densities at 100 K of 1.672 g·cm$^{-3}$ for **3** and 1.766 g·cm$^{-3}$ for **5**, respectively (Figure 2).

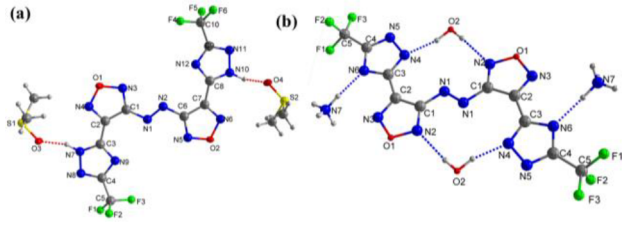

**Figure 2.** (a) Thermal ellipsoid plot (50%) and labeling scheme for **3**·2DMSO. (b) Thermal ellipsoid plot (50%) and labeling scheme for **5**·2$H_2O$. Dashed lines indicate strong hydrogen bonding.

Compound **3** crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell, while **5** crystallizes in the monoclinic space group $P2_1/n$ with two molecules per unit cell. The bond lengths of compound **3** and anion of **5** are comparable within the limits of error in contrast to their bond angles (Supporting Information). In both compounds **3** and **5**, the azo bond adopts a stable *E* configuration due to its lower energy relative to the *Z* configuration. The bond length of the azo bridge of N═N in **3** has an average value of 1.246 Å compared to a slightly longer value of 1.261 Å for the anion of the ammonium salt **5**. In **3**, two furazan rings, triazole rings, and an azo linkage are nearly planar with a torsion angle of C6–N2–N1–C1, −178.53°(15); N7–C3–C2–N4, 11.7°(3); N6–C7–C8–N10, 7.5°(3). It is the same in the anion of **5**, where the furazan ring is still coplanar with the azo linkage and triazole ring with torsion angles of N1$^1$–N1–C1–N2, 5.6°(5); N3–C2–C3–N6, −3.3°(5). In the packing system of **3**, only two pairs of hydrogen bonds which exist between the triazole NH of compound **3** and cosolvent DMSO (N10–H10–O4; N7–H7–O3), while **5** has four intermolecular hydrogen bonds between the cationic NH4 moieties, two water molecules, and the anion (Figure 2).

Suitable crystals were obtained for **4** and **6** by slow evaporation of their saturated solutions in chloroform and methanol, respectively. Their crystal structures are given in Figure 3. Compound **4** crystallizes in the triclinic space group *P*-1, whereas its ammonium salt **6** crystallizes in monoclinic space group $P2_1/n$ with crystal densities at 100 K of 1.883 g·cm$^{-3}$ for **4** and 1.711 g·cm$^{-3}$ for **6**, respectively.

It is noteworthy that in the crystal structure of **4**, due to steric hindrance of trifluoromethyl triazole unit, the molecular structure is bent into a "U" shape. In this case, both furazan rings in compound **4** are oriented in the same direction, while they are oriented oppositely in the anion of **6**. In **4**, atoms of the furazan and triazole rings are planar, while the furazan and triazole rings are laid out of the plane from one another. The dihedral angles between the mean planes through the furazan ring **A** and furazan ring **B**, furazan ring **A** and triazole ring **A′**, and furazan ring **B** and triazole ring **B′** were found to be

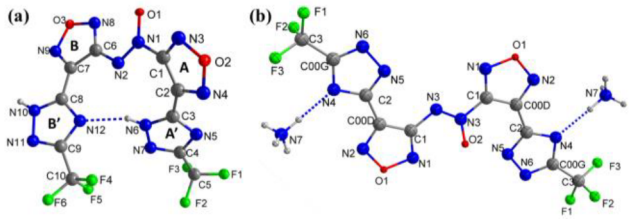

**Figure 3.** (a) Thermal ellipsoid plot (50%) and labeling scheme for **4**·$CHCl_3$. For clarity, the $CHCl_3$ molecule is omitted in **4**·$CHCl_3$. (b) Thermal ellipsoid plot (50%) and labeling scheme for **6**·2MeOH. For clarity, two MeOH molecules are omitted in **4**·$CHCl_3$. Dashed lines indicate strong hydrogen bonding.

42.35°, 34.15°, and 17.59°, respectively (**4**). In **6**, the furazan ring and the triazole ring are nearly coplanar (Figure 3b), which is seen from the torsion angles of C1–C00D–C2–N4, 168.45°(14). In **4**, there is an intramolecular hydrogen bond between one of the triazole NH groups and the nitrogen atom of another triazole ring (N6–H6···N12), while the ammonium salt **6** has hydrogen bond interaction between cation $NH_4$ proton and triazole ring nitrogen atom (N7–H7A···N4). The bond lengths and bond angles in compounds **4** and **6** resemble compounds **3** and **5** (Supporting Information).

The physicochemical properties for all new compounds and standard explosive energetic properties for comparison are reported in Table 2. The thermal stabilities (onset temperature) of all compounds were measured by differential scanning calorimetry (DSC) with a heating rate of 5 °C min$^{-1}$. All new compounds melt prior to decomposition. It is interesting that both neutral compounds **3** and **4** have high thermal stabilities (**3**, $T_{dec}$ = 272 °C; **4**, $T_{dec}$ = 276 °C) relative to their ammonium salts (**5**, $T_{dec}$ = 268 °C; **6**, $T_{dec}$ = 165 °C). Densities were measured by using a gas pycnometer at 25 °C and were found to be moderately high within the range from 1.78–1.84 g·cm$^{-3}$. As expected, both the neutral azo compound **3** (1.82 g·cm$^{-3}$) and azoxy compound **4** (1.84 g·cm$^{-3}$) have higher densities than their ammonium salts. The heats of formation for the neutral compounds **3** and **4** and ammonium salts **5** and **6** were determined by using the Gaussian 03 suite of programs (Supporting Information).[15] Due to the presence of the C–F bonds, all of the new compounds exhibit negative heats of formation between the range of −471 kJ mol$^{-1}$/−0.96 kJ g$^{-1}$ to −307 kJ mol$^{-1}$/−0.70 kJ g$^{-1}$. In order to evaluate the possibility of practical application in the field of energetic materials, the detonation properties were calculated with the Explo5 (version 6.01) code program[16] based on the measured densities and calculated heats of formation. Lower detonation properties were expected due to the high negative heats of formation for all high fluorinated derivatives. Interestingly, both the ammonium salts, **5** ($vD$ = 7173 m s$^{-1}$; $P$ = 21.55 GPa) and **6** ($vD$ = 7389 m s$^{-1}$; $P$ = 23.02 GPa) have detonation properties comparable with TNT ($vD$ = 6881 m s$^{-1}$; $P$ = 19.5 GPa) (Table 2). Impact and friction sensitivity values were measured by using BAM drop hammer and friction tester techniques, and all new compounds were found to be insensitive (IS > 40 J, FS > 360 N) to impact and friction.[17]

In summary, we have designed and synthesized two new heterocyclic compounds, **3** and **4**, with the combination of azo- or azoxy-bridged mixed heterocycles of furazan and triazoles by selective oxidation of 4-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-1,2,5-oxadiazol-3-amine, **2**. Ammonium salts **5** and **6**



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Table 2. Physicochemical and Energetic Properties of 3−6 in Comparison with TNT

| compd | $\rho^a$ (g·cm$^{-3}$) | $vD^b$ (m s$^{-1}$) | $P^c$ (GPa) | $\Delta_f H^{\circ d}$ (kJ mol$^{-1}$/kJ g$^{-1}$) | $T_m{}^e$ (°C) | $T_{dec}{}^f$ (°C) | IS$^g$ (J) | FS$^h$ (N) |
|---|---|---|---|---|---|---|---|---|
| **3** | 1.82 | 6383 | 20.86 | −307/−0.70 | 205 | 272 | >40 | >360 |
| **4** | 1.84 | 6505 | 21.23 | −414/−0.91 | 141 | 276 | >40 | >360 |
| **5** | 1.78 | 7173 | 21.55 | −402/−0.85 | 140 | 268 | >40 | >360 |
| **6** | 1.82 | 7389 | 23.02 | −476/−0.97 | 140 | 165 | >40 | >360 |
| TNT[i] | 1.65 | 6881 | 19.5 | −59/−0.26 | 81 | 300 | 15 | 353 |

[a]Density measured by a gas pycnometer at 25 °C. [b]Calculated detonation velocity. [c]Calculated detonation pressure. [d]Calculated molar enthalpy of formation in solid state. [e]Melting temperature (onset). [f]Decomposition temperature (onset). [g]Impact sensitivity. [h]Friction sensitivity. [i]Reference 11a.

were prepared in very good yields. All four new compounds were fully characterized by multinuclear NMR, FTIR, and elemental analysis. All new structures of **3**−**6** were confirmed by single-crystal X-ray analysis. Thermostabilities and crystal densities were measured, and energetic properties were calculated. Ammonium salts of **5** and **6** were found to have detonation properties comparable with TNT.

## EXPERIMENTAL SECTION

***Caution!*** Although no explosions or detonations occurred during the preparation or handling of these nitrogen-rich compounds, appropriate safety precautions (protective gloves and coats, face shield, and explosion-proof baffle) must be followed to ensure safety.

**General Information.** Reagents were purchased from Aldrich and Acros Organics and were used as received. $^1$H, $^{13}$C, and $^{19}$F NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13, 75.48, and 282.40 MHz, respectively, by using DMSO-$d_6$ or acetone-$d_6$ as the solvent and locking solvent. Tetramethylsilane, trichlorofluoromethane, and nitromethane are used as references for $^1$H, $^{13}$C, $^{19}$F, and $^{15}$N NMR spectra, respectively. The $^{15}$N spectra were obtained on a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz. The melting and decomposition (onset) points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q2000) at a scan rate of 5 °C min$^{-1}$. IR spectra were recorded using KBr pellets for solids on a Nicolet Thermo model AVATAR 370 spectrometer. Density was measured at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses (C, H, N) was determined using a Vario Micro cube Elementar Analyzer. The sensitivities to impact (IS) and friction (FS) were determined according to BAM standards.

**4-(3-(Trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-1,2,5-oxadiazol-3-amine 2.** 4-Amino-1,2,5-oxadiazole-3-carbohydrazonamide, **1**,[1] (5.0 g, 35.2 mmol) was dissolved in trifluoracetic acid (30 mL) and heated at 65 °C overnight. After being cooled to room temperature, excess amounts of trifluoracetic acid were removed with an air blower to give a colorless solid. The solid was dissolved in ethylene glycol (20 mL) and heated slowly using an oil bath at 120 °C for 2 h. After being cooled to room temperature, the reaction mixture was poured into distilled water (150 mL) and stirred at room temperature for 0.5 h to form a colorless precipitate that was collected by filtration and dried by air blowing to give 4-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-1,2,5-oxadiazol-3-amine, **2** (5.90 g, 78%). White solid. $T_m$: 153−155 °C (onset). $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 6.45 (s, 2H, $NH_2$). $^{13}$C{$^1$H}NMR (75.4 MHz, DMSO-$d_6$): $\delta$ 155.2, 152.6 (q, C−F, $J_{C-F}$ = 39.3 Hz), 145.8, 136.6, 119.2 (q, C−F, $J_{C-F}$ = 269.2 Hz). $^{19}$F NMR (282 MHz, DMSO-$d_6$): $\delta$ −63.92; IR (KBr pellet): $\upsilon$ 3571, 3455, 3323, 3062, 2960, 2775, 1642, 1615, 1574, 1506, 1456, 1417, 1329, 1227, 1162, 1042, 1006, 974, 916, 916, 754, 601, 570, 460 cm$^{-1}$. Anal. Calcd for $C_5H_3F_3N_6O$ (220.11): C, 27.28; H, 1.37; N, 38.18. Found: C, 27.30; H, 1.48; N, 38.33.

**1,2-Bis(4-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-1,2,5-oxadiazol-3-yl)diazene, 3.** 4-(3-(Trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-1,2,5-oxadiazol-3-amine, **2** (1.0 g, 4.5 mmol), was dissolved in 6 M hydrochloric acid (45 mL) and cooled to 0 °C. To this was added dropwise potassium permanganate (0.71 g, 4.5 mmol) in distilled water (3.0 mL). The resulting mixture was warmed to room temperature and stirred for 24 h. Then the reaction mixture was diluted by addition of 5% hydrogen peroxide until the color changed. A yellow precipitate was formed, collected by filtration, washed with excess water (10 mL), and dried to give **3** (0.83 g, 83%). Yellow solid. $T_m$: 205−208 °C (onset), $T_d$: 272 °C (onset). $^1$H NMR (300 MHz, acetone-d$_6$): $\delta$ 14.81 (s, 2H, NH). $^{13}$C{$^1$H}NMR (125 MHz, DMSO-$d_6$): $\delta$ 161.8, 152.9 (q, C−F, $J_{C-F}$ = 39.4 Hz), 143.8, 141.2, 119.0 (q, C−F, $J_{C-F}$ = 268.1 Hz). $^{19}$F NMR (282 MHz, DMSO-$d_6$): $\delta$ −64.11. $^{15}$N NMR (50.66 MHz, DMSO-$d_6$ + 1 drop $D_2O$): $\delta$ 137.20, 43.24, 30.46, −88.43, −127.84, −150.33. IR (KBr pellet): $\nu$ 3153, 1565, 1511, 1441, 1344, 1314, 1222, 1049, 995, 935, 882, 776, 754, 705, 624 cm$^{-1}$. Anal. Calcd for $C_{10}H_2F_6N_{12}O_2$ (436.03): C, 27.54; H, 0.46; N, 38.53. Found: C, 27.65; H, 0.53; N, 38.96.

**4,4′-(1-($\lambda^1$-Oxidanyl)-1$\lambda^4$-diazene-1,2-diyl)bis(3-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-1,2,5-oxadiazole, 4.** Concentrated $H_2SO_4$ (5 g) and 30% $H_2O_2$ (10 mL) were cooled to 15 °C using an ice-cold water bath and stirred for 10 min. To this was added 4-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)-1,2,5-oxadiazol-3-amine **2** (1.0 g, 4.5 mmol), and the resulting mixture was stirred at room temperature for 24 h. A colorless precipitate was formed and collected by filtration. The solid was washed with cold water (5 mL) and dried with an air blower to give a colorless compound, **4** (0.73 g, 73%). Colorless solid. $T_m$: 141−143 °C (onset), $T_d$: 276 °C (onset). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 6.47 (s, 2H, NH); $^{13}$C{$^1$H}NMR (125 MHz, DMSO-$d_6$): $\delta$ 158.4, 155.3, 152.7 (dq, C−F, $J_{1C-F}$ = 40.2 Hz; $J_{2C-F}$ = 66.1 Hz), 145.9, 153.8, 143.0, 141.1, 136.6, 118.9 (dq, C−F, $J_{1C-F}$ = 13.4 Hz; $J_{2C-F}$ = 268.6 Hz). $^{19}$F NMR (282 MHz, DMSO-$d_6$): $\delta$ −64.13, −64.26. $^{15}$N NMR (50.66 MHz, DMSO-$d_6$ + 1 drop $D_2O$): $\delta$ 45.79, 35.10, 32.59, 27.78, −68.17, −72.16, −126.40, −128.65. IR (KBr pellet): $\nu$ 3144, 1632, 1570, 1496, 1433, 1365, 1318, 1241, 1161, 1039, 992, 907, 752, 612, 462 cm$^{-1}$. Anal. Calcd for $C_{10}H_2F_6N_{12}O_3$ (452.02): C, 26.56; H, 0.45; N, 37.17. Found: C, 26.00; H, 0.71; N, 36.69.

**Diammonium 5,5′-(Diazene-1,2-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(3-(trifluoromethyl)-1,2,4-triazol-1-ide), 5.** Compound **3** (0.5 g, 1.1 mmol) was dissolved in acetonitrile (5 mL) and aqueous ammonia (0.5 mL) in acetonitrile (2 mL) at room temperature. The resulting mixture was stirred at room temperature for 30 min, and a yellow solid precipitated. The precipitate was collected by filtration and dried at room temperature to give pure compound **5** (0.52 g, 97%). Yellow solid. $T_m$: 140−142 °C (onset), $T_d$: 268 °C (onset). $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 7.29 (s, 8H, $NH_4$). $^{13}$C{$^1$H}NMR (125 MHz, DMSO-$d_6$): $\delta$ 162.3, 154.3 (q, C−F, $J_{C-F}$ = 34.1 Hz), 149.0, 146.0, 121.7 (q, C−F, $J_{C-F}$ = 269.9 Hz). $^{19}$F NMR (282 MHz, DMSO-$d_6$): $\delta$ −61.28. IR (KBr pellet): $\nu$ 3365, 2981, 2741, 2179, 1850, 1701, 1587, 1481, 1439, 1411, 1324, 1204, 1139, 1098, 1043, 1020, 994, 909, 876, 777, 753, 700, 609, 586, 564, 486, 423 cm$^{-1}$. Anal. Calcd for $C_{10}H_8F_6N_{14}O_2$ (470.08): C, 25.54; H, 1.71; N, 41.70. Found: C, 25.48; H, 1.827; N, 42.00.

**Diammonium 5,5′-((1-($\lambda^1$-Oxidanyl)-1$\lambda^4$-diazene-1,2-diyl)-bis(1,2,5-oxadiazole-4,3-diyl))bis(3-(trifluoromethyl)-1,2,4-triazol-1-ide), 6.** Compound **4** (0.5 g, 1.1 mmol) was dissolved in acetonitrile (3 mL), and aqueous ammonia (0.5 mL) was added dropwise at room temperature. The resulting mixture was stirred at room temperature for 30 min, and a yellow precipitate was formed.


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The precipitate was collected by filtration and dried at room temperature to give pure compound **6** (0.46 g, 86%). Pale yellow solid. $T_m$: 140−143 °C(onset), $T_d$: 165 °C (onset). $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 7.18 (s, 8H, $NH_4$). $^{13}$C{$^1$H}NMR (125 MHz, DMSO-$d_6$): $\delta$ 156.7, 154.2 (dq, C−F, $J_{1C-F}$ = 34.0 Hz; $J_{2C-F}$ = 50.9 Hz), 149.3, 147.5, 145.2, 144.0, 121.6 (dq, C−F, $J_{1C-F}$ = 22.1 Hz; $J_{2C-F}$ = 267.7 Hz). $^{19}$F NMR (282 MHz, DMSO-$d_6$): $\delta$ −61.11, −61.21. $^{15}$N NMR (50.66 MHz, DMSO-$d_6$): $\delta$ 35.47, 29.21, 28.52, 20.88, −48.33, −50.88, −51.39, −53.65, −59.44, −63.12, −132.23, −132.81. IR (KBr pellet): $\nu$ 3660, 3310, 3048, 2816, 1848, 1699, 1599, 1483, 1443, 1374, 1216, 1157, 1128, 1085, 1027, 1017, 990, 931, 904, 874, 772, 751, 600, 561, 503, 459 cm$^{-1}$. Anal. Calcd for $C_{10}H_8F_6N_{14}O_3$ (486.25): C, 24.70; H, 1.66; N, 40.33; found: C, 24.66; H, 1.47; N, 39.43.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00531.

$^1$H, $^{13}$C, and $^{19}$F NMR spectra for new compounds, X-ray crystal diffraction data and crystal structures for compounds **3**−**6** (PDF)

### Accession Codes

CCDC 2057052−2057055 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

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