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# Energetic Dinitromethyl Groups Functionalized Azofurazan and Its Azofurazanate

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**X-Ray crystallography data**

**Table S1.** Crystal data and structure refinement for **2** and **3**.

| Identification code | **2** | **3** |
|---|---|---|
| CCDC number | 1473226 | 1473225 |
| Empirical formula | $C_6 F_2 N_{10} O_{10}$ | $C_6H_2N_{10}O_{10}$ |
| Formula weight | 410.16 | 374.18 |
| Temperature/K | 150(2) K | 150(2) |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| *a*/Å | 7.2868(5) | 7.3983(9) |
| *b*/Å | 7.7602(5) | 7.6242(9) |
| *c*/Å | 12.5498(8) | 11.7823(14) |
| *α*/° | 90 | 90 |
| *β*/° | 90.9520(10) | 94.006(2) |
| *γ*/° | 90 | 90 |
| Volume/Å$^3$ | 709.56(8) | 662.97(14) |
| *Z* | 2 | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.920 | 1.874 |
| μ/mm$^{-1}$ | 0.195 | 0.178 |
| F(000) | 408 | 376 |
| Crystal size/mm$^3$ | 0.460 × 0.375 × 0.210 | 0.320 × 0.302 × 0.060 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.086 to 29.934 | 3.155 to 30.037 |
| Index ranges | -10<=h<=10,<br>-10<=k<=10,<br>-16<=l<=17 | -9<=h<=10,<br>-10<=k<=10,<br>-15<=l<=16 |
| Reflections collected | 7608 | 6857 |
| Independent reflections | 2005 [$R_{int}$ = 0.0146] | 1860 [$R_{int}$ = 0.0386] |
| Data/restraints/parameters | 2005 / 0 / 127 | 1860 / 0 / 118 |
| Goodness-of-fit on $F^2$ | 1.044 | 1.043 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0298,<br>$wR_2$ = 0.0768 | $R_1$ = 0.0418,<br>$wR_2$ = 0.0811 |
| Final R indexes [all data] | $R_1$ = 0.0316,<br>$wR_2$ = 0.0783 | $R_1$ = 0.0706,<br>$wR_2$ = 0.0903 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.391 and -0.244 | 0.397 and -0.218 |

**Table S2**. Bond lengths [Å] and angles [°] for **2**.

| | |
|---|---|
| O(1)-N(3) | 1.2083(12) |
| O(2)-N(3) | 1.2116(12) |
| N(3)-C(4) | 1.5332(12) |
| C(4)-F(8) | 1.3332(10) |
| C(4)-C(9) | 1.4937(12) |
| C(4)-N(5) | 1.5436(12) |
| N(5)-O(7) | 1.2091(12) |
| N(5)-O(6) | 1.2102(12) |
| C(9)-N(10) | 1.3007(12) |
| C(9)-C(13) | 1.4317(12) |
| N(10)-O(11) | 1.3760(10) |
| O(11)-N(12) | 1.3693(11) |
| N(12)-C(13) | 1.3077(12) |
| C(13)-N(14) | 1.4053(12) |
| N(14)-N(14)#1 | 1.2586(15) |

| | |
|---|---|
| O(1)-N(3)-O(2) | 128.18(9) |
| O(1)-N(3)-C(4) | 116.09(8) |
| O(2)-N(3)-C(4) | 115.72(8) |
| F(8)-C(4)-C(9) | 113.73(7) |
| F(8)-C(4)-N(3) | 108.47(7) |
| C(9)-C(4)-N(3) | 112.11(7) |
| F(8)-C(4)-N(5) | 107.15(7) |
| C(9)-C(4)-N(5) | 109.04(7) |
| N(3)-C(4)-N(5) | 105.94(7) |
| O(7)-N(5)-O(6) | 128.06(9) |
| O(7)-N(5)-C(4) | 116.53(8) |
| O(6)-N(5)-C(4) | 115.40(8) |
| N(10)-C(9)-C(13) | 108.80(8) |
| N(10)-C(9)-C(4) | 119.98(8) |
| C(13)-C(9)-C(4) | 131.07(8) |
| C(9)-N(10)-O(11) | 105.58(7) |
| N(12)-O(11)-N(10) | 111.45(7) |
| C(13)-N(12)-O(11) | 105.55(8) |
| N(12)-C(13)-N(14) | 118.56(8) |
| N(12)-C(13)-C(9) | 108.62(8) |
| N(14)-C(13)-C(9) | 132.81(8) |
| N(14)#1-N(14)-C(13) | 111.34(9) |

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+2

**Table S3**. Torsion angles [°] for **2**.

| | |
|---|---|
| O(1)-N(3)-C(4)-F(8) | -34.26(11) |
| O(2)-N(3)-C(4)-F(8) | 146.75(9) |
| O(1)-N(3)-C(4)-C(9) | -160.68(9) |
| O(2)-N(3)-C(4)-C(9) | 20.33(12) |
| O(1)-N(3)-C(4)-N(5) | 80.49(10) |
| O(2)-N(3)-C(4)-N(5) | -98.49(10) |
| F(8)-C(4)-N(5)-O(7) | 145.74(8) |
| C(9)-C(4)-N(5)-O(7) | -90.76(10) |
| N(3)-C(4)-N(5)-O(7) | 30.09(11) |
| F(8)-C(4)-N(5)-O(6) | -35.60(10) |
| C(9)-C(4)-N(5)-O(6) | 87.91(9) |
| N(3)-C(4)-N(5)-O(6) | -151.25(8) |
| F(8)-C(4)-C(9)-N(10) | 122.76(9) |
| N(3)-C(4)-C(9)-N(10) | -113.72(9) |
| N(5)-C(4)-C(9)-N(10) | 3.26(11) |
| F(8)-C(4)-C(9)-C(13) | -52.30(13) |
| N(3)-C(4)-C(9)-C(13) | 71.22(12) |
| N(5)-C(4)-C(9)-C(13) | -171.80(9) |
| C(13)-C(9)-N(10)-O(11) | 0.09(10) |
| C(4)-C(9)-N(10)-O(11) | -175.98(7) |
| C(9)-N(10)-O(11)-N(12) | 0.26(10) |
| N(10)-O(11)-N(12)-C(13) | -0.52(11) |
| O(11)-N(12)-C(13)-N(14) | 179.92(8) |
| O(11)-N(12)-C(13)-C(9) | 0.55(11) |
| N(10)-C(9)-C(13)-N(12) | -0.42(11) |
| C(4)-C(9)-C(13)-N(12) | 175.06(9) |
| N(10)-C(9)-C(13)-N(14) | -179.66(10) |
| C(4)-C(9)-C(13)-N(14) | -4.18(17) |
| N(12)-C(13)-N(14)-N(14)#1 | 174.46(10) |
| C(9)-C(13)-N(14)-N(14)#1 | -6.36(16) |

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+2

**Table S4**. Bond lengths [Å] and angles [°] for **3**.

| | |
|---|---|
| O(1)-N(3) | 1.2175(18) |
| O(2)-N(3) | 1.2142(17) |
| N(3)-C(4) | 1.5169(17) |
| C(4)-C(8) | 1.491(2) |
| C(4)-N(5) | 1.515(2) |
| C(4)-H(4) | 1.0000 |
| N(5)-O(6) | 1.2155(17) |
| N(5)-O(7) | 1.2197(17) |

| | |
|---|---|
| O(8)-N(11) | 1.3678(16) |
| O(8)-N(9) | 1.3814(17) |
| C(8)-N(9) | 1.2982(19) |
| C(8)-C(12) | 1.4319(19) |
| N(11)-C(12) | 1.302(2) |
| C(12)-N(13) | 1.4069(18) |
| N(13)-N(13)#1 | 1.262(2) |

| | |
|---|---|
| O(2)-N(3)-O(1) | 126.83(13) |
| O(2)-N(3)-C(4) | 115.45(12) |
| O(1)-N(3)-C(4) | 117.66(12) |
| C(8)-C(4)-N(5) | 111.31(11) |
| C(8)-C(4)-N(3) | 108.08(11) |
| N(5)-C(4)-N(3) | 107.13(11) |
| C(8)-C(4)-H(4) | 110.1 |
| N(5)-C(4)-H(4) | 110.1 |
| N(3)-C(4)-H(4) | 110.1 |
| O(6)-N(5)-O(7) | 127.05(14) |
| O(6)-N(5)-C(4) | 115.55(12) |
| O(7)-N(5)-C(4) | 117.40(13) |
| N(11)-O(8)-N(9) | 111.32(11) |
| N(9)-C(8)-C(12) | 108.32(13) |
| N(9)-C(8)-C(4) | 121.61(12) |
| C(12)-C(8)-C(4) | 130.05(13) |
| C(8)-N(9)-O(8) | 105.73(11) |
| C(12)-N(11)-O(8) | 105.33(12) |
| N(11)-C(12)-N(13) | 119.42(13) |
| N(11)-C(12)-C(8) | 109.29(13) |
| N(13)-C(12)-C(8) | 131.29(14) |
| N(13)#1-N(13)-C(12) | 111.20(14) |

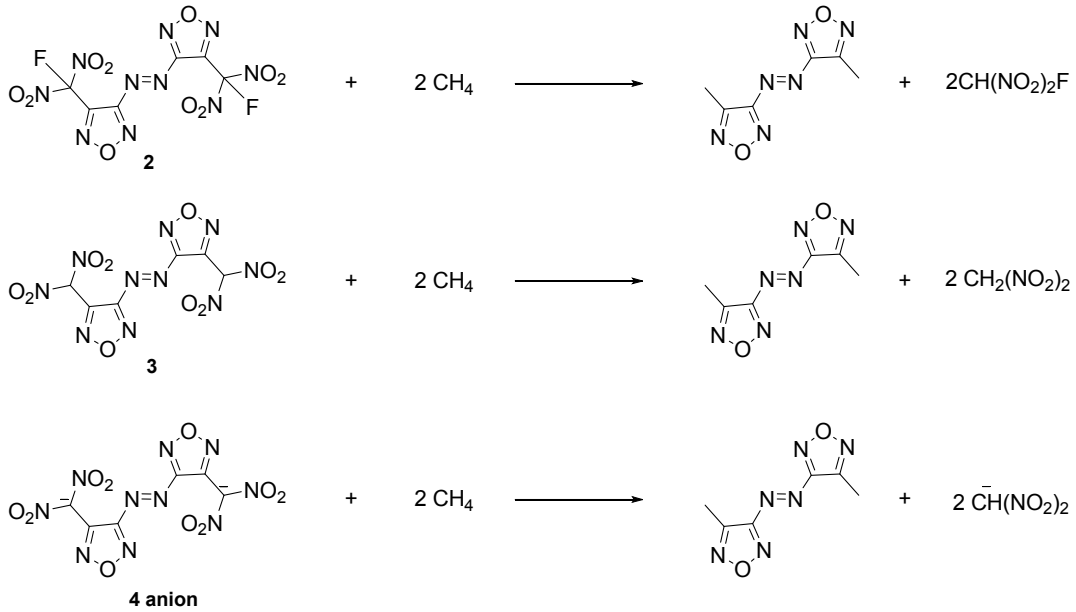
Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+2

**Table S5**. Torsion angles [°] for **3**.

| | |
|---|---|
| O(2)-N(3)-C(4)-C(8) | -81.46(15) |
| O(1)-N(3)-C(4)-C(8) | 96.08(15) |
| O(2)-N(3)-C(4)-N(5) | 158.50(13) |
| O(1)-N(3)-C(4)-N(5) | -23.96(17) |
| C(8)-C(4)-N(5)-O(6) | 163.63(12) |
| N(3)-C(4)-N(5)-O(6) | -78.42(15) |
| C(8)-C(4)-N(5)-O(7) | -16.13(17) |
| N(3)-C(4)-N(5)-O(7) | 101.82(14) |

| | |
|---|---|
| N(5)-C(4)-C(8)-N(9) | 113.15(14) |
| N(3)-C(4)-C(8)-N(9) | -4.23(18) |
| N(5)-C(4)-C(8)-C(12) | -68.66(18) |
| N(3)-C(4)-C(8)-C(12) | 173.96(13) |
| C(12)-C(8)-N(9)-O(8) | -0.52(15) |
| C(4)-C(8)-N(9)-O(8) | 178.02(12) |
| N(11)-O(8)-N(9)-C(8) | 0.12(15) |
| N(9)-O(8)-N(11)-C(12) | 0.36(15) |
| O(8)-N(11)-C(12)-N(13) | 178.96(11) |
| O(8)-N(11)-C(12)-C(8) | -0.67(15) |
| N(9)-C(8)-C(12)-N(11) | 0.79(16) |
| C(4)-C(8)-C(12)-N(11) | -177.59(14) |
| N(9)-C(8)-C(12)-N(13) | -178.79(14) |
| C(4)-C(8)-C(12)-N(13) | 2.8(3) |
| N(11)-C(12)-N(13)-N(13)#1 | -176.88(15) |
| C(8)-C(12)-N(13)-N(13)#1 | 2.7(2) |

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+2




**Scheme S1.** Isodesmic reactions for **2**, **3** and **4** anion