Electronic Supplementary Information

1,1-Diamino-2,2-dinitroethene (FOX-7) and 1-amino-1-hydrazino-2,2-dinitroethene (HFOX) as amphotères: Bases with strong acids

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(Compounds are numbered as in the paper)

1. X-ray crystallography:

A colorless prism of dimensions 0.44 x 1.01 x 1.28 mm^3 (**3a**), a colorless prism of 0.37 x 0.14 x 0.11 mm^3 (**3b**), a colorless plate crystal of dimensions 0.82 x 0.10 x 0.07 mm^3 (**4a**), and a yellow plate of 0.27 x 0.23 x 0.07 mm^3 (**9**) were mounted with a MiteGen MicroMesh and a small amount of Cargille Immersion Oil (for salts **3a**, **3b**, and **4a**) or a Nylon loop with paratone oil (compound **9**). For all salts, data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK$_\alpha$ radiation (λ = 0.71073). An Oxford Cobra low temperature device was used to keep the crystals at a constant 124(2) K [**3a** and **3b**], and 150(2) K [**4a**] during data collection. For compound **9**, data were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using omega and phi scans of 1.0° per frame for 30 s. The total number of images was based on results from the program COSMO[1] where redundancy was expected to be 4.0 and completeness to 0.83 Å to 100%.

For all the salts, data collection was performed, and the unit cell was initially refined using APEX2 [v2009.3-0].[2] Data reduction was performed using SAINT [v7.60A][3] and XPREP [v2008/2].[4] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2008/1].[5] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v2008/4] system of programs (**3a**, **3b**, and **4a**).[6] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model. Details of the data collection and refinement are given in Table S1.

For hydrazone **9**, cell parameters were retrieved using APEX II software[7] and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[8] which corrects for Lp. Scaling and absorption corrections were applied using SADABS[9] multi-scan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on F^2, SHELXL-97[10a], which are incorporated in OLEX2.[10b]. The structure was solved in the space group P$\bar{1}$ (# 2). All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model.

2. Crystal data and structural refinement:

Table S1. Crystallographic data for salts **3a**, **3b**, **4a**, and compound **9**

	3a	3b	4a	9
Formula	$C_3H_5F_3N_4O_7S$	$C_2H_5N_4O_8Cl$	$C_5H_9F_3N_6O_7S$	$C_5H_9N_5O_4$
MW	298.17	248.55	354.24	203.17
CCDC	1008326	1008327	1008328	1008325
T [K]	150 (2)	150 (2)	150 (2)	174 (2)
Wavelength (Å)	0.71073	0.71073	0.71073	1.54178
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P 121/c1	P-1	P-1	P-1
a (Å)	7.5409(4)	10.3533(11)	6.2235(9)	6.68570(10)
b (Å)	11.4812(6)	13.0615(14)	10.5855(15)	6.89930(10)
c (Å)	12.3048(6)	20.060(2)	11.8361(17)	10.2681(2)
α (°)	90	107.534(2)	111.318(2)	76.7114(10)
β (°)	106.8020(10)	94.518(2)	93.653(2)	79.0212(10)
γ (°)	90	95.584(2)	102.778(2)	75.8661(10)
Volume (Å^3)	1019.85(9)	2557.6(5)	699.44(17)	442.447(13)
Z	4	12	2	2
Density (calculated) (g cm^{-3})	1.942	1.936	1.682	1.525
Absorption coefficient	0.404	0.489	0.313	1.147
F(000)	600	1512	360	212
Crystal size (mm^3)	0.44 x 1.01 x 1.28	0.37 x 0.14 x 0.11	0.60 x 0.27 x 0.25	0.27 x 0.23 x 0.07
Theta range for data collection (°)	2.48 to 30.52	1.99 to 30.56	1.87 to 26.47	4.47 to 71.81
Index ranges	-10<=h<=10, -16<=k<=16, -17<=l<=17	-14<=h<=14, -18<=k<=18, -28<=l<=28	-7<=h<=7, -13<=k<=12, -14<=l<=14	$-8 \leq h \leq 8, -7 \leq k \leq 8, -12 \leq l \leq 12$
Reflections collected	16143	41318	6266	6216
Independent reflections	3116 [R(int) = 0.0591]	15578 [R(int) = 0.1209]	2825 [R_{int} = 0.0169]	1680

Table S1 (continued). Crystallographic data for salts **3a**, **3b**, **4a**, and compound **9**

	3a	3b	4a	9
Absorption correction	Multi-scan	Multi-scan	Semi-empirical from equivalents	Multi-scan
Max. and Min. Transmission	0.8423 and 0.6259		0.9258 and 0.8344	0.7535 and 0.6458
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3116/0/163	15578/53/870	2825/0/215	1680/0/141
Goodness-of-fit on F2	1.058	1.024	1.039	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0335, wR2 = 0.0877	R1 = 0.0481, wR2 = 0.1275	R_1 = 0.0338, wR_2 = 0.0875	R_1 = 0.0323, wR_2 = 0.0854
R indices (all data)	R1 = 0.0365, wR2 = 0.0896	R1 = 0.0592, wR2 = 0.1366	R_1 = 0.0388, wR_2 = 0.0910	R_1 = 0.0401, wR_2 = 0.0900
Largest diff. peak and hole (e $Å^{-3}$)	0.499 and -0.463	1.158 and -0.915	0.587 and -0.375	0.24 and -0.17

3. Selected bond lengths and bond angles:

Salt **3a**

Table S2. Bond lengths (Å) of **3a.**

C1-N4	1.3032(15)	N8-O10	1.2107(15)
C1-N3	1.3068(14)	S11-O15	1.4405(9)
C1-C2	1.5179(15)	S11-O13	1.4436(9)
C2-N5	1.5111(15)	S11-O14	1.4539(9)
C2-N8	1.5164(14)	S11-C12	1.8358(12)
N5-O7	1.2119(14)	C12-F17	1.3108(15)
N5-O6	1.2158(14)	C12-F16	1.3167(16)
N8-O9	1.2082(16)	C12-F18	1.3186(14)

Table S3. Bond angles (°) of **3a**

N4-C1-N3	123.79(11)	O13-S11-C12	104.18(6)
N4-C1-C2	120.39(10)	O14-S11-C12	104.77(6)
N3-C1-C2	115.82(10)	F17-C12-F16	108.54(12)
N5-C2-N8	107.67(9)	F17-C12-F18	107.62(12)
N5-C2-C1	112.17(9)	F16-C12-F18	107.81(12)
N8-C2-C1	110.89(9)	F17-C12-S11	111.21(9)
O7-N5-O6	126.09(12)	F16-C12-S11	110.30(9)
O7-N5-C2	117.87(10)	F18-C12-S11	111.23(9)
O6-N5-C2	116.04(10)		
O9-N8-O10	127.54(11)		
O9-N8-C2	114.47(11)		
O10-N8-C2	117.95(10)		
O15-S11-O13	115.32(6)		
O15-S11-O14	114.15(6)		
O13-S11-O14	113.24(6)		
O15-S11-C12	103.47(6)		

Salt **3b**

Table S3. Bond lengths (Å) of **3b.**

C1A-N4A	1.298(2)	N5D-O6D	1.204(4)
C1A-N3A	1.308(2)	N5D'-O6D'	1.190(7)
C1A-C2A	1.516(2)	N5D'-O7D'	1.259(8)
C2A-N5A	1.517(2)	O6D'-O6D'#1	1.797(10)
C2A-N8A	1.520(2)	N8D-O9D	1.198(5)
N5A-O7A	1.2151(17)	N8D-O10D	1.201(7)
N5A-O6A	1.2161(17)	N8D'-O10'	1.203(5)
N8A-O9A	1.189(2)	N8D'-O9D'	1.214(4)
N8A-O10A	1.192(2)	C1E-N3E	1.299(2)
C1B-N3B	1.292(2)	C1E-N4E	1.3049(19)
C1B-N4B	1.309(2)	C1E-C2E	1.518(2)
C1B-C2B	1.5179(19)	C2E-N5E	1.509(2)
C2B-N8B	1.509(2)	C2E-N8E	1.517(2)
C2B-N5B	1.515(2)	N5E-O7E	1.211(2)
N5B-O7B	1.2054(19)	N5E-O6E	1.218(2)
N5B-O6B	1.209(2)	N8E-O9E	1.2156(18)
N8B-O9B	1.212(2)	N8E-O10E	1.218(2)
N8B-O10B	1.231(3)	C1F-N4F	1.298(2)
C1C-N3C	1.298(2)	C1F-N3F	1.3060(19)
C1C-N4C	1.3077(19)	C1F-C2F	1.5159(19)
C1C-C2C	1.514(2)	C2F-N8F	1.506(2)
C2C-N5C	1.511(2)	C2F-N5F	1.5259(19)
C2C-N8C	1.523(2)	N5F-O6F	1.2120(19)
N5C-O6C	1.2119(19)	N5F-O7F	1.216(2)
N5C-O7C	1.222(2)	N8F-O10F	1.215(2)
N8C-O10C	1.206(2)	N8F-O9F	1.2163(19)
N8C-O9C	1.211(2)	Cl1A-O4A	1.4329(14)
C1D-N4D	1.288(2)	Cl1A-O2A	1.4341(15)
C1D-N3D	1.2983(19)	Cl1A-O1A	1.4344(14)
C1D-C2D	1.517(2)	Cl1A-O3A	1.4363(13)
C2D-N8D	1.376(4)	Cl1B-O3B	1.4283(13)
C2D-N5D	1.440(3)	Cl1B-O2B	1.4368(14)
C2D-N8D'	1.627(4)	Cl1B-O1B	1.4434(14)

Table S3 (continued). Bond lengths (Å) of **3b.**

C2D-N5D'	1.648(5)	Cl1B-O4B	1.4459(15)
N5D-O7D	1.137(7)	Cl1C-O4C	1.4305(14)

Cl1C-O2C	1.4341(14)	Cl1E-O1E	1.4341(14)
Cl1C-O3C	1.4392(13)	Cl1E-O4E	1.4441(12)
Cl1C-O1C	1.4414(14)	Cl1E-O2E	1.4476(12)
Cl1D-O2D	1.4232(13)	Cl1F-O2F	1.4264(14)
Cl1D-O4D	1.4386(13)	Cl1F-O3F	1.4292(16)
Cl1D-O3D	1.4403(12)	Cl1F-O4F	1.4328(15)
Cl1D-O1D	1.4493(14)	Cl1F-O1F	1.4403(13)
Cl1E-O3E	1.4299(13)		

Table S4. Bond angles (°) of **3b.**

N4A-C1A-N3A	124.15(14)	O9B-N8B-C2B	115.1(2)
N4A-C1A-C2A	116.72(13)	O10B-N8B-C2B	116.92(16)
N3A-C1A-C2A	119.12(14)	N3C-C1C-N4C	124.07(14)
C1A-C2A-N5A	111.49(11)	N3C-C1C-C2C	116.37(13)
C1A-C2A-N8A	109.31(13)	N4C-C1C-C2C	119.56(14)
N5A-C2A-N8A	108.60(12)	N5C-C2C-C1C	113.52(13)
O7A-N5A-O6A	126.55(15)	N5C-C2C-N8C	107.10(13)
O7A-N5A-C2A	116.01(12)	C1C-C2C-N8C	109.34(12)
O6A-N5A-C2A	117.41(12)	O6C-N5C-O7C	126.85(18)
O9A-N8A-O10A	125.52(18)	O6C-N5C-C2C	115.70(16)
O9A-N8A-C2A	115.13(16)	O7C-N5C-C2C	117.38(14)
O10A-N8A-C2A	119.31(14)	O10C-N8C-O9C	127.06(18)
N3B-C1B-N4B	123.36(13)	O10C-N8C-C2C	118.46(16)
N3B-C1B-C2B	115.69(13)	O9C-N8C-C2C	114.48(17)
N4B-C1B-C2B	120.95(14)	N4D-C1D-N3D	124.17(16)
N8B-C2B-N5B	106.93(13)	N8D-C2D-N8D'	20.42(19)
N8B-C2B-C1B	112.53(13)	N8D-C2D-N5D'	109.7(3)
N5B-C2B-C1B	111.60(11)	N5D-C2D-N5D'	26.21(16)
O7B-N5B-O6B	127.38(16)	N5D'-O6D'-O6D'#1	131.7(5)
O7B-N5B-C2B	118.06(14)	O9D-N8D-O10D	128.5(5)
O6B-N5B-C2B	114.51(14)	O9D-N8D-C2D	123.6(4)

Table S4 (continued). Bond angles (°) of **3b.**

O9B-N8B-O10B	127.8(2)	O3B-Cl1B-O2B	110.21(8)
O10'-N8D'-O9D'	127.3(4)	O10D-N8D-C2D	107.8(4)
O10'-N8D'-C2D	115.7(3)	O2B-Cl1B-O1B	111.28(9)
O9D'-N8D'-C2D	117.0(3)	O3B-Cl1B-O4B	109.79(10)
N3E-C1E-N4E	124.18(14)	O2B-Cl1B-O4B	108.94(9)
N3E-C1E-C2E	115.42(13)	O1B-Cl1B-O4B	107.69(9)

N4E-C1E-C2E	120.39(14)	O4C-Cl1C-O2C	110.60(10)
N5E-C2E-N8E	106.20(13)	O4C-Cl1C-O3C	110.05(9)
N5E-C2E-C1E	112.38(12)	O2C-Cl1C-O3C	108.74(9)
N8E-C2E-C1E	110.34(12)	O4C-Cl1C-O1C	108.97(9)
O7E-N5E-O6E	126.81(16)	O2C-Cl1C-O1C	109.58(9)
O7E-N5E-C2E	116.73(15)	O3C-Cl1C-O1C	108.88(8)
O6E-N5E-C2E	116.47(14)	O2D-Cl1D-O4D	110.59(8)
O9E-N8E-O10E	127.28(16)	O2D-Cl1D-O3D	110.96(9)
O9E-N8E-C2E	115.88(14)	O4D-Cl1D-O3D	108.94(8)
O10E-N8E-C2E	116.80(13)	O2D-Cl1D-O1D	108.61(9)
N4F-C1F-N3F	123.83(14)	O4D-Cl1D-O1D	108.49(10)
N4F-C1F-C2F	121.11(13)	O3D-Cl1D-O1D	109.21(8)
N3F-C1F-C2F	115.06(14)	O3E-Cl1E-O1E	110.07(9)
N8F-C2F-C1F	113.70(12)	O3E-Cl1E-O4E	109.92(9)
N8F-C2F-N5F	106.75(11)	O1E-Cl1E-O4E	109.32(8)
C1F-C2F-N5F	111.19(12)	O3E-Cl1E-O2E	109.62(8)
O6F-N5F-O7F	127.87(15)	O1E-Cl1E-O2E	109.86(9)
O6F-N5F-C2F	117.38(14)	O4E-Cl1E-O2E	108.02(8)
O7F-N5F-C2F	114.59(13)	O2F-Cl1F-O3F	108.84(10)
O10F-N8F-O9F	126.11(16)	O2F-Cl1F-O4F	109.94(9)
O10F-N8F-C2F	117.24(14)	O3F-Cl1F-O4F	108.63(12)
O9F-N8F-C2F	116.62(14)	O2F-Cl1F-O1F	111.06(9)
O4A-Cl1A-O2A	109.24(11)	O3F-Cl1F-O1F	109.16(9)
O4A-Cl1A-O1A	108.74(9)	O4F-Cl1F-O1F	109.18(10)
O2A-Cl1A-O1A	109.56(11)	O3B-Cl1B-O1B	108.90(8)
O4A-Cl1A-O3A	110.41(9)		
O2A-Cl1A-O3A	108.84(9)		
O1A-Cl1A-O3A	110.03(8)		

Salt **4a**

Table S5. Bond lengths (Å) of **4a.**

C(1)-N(3)	1.507(2)	C(1)-C(2)	1.514(2)
C(1)-N(6)	1.516(2)	C(1)-H(1)	1.0000
C(2)-N(10)	1.292(2)	C(2)-N(9)	1.325(2)
N(3)-O(5)	1.209(2)	N(3)-O(4)	1.213(2)
N(6)-O(8)	1.202(2)	N(6)-O(7)	1.221(2)
N(9)-H(9A)	0.84(2)	N(9)-H(9B)	0.83(2)
N(10)-N(11)	1.4482(19)	N(11)-H(11C)	0.88(2)
N(11)-H(11B)	0.84(2)	N(11)-H(11A)	0.88(2)
C(12)-F(15)	1.318(2)	C(12)-F(13)	1.325(2)
C(12)-F(14)	1.326(2)	C(12)-S(16)	1.8202(18)
S(16)-O(17)	1.4352(12)	S(16)-O(19)	1.4404(12)
S(16)-O(18)	1.4473(12)	C(21)-N(22)	1.130(2)
C(21)-C(20)	1.450(3)	C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800	C(20)-H(20C)	0.9800

Table S6. Bond angles (Å) of **4b**.

N(3)-C(1)-C(2)	109.80(13)	N(3)-C(1)-N(6)	107.87(13)
C(2)-C(1)-N(6)	113.06(14)	N(3)-C(1)-H(1)	108.7
C(2)-C(1)-H(1)	108.7	N(6)-C(1)-H(1)	108.7
N(10)-C(2)-N(9)	131.67(16)	N(10)-C(2)-C(1)	113.51(14)
N(9)-C(2)-C(1)	114.81(14)	O(5)-N(3)-O(4)	126.67(16)
O(5)-N(3)-C(1)	119.00(15)	O(4)-N(3)-C(1)	114.32(14)
O(8)-N(6)-O(7)	126.33(18)	O(8)-N(6)-C(1)	119.30(15)
O(7)-N(6)-C(1)	114.37(17)	C(2)-N(9)-H(9A)	117.4(14)
C(2)-N(9)-H(9B)	120.5(14)	H(9A)-N(9)-H(9B)	122(2)
C(2)-N(10)-N(11)	112.75(13)	N(10)-N(11)-H(11C)	112.9(13)
N(10)-N(11)-H(11B)	106.1(14)	H(11C)-N(11)-H(11B)	108.1(19)
N(10)-N(11)-H(11A)	109.9(14)	H(11C)-N(11)-H(11A)	111.7(18)
H(11B)-N(11)-H(11A)	107.8(18)	F(15)-C(12)-F(13)	108.67(17)
F(15)-C(12)-F(14)	108.49(16)	F(13)-C(12)-F(14)	107.91(16)
F(15)-C(12)-S(16)	110.85(13)	F(13)-C(12)-S(16)	110.85(13)
F(14)-C(12)-S(16)	109.99(13)	O(17)-S(16)-O(19)	115.82(8)
O(17)-S(16)-O(18)	115.24(7)	O(19)-S(16)-O(18)	112.79(8)
O(17)-S(16)-C(12)	103.69(8)	O(19)-S(16)-C(12)	104.22(8)
O(18)-S(16)-C(12)	103.00(8)	N(22)-C(21)-C(20)	179.4(2)
C(21)-C(20)-H(20A)	109.5	C(21)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5	C(21)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5	H(20B)-C(20)-H(20C)	109.5

Compound **9**

Table S7. Bond lengths (Å) of **9**

O(1)-N(4)	1.2431(16)	N(3)-C(4)	1.3157(18)
O(2)-N(4)	1.2177(16)	N(4)-N(5)	1.4295(18)
O(3)-N(5)	1.2640(15)	N(5)-C(5)	1.3892(18)
O(4)-N(5)	1.2342(15)	C(1)-C(2)	1.492(2)
N(1)-N(2)	1.3908(16)	C(2)-C(3)	1.499(2)
N(1)-C(2)	1.283(2)	C(4)-C(5)	1.4462(18)
N(2)-C(4)	1.3360(18)		

Table S8. Bond angles (°) of **9.**

C(2)-N(1)-N(2)	114.81(12)	N(1)-C(2)-C(3)	116.29(14)
C(4)-N(2)-N(1)	117.83(11)	C(1)-C(2)-C(3)	119.04(14)
O(1)-N(4)-C(5)	117.83(11)	N(2)-C(4)-C(5)	119.75(11)
O(2)-N(4)-O(1)	122.09(12)	N(3)-C(4)-N(2)	117.86(12)
O(2)-N(4)-C(5)	120.04(12)	N(3)-C(4)-C(5)	122.38(12)
O(3)-N(5)-C(5)	118.39(11)	N(4)-C(5)-C(4)	120.52(11)
O(4)-N(5)-O(3)	120.29(11)	N(5)-C(5)-N(4)	116.58(11)
O(4)-N(5)-C(5)	121.27(12)	N(5)-C(5)-C(4)	122.86(12)
N(1)-C(2)-C(1)	124.67(13)		

4. Theoretical studies:

Energetic performances were calculated using Explo5 v6.01. The heats of formation for all the compounds were calculated using Gaussian 03 (Revision D. 01).[11]The geometric optimization of the structures was based on single-crystal structures, and frequency analyses were carried out using the B3LYP functional with 6-31+G** basis set. Single-point energies were calculated at the MP2/6-311++G** level.[12] Atomization energies for compounds (**3a**), (**3b**), (**4a**), and (**4b**) were calculated using the G2 ab initio method.[13] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. The standard heats of formation of the salts were calculated based on the Born-Haber energy cycle (Scheme 1) and Equation (1).[1c,14]
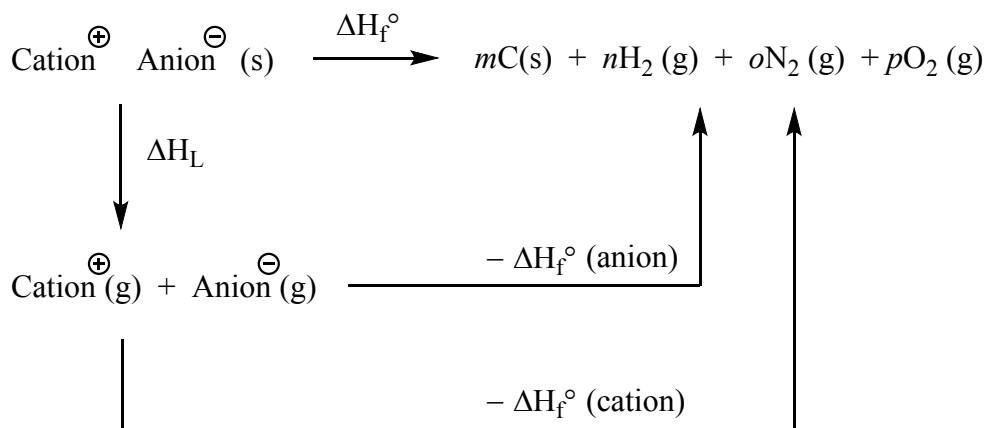
(*"*m, n, o, p*" represent the number of moles of each product)

Figure 1. Born-Haber cycle for formation of energetic salts.

$$\Delta H_f° \text{ (salt, 298K)} = \Delta H_f° \text{ (cation, 298K)} + \Delta H_f° \text{ (anion, 298K)} - \Delta H_L \qquad (1)$$

The lattice energy (ΔH_L) of the salts M_pX_q are calculated using Equation (2) suggested by Jenkins, et al.[15]:

$$\Delta H_L = U_{POT} + [p(n_M/2\text{-}2) + q(n_x/2\text{-}2)]RT \qquad (2)$$

where n_M and n_x are dependent on the ions of M^{p+} and X^{q-} (q and p represent the charges on the cation and anion) and assigned values 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The lattice potential energy, U_{POT}, (reported as kJ mol^{-1}) can be calculated from Equation (3):

$$U_{POT} = \gamma[\rho_m(M_m)^{1/3} + \delta \qquad (3)$$

where ρ_m is the density (gcm^{-3}), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ mol^{-1}cm) and δ (kJ mol^{-1}) values are obtained from the literature.[16, 17]

The densities were calculated according to a reliable method by our group.[18] The volume of FOX-7 and HFOX were calculated by taking the reported volume of the parent compounds from their crystal structure reports and adding 7Å (volume for a hydrogen bonded to carbon) to the volume to incorporate the added proton for the cations according (FOX-7 cation vol. = 136.98, HFOX cation vol. = 155.75).[18] The volumes for the following anions were taken from the literature: (trinitromethanide, dinitroamide, nitrate, triflate, and perchlorate)[18]and NTO.

As mentioned in the manuscript, our initial investigation began with calculations of energetic salts containing FOX-7 and HFOX cations. Salts containing counter anions such as nitrate (**10a**, **11a**), trinitromethanide (**10b**, **11b**), dinitroamide (**10c**, **11c**), and 3-nitro-1,2,4-
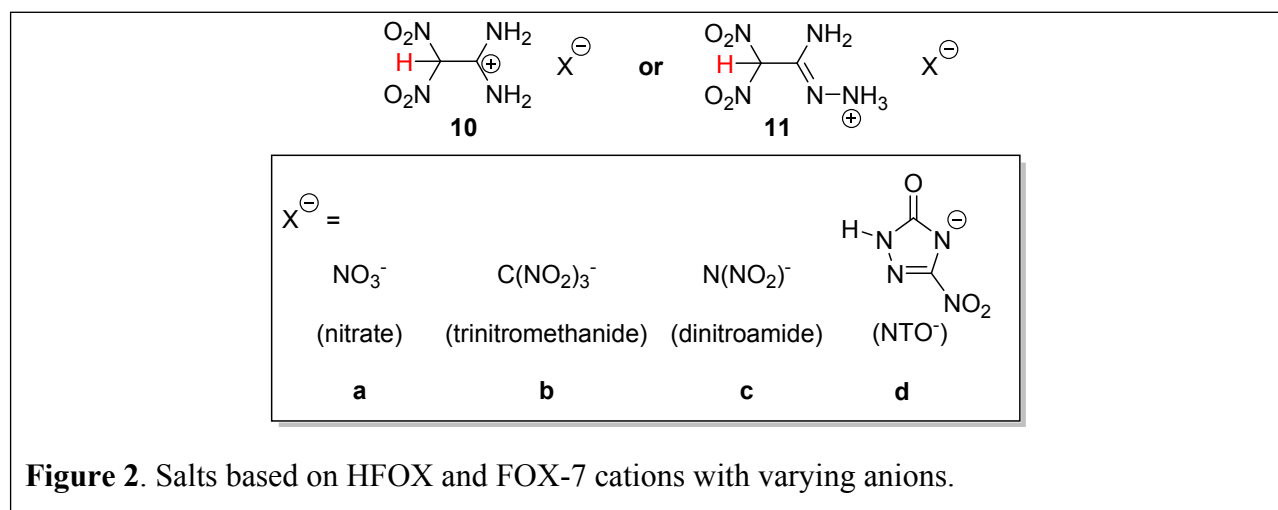

Figure 2. Salts based on HFOX and FOX-7 cations with varying anions.

triazol-5-one (NTO; [**10d**, **11d**]) were examined (Figure 2). The calculated energetic properties

were found to exceed that of TNT, FOX-7 and RDX, which supports the usefulness of FOX-7 and HFOX cations as building blocks for energetic salts (Table S9). Salt **11c** (8907 ms^{-1}) has the highest detonation velocity among the salts, exceeding the values of TNT, FOX-7 and RDX. The remaining salts all exceed TNT while salts **10c-d** and **11b-d** are either comparable or slightly better than FOX-7. With the exception of **11a**, the detonation pressures of the salts approach those of FOX-7 and RDX.

Table S9. Calculated energetic properties of salts based on HFOX and FOX-7 cations with varying anions.

	Compounds	ρ^a	Vol.[b] (Å)	$\Delta H_{f(cation)}{}^c$ (kJ/mol)	$\Delta H_{f(anion)}{}^d$ (kJ/mol)	$\Delta H_f{}^e$ (kJ/mol)	P^f (Gpa)	D^g (ms^{-1})	Isp^h (s)
	10a	1.753	199.98	659.7	-300.5	-150.8	31.8	8670	262
FOX-7 cation salts	**10b**	1.793	276.98	659.7	-287.0	-96.0	31.5	8605	257
	10c	1.811	233.98	659.7	-156.2	14.0	32.9	8793	259
	10d	1.784	258.98	659.7	63.9	246.8	33.9	8728	267
	11a	1.595	219.75	799.5	-300.5	1.50	26.2	8163	274
HFOX cation salts	**11b**	1.758	296.75	799.5	-287.0	52.0	32.4	8706	266
	11c	1.767	253.75	799.5	-156.2	164.0	33.8	8907	270
	11d	1.746	278.75	799.5	63.9	395.5	33.5	8750	274
	TNT	1.65	-	-	-	-59.3	21.3	7304	211
Standard energetic compounds	**FOX-7**	1.88	-	-	-	-134.1	35.2	8771	240
	RDX	1.82	-	-	-	70.3	35.8	8864	267

a) Calculated density [ref. 19]. b) Calculated volumes. c) Cation heat of formation. d) Anion heat of formation. e) Heat of formation. f) Detonation pressure. g) Detonation velocity. h) Specific impulse [calculated at an isobaric pressure of 70 bar and initial temperature of 3,300 K].

The specific impulse values of salts **10** and **11** are increased with the suggested counter anions with values that exceed TNT, FOX-7 and RDX (excluding **10b** and **10c**). By varying the counter anion, it can be seen that the properties of salts based on the FOX-7 and HFOX cations can be modified.

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