Electronic Supplementary Information

From BTO^{2-} to $HBTO^{-}$ insensitive energetic salt: Route to boost energy

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1. Single-crystal X-ray diffraction analysis of **3**·2H_2O

Table S1. Crystal data and structure refinement for **3**·2H_2O

	3·2H_2O
CCDC	1903600
Empirical formula	$C_6H_{14}N_{18}O_4$
Formula weight	402.35
Temperature / K	205
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	8.9135(17)
b / Å	14.392(3)
c / Å	6.7544(14)
α /°	90.00
β /°	110.499(4)
γ /°	90.00
Volume / Å^3	811.6(3)
Z	2
ρ_{calc} / g cm^{-3}	1.646
μ / mm^{-1}	0.138
F(000)	416.0
Crystal size / mm^3	0.25×0.12×0.05
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.878 to 55.272
Index ranges	$-11 \le h \le 9$, $-18 \le k \le 18$, $-7 \le l \le 8$
Reflections collected	6965
Independent reflections	1869 [R_{int} = 0.0535, R_{sigma} = 0.0552]
Data / restraints / parameters	1869 / 0 / 131
Goodness-of-fit on F^2	1.030
Final R indexes [$I >= 2\sigma(I)$]	R_1 = 0.0556, wR_2 = 0.1599
Final R indexes [all data]	R_1 = 0.0779, wR_2 = 0.1751
Largest diff. peak / hole / e Å^{-3}	0.62 / -0.66

Table S2. Selected bond lengths for **3**·2H_2O

parameter		bond length (Å)	parameter		bond length (Å)
O1	N6	1.315(2)	N5	C1	1.320(3)
O2	H2A	0.8501	N9	N8	1.347(3)
O2	H2B	0.8501	N9	C3	1.337(3)
N2	N1	1.403(3)	N3	C2	1.293(3)
N2	C2	1.386(3)	N6	N7	1.343(3)
N2	C1	1.358(3)	N6	C3	1.350(3)
N4	H4	0.87	N1	H1A	0.8633
N4	N3	1.384(3)	N1	H1B	0.8629
N4	C1	1.327(3)	N7	N8	1.316(3)
N5	H5A	0.87	C2	C2[1]	1.453(4)
N5	H5B	0.87	C3	C3[2]	1.428(5)

[1]-X,1-Y,-Z; [2]1-X,1-Y,1-Z

Table S3. Selected bond angles for **3**·2H_2O

parameter			bond angle (°)	parameter			bond angle (°)
H2A	O2	H2B	109.5	N7	N6	C3	108.9(2)
C2	N2	N1	132.49(19)	N2	N1	H1A	110.1
C1	N2	N1	121.26(19)	N2	N1	H1B	109.1
C1	N2	C2	106.2(2)	H1A	N1	H1B	109
N3	N4	H4	124.2	N8	N7	N6	105.9(2)
C1	N4	H4	124.2	N7	N8	N9	111.3(2)
C1	N4	N3	111.61(19)	N2	C2	C2[1]	123.9(3)
H5A	N5	H5B	120	N3	C2	N2	111.55(19)
C1	N5	H5A	120	N3	C2	C2[1]	124.6(3)
C1	N5	H5B	120	N4	C1	N2	106.2(2)
C3	N9	N8	105.9(2)	N5	C1	N2	124.9(2)
C2	N3	N4	104.39(19)	N5	C1	N4	128.9(2)
O1	N6	N7	122.1(2)	N9	C3	N6	108.0(2)
O1	N6	C3	129.0(2)	N9	C3	C3[2]	127.2(3)
N6	C3	C3[2]	124.8(3)				

[1]-X,1-Y,-Z; [2]1-X,1-Y,1-Z

Table S4. Selected torsion angles for **3**·2H_2O

parameter				torsion angle (°)	parameter				torsion angle (°)
O1	N6	N7	N8	178.9(2)	N7	N6	C3	N9	0.3(3)
O1	N6	C3	N9	-178.9(2)	N7	N6	C3	C3	178.4(3)
O1	N6	C3	C3	-0.8(5)	N8	N9	C3	N6	-0.1(3)
N4	N3	C2	N2	-0.4(3)	N8	N9	C3	C3	-178.2(3)
N4	N3	C2	C2	179.2(3)	C2	N2	C1	N4	-1.7(3)
N3	N4	C1	N2	1.5(3)	C2	N2	C1	N5	178.0(2)
N3	N4	C1	N5	-178.2(2)	C1	N2	C2	N3	1.4(3)
N6	N7	N8	N9	0.4(3)	C1	N2	C2	C2	-178.3(3)
N1	N2	C2	N3	178.7(2)	C1	N4	N3	C2	-0.7(3)
N1	N2	C2	C2	-1.0(5)	C3	N9	N8	N7	-0.2(3)
N1	N2	C1	N4	-179.4(2)	C3	N6	N7	N8	-0.4(3)
N1	N2	C1	N5	0.3(4)					

[1]1-X,1-Y,1-Z; [2]-X,1-Y,-Z

Table S5. Hydrogen bonds for **3**·2H_2O

Donor--H...Acceptor			D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N(1)	--H(1A)	..N(7)	0.86	2.54	3.327(3)	151
N(1)	--H(1B)	..N(5)	0.86	2.43	2.842(3)	110
N(1)	--H(1B)	..O(1)	0.86	2.49	3.335(3)	167
O(2)	--H(2A)	..O(1)	0.85	1.92	2.746(3)	163
O(2)	--H(2A)	..N(6)	0.85	2.57	3.208(3)	133
O(2)	--H(2B)	..N(9)	0.85	2.06	2.853(3)	155
N(4)	--H(4)	..O(2)	0.87	1.76	2.593(3)	160
N(5)	--H(5A)	..N(8)	0.87	2.09	2.928(4)	162
N(5)	--H(5B)	..N(1)	0.87	2.56	2.842(3)	100
N(5)	--H(5B)	..O(1)	0.87	2.08	2.935(3)	168

2. Single-crystal X-ray diffraction analysis of **4**

Table S6. Crystal data and structure refinement for **4**

	4
CCDC	1903599
Empirical formula	$C_8H_{12}N_{26}O_4$
Formula weight	536.44
Temperature / K	205
Crystal system	triclinic
Space group	P-1
a / Å	6.4179(5)
b / Å	7.4575(5)
c / Å	10.8598(8)
α /°	74.881(5)
β /°	74.297(5)
γ /°	88.026(6)
Volume / Å^3	482.68(6)
Z	1
ρ_{calc} / g cm^{-3}	1.845
μ / mm^{-1}	0.153
F(000)	274.0
Crystal size / mm^3	0.18×0.12×0.11
Radiation	MoK*α* (λ = 0.71073)
2*θ* range for data collection/°	4.036 to 55.594
Index ranges	$-8 \le h \le 8$, $-9 \le k \le 9$, $-14 \le l \le 13$
Reflections collected	8188
Independent reflections	2264 [R_{int} = 0.0932, R_{sigma} = 0.0715]
Data / restraints / parameters	2264 / 2 / 177
Goodness-of-fit on F^2	1.009
Final *R* indexes [$I >= 2\sigma(I)$]	R_1 = 0.0579, wR_2 = 0.1584
Final *R* indexes [all data]	R_1 = 0.0902, wR_2 = 0.1748
Largest diff. peak / hole / e Å^{-3}	0.65 / -0.65

Table S7. Selected bond lengths for **4**

parameter		bond length (Å)	parameter		bond length (Å)
O1	N2AA	1.328(3)	N4AA	N5	1.342(3)
O1	H1	0.87(2)	N4AA	C6	1.333(3)
N2	N3	1.299(3)	N2AA	C7	1.343(3)
N2	N2AA	1.332(3)	N6	C7	1.329(3)
N3	N6	1.357(3)	N1	H1A	0.87
O4	N4AA	1.317(3)	N1	H1B	0.87
N3AA	C0AA	1.348(3)	N1	C0AA	1.322(3)
N3AA	C1AA	1.379(3)	C1AA	C1AA^1	1.459(5)
N3AA	N4	1.388(3)	N4	H4A	0.8637
N0AA	N1AA	1.376(3)	N4	H4B	0.8637
N0AA	C1AA	1.294(3)	N5	N8	1.295(3)
N1AA	H1AA	0.87	C6	C7	1.442(4)

N1AA	C0AA	1.334(4)	C6	N9	1.342(3)
N8	N9	1.347(3)			

[1]-X,2-Y,2-Z

Table S8. Selected bond angles for **4**

parameter			bond angle (°)	parameter			bond angle (°)
N2AA	O1	H1	98(4)	H1A	N1	H1B	120
N3	N2	N2AA	106.3(2)	C0AA	N1	H1A	120
N2	N3	N6	111.0(2)	C0AA	N1	H1B	120
C0AA	N3AA	C1AA	106.2(2)	N1AA	C0AA	N3AA	106.5(2)
C0AA	N3AA	N4	121.0(2)	N1	C0AA	N3AA	123.3(3)
C1AA	N3AA	N4	132.4(2)	N1	C0AA	N1AA	130.1(3)
C1AA	N0AA	N1AA	104.6(2)	N3AA	C1AA	C1AA[1]	123.4(3)
N0AA	N1AA	H1AA	124.5	N0AA	C1AA	N3AA	111.6(2)
C0AA	N1AA	N0AA	111.0(2)	N0AA	C1AA	C1AA[1]	125.0(3)
C0AA	N1AA	H1AA	124.5	N3AA	N4	H4A	109.1
O4	N4AA	N5	122.6(2)	N3AA	N4	H4B	110.3
O4	N4AA	C6	128.6(2)	H4A	N4	H4B	108.8
C6	N4AA	N5	108.8(2)	N8	N5	N4AA	106.4(2)
O1	N2AA	N2	123.5(2)	N4AA	C6	C7	124.5(2)
O1	N2AA	C7	127.1(2)	N4AA	C6	N9	108.2(2)
N2	N2AA	C7	109.4(2)	N9	C6	C7	127.3(2)
C7	N6	N3	105.7(2)	N2AA	C7	C6	125.6(2)
N5	N8	N9	111.4(2)	N6	C7	N2AA	107.6(2)
C6	N9	N8	105.3(2)	N6	C7	C6	126.8(2)

[1]-X,2-Y,2-Z

Table S9. Selected torsion angles for **4**

parameter	torsion angle (°)	parameter	torsion angle (°)
O1-N2AA-C7-N6	-179.3(2)	C0AA-N3AA-C1AA-N0AA	-0.9(3)
O1-N2AA-C7-C6	1.4(4)	C0AA-N3AA-C1AA-C1AA	177.8(3)
N2-N3-N6-C7	1.0(3)	C1AA-N3AA-C0AA-N1AA[1]	1.1(3)
N2-N2AA-C7-N6	0.5(3)	C1AA-N3AA-C0AA-N1	178.5(2)
N2-N2AA-C7-C6	-178.8(2)	C1AA-N0AA-N1AA-C0AA	0.4(3)
N3-N2-N2AA-O1	179.9(2)	N4-N3AA-C0AA-N1AA	175.0(2)
N3-N2-N2AA-C7	0.1(3)	N4-N3AA-C0AA-N1	-7.5(4)
N3-N6-C7-N2AA	-0.9(3)	N4-N3AA-C1AA-N0AA	-173.8(2)
N3-N6-C7-C6	178.5(2)	N4-N3AA-C1AA-C1AA[1]	4.9(5)
O4-N4AA-N5-N8	179.4(2)	N5-N4AA-C6-C7	-177.3(2)
O4-N4AA-C6-C7	2.5(4)	N5-N4AA-C6-N9	0.5(3)
O4-N4AA-C6-N9	-179.7(2)	N5-N8-N9-C6	-0.4(3)
N0AA-N1AA-C0AA-N3AA	-0.9(3)	C6-N4AA-N5-N8	-0.7(3)
N0AA-N1AA-C0AA-N1	-178.2(3)	C7-C6-N9-N8	177.7(3)
N1AA-N0AA-C1AA-N3AA	0.3(3)	N9-C6-C7-N2AA	1.4(4)
N1AA-N0AA-C1AA-C1AA[1]	-178.4(3)	N9-C6-C7-N6	-177.8(3)
N4AA-N5-N8-N9	0.7(3)	N4AA-C6-N9-N8	-0.1(3)
N4AA-C6-C7-N2AA	178.8(2)	N2AA-N2-N3-N6	-0.7(3)
N4AA-C6-C7-N6	-0.4(4)		

[1]-X,2-Y,2-Z

Table S10. Hydrogen bonds for **4**

Donor--H...Acceptor			D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
O1	--H1	..O4	0.87(4)	1.64(3)	2.479(3)	162(5)
O1	--H1	..N4AA	0.87(4)	2.48(3)	3.150(3)	135(4)
N1AA	--H1AA	..N9	0.87	2.11	2.919(3)	156
N1	--H1A	..N6	0.87	2.19	2.926(3)	142
N1	--H1B	..N4	0.87	2.5	2.793(3)	100
N1	--H1B	..N9	0.87	2.38	3.209(4)	159
N4	--H4A	..O1	0.86	2.54	3.399(3)	173
N4	--H4B	..N8	0.86	2.46	3.000(3)	121

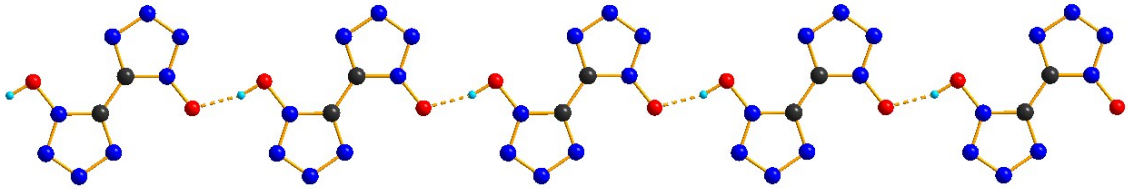


Fig. S1 The long chain of $HBTO^-$ anions along the *b* axis by formation of very strong hydrogen bonds O1-H1...O4.

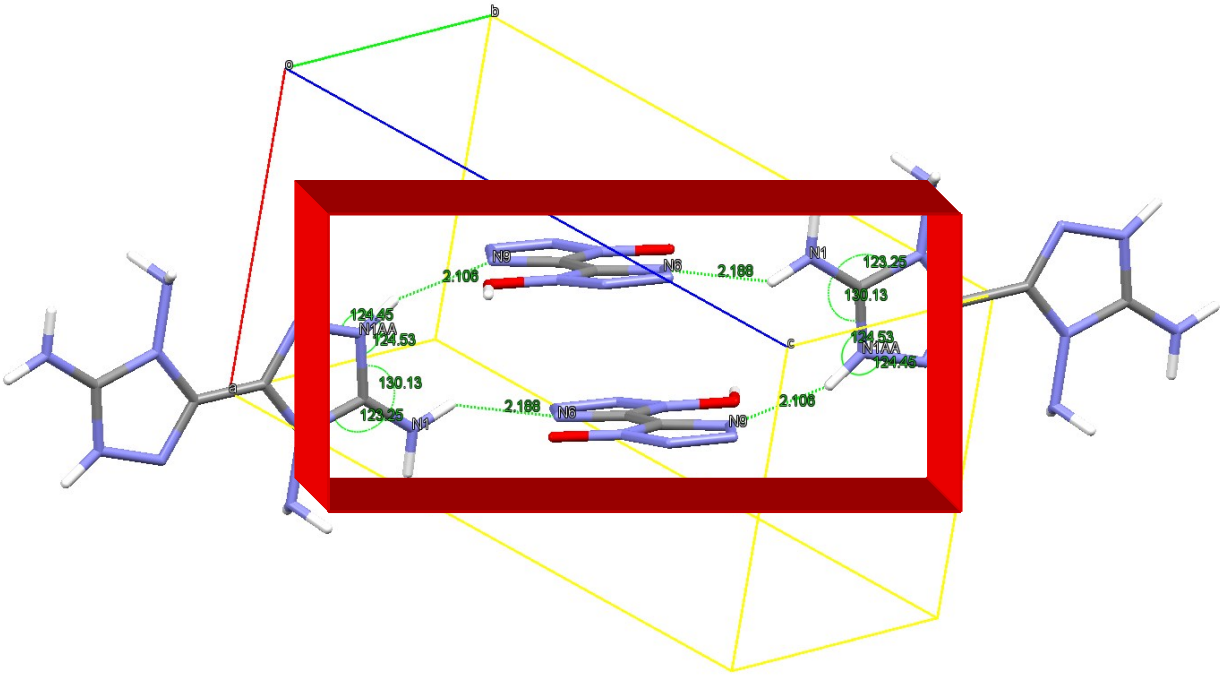


Fig. S2 The anions of the adjacent layers are fixed in a rectangular (in red) by hydrogen bonds with the cations.

3. Calculation of heats of formation

For energetic salts, the solid-phase heats of formation are calculated on the basis of a Born-Haber energy cycle (Scheme S1).

Based on a Born-Haber energy cycle, the heat of formation of a salt can be simplified by the formula given in Equation (1):

ΔH_f^o (salt, 298 K) = ΔH_f^o (cation, 298K) + ΔH_f^o (anion, 298K) – ΔH_L (1)

where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al.[2] [Eq. (2)]

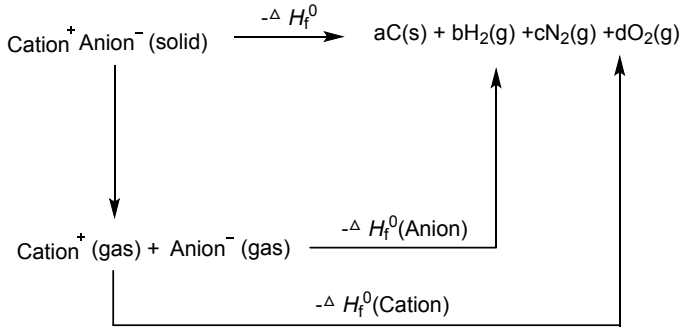
$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$ (2)

where n_M and n_X depend on the nature of the ions, M_p^+ and X_q^-, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

U_{POT} [kJ mol^{-1}] = $\gamma(\rho_m/M_m)^{1/3} + \delta$ (3)

Where ρ_m/g cm^{-3} is the density, M_m is the chemical formula mass of the ionic material, and values for the coefficients γ/ kJ mol^{-1} cm and δ/kJ mol^{-1} are taken from the literature[3].



Scheme S1. Born-Haber cycle for the formation of energetic salts

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2 H. D. B. Jenkins, D. Tudela and L. Glasser, *Inorg. Chem.*, 2002, **41**, 2364-2367.

3 H. D. B. Jenkins, H. K. Roobottom, J. Passmore and L. Glasser, *Inorg. Chem.*, 1999, **38**, 3609-3620.