Insensitive nitrogen-rich compounds with a planar 2D configuration based on imidazole-tetrazole

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Content

1 Crystallographic data

Table S1. Crystallographic data of **NABTI**·DMSO·H$_2$O

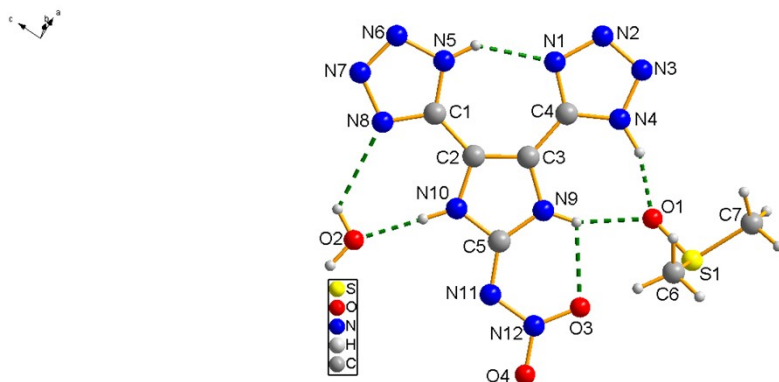| Compound	**NABTI**·DMSO·H$_2$O
CCDC number	2102547
Chemical formula	C$_5$H$_4$N$_{12}$O$_2$·C$_2$H$_6$SO·H$_2$O
Formula mass	360.35
Crystal system	triclinic
Space group	P-1
a, b, c [Å]	7.3452(3), 7.7532(4), 13.1160(6)
α, β, γ [°]	81.172(2), 87.255(2), 80.148(2)
Volume [Å^3]	727.03(6)
Temperature [K]	170
Z	2
μ [mm^{-1}]	0.271
ρ [g cm^{-3}]	1.646
F (000)	372.0
θ range [°]	5.392 to 52.84
Index ranges	-9 ≤ h ≤ 9; -9 ≤ k ≤ 9; -16 ≤ l ≤ 15
Reflections collected	8362
Independent reflections	2956
Data/restraints/parameters	2956 / 0 / 226
R1 / wR2 [all data]	0.0487 / 0.0910
R1 / wR2 [I > 2σ(I)]	0.0361 / 0.0819
Goodness-of-fit on F^2	1.048

Figure S1. Molecular structure of **NABTI**·DMSO·H$_2$O

Table S2. Hydrogen bond of **NABTI**·DMSO·H$_2$O

D-H···A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

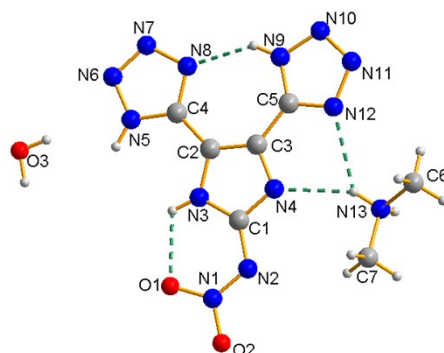|				
O2-H2A⋯N8	0.87	2.46	3.036(2)	125.00
O2-H2B⋯O4	0.87	2.56	3.047(2)	116.00
O2-H2B⋯N11	0.87	2.02	2.887(2)	171.00
N4-H4⋯O1	0.96(2)	1.69(2)	2.612(2)	160.00(2)
N5-H5⋯N1	0.88	2.04	2.786(2)	142.00
N5-H5⋯N2	0.88	2.44	3.044(2)	126.00
N9-H9⋯O1	0.88	1.91	2.737(2)	157.00
N9-H9⋯O3	0.88	2.13	2.595(2)	112.00
N10-H10⋯O2	0.88	1.80	2.684(2)	179.00
C6-H6A⋯O4	0.98	2.27	3.199(3)	158.00
C6-H6B⋯O3	0.98	2.59	3.552(3)	167.00
C7-H7B⋯N6	0.98	2.61	3.367(3)	135.00

Symmetry transformations used to generate equivalent atoms:

1-x,-y,-z   # 1-x,1-y,-z   # 1+x,y,z   # 2-x,1-y,1-z

x,y,-1+z   # 1+x,y,z

Table S3. Crystallographic data of 4·H$_2$O

Compound	**4**·H$_2$O
CCDC number	2096613
Chemical formula	$C_7H_{11}N_{13}O_2 \cdot H_2O$
Formula mass	327.30
Crystal system	triclinic
Space group	P-1
a, b, c [Å]	6.4345(5), 9.3017(7), 11.9277(9)
α, β, γ [º]	76.640(2), 84.469(3), 81.237(2)
Volume [Å^3]	685.08(9)
Temperature [K]	296(2)
Z	2
μ [mm^{-1}]	0.271
ρ [g cm^{-3}]	1.587
F (000)	340
θ range [°]	2.271 to 27.506
Index ranges	-8 ≤ h ≤ 8; -12 ≤ k ≤ 12; -15 ≤ l ≤ 15
Reflections collected	10334
Independent reflections	3109
Data/restraints/parameters	3109 / 0 / 216
R1 / wR2 [all data]	0.0546 / 0.1036
R1 / wR2 [I > 2σ(I)]	0.0387 / 0.0953

Compound	**4**·H$_2$O
Goodness-of-fit on F^2	1.041

Figure S2. Molecular structure of **4**·H$_2$O

Table S4. Hydrogen bond of **4**·H$_2$O

D-H···A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3B)···N(11) #1	0.83(2)	2.08(2)	2.9000(17)	170(2)
O(3)-H(3A)···N(7) #2	0.90(2)	2.01(2)	2.9051(18)	172.3(19)
C(6)-H(6A)···O(2)#3	0.96	2.62	3.468(3)	147.0
N(13)-H(13B)···O(3)#4	0.89	2.50	3.0895(18)	124.5
N(13)-H(13B)···O(3)#5	0.89	2.03	2.8475(17)	152.1
N(13)-H(13A)···N(12)	0.89	2.42	3.1183(18)	135.9
N(13)-H(13A)···N(4)	0.89	2.23	3.0325(17)	149.8
N(9)-H(9)···N(10)#6	0.86	2.65	3.1043(17)	114.6
N(9)-H(9)···N(8)	0.86	2.03	2.7577(16)	142.1
N(5)-H(5)···O(2)#7	0.86	1.94	2.6760(16)	142.8
N(5)-H(5)···O(1)#7	0.86	2.40	3.2143(16)	158.0
N(5)-H(5)···N(1)#7	0.86	2.53	3.3806(17)	171.5
N(3)-H(3)···O(1)#7	0.86	2.08	2.9325(15)	170.5
N(3)-H(3)···O(1)	0.86	2.13	2.5885(15)	113.0

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1   #2 x,y-1,z   #3 x+1,y,z   #4 -x+1,-y+1,-z+1
#5 x,y+1,z-1   #6 -x+2,-y+2,-z+1   #7 -x,-y+1,-z+1

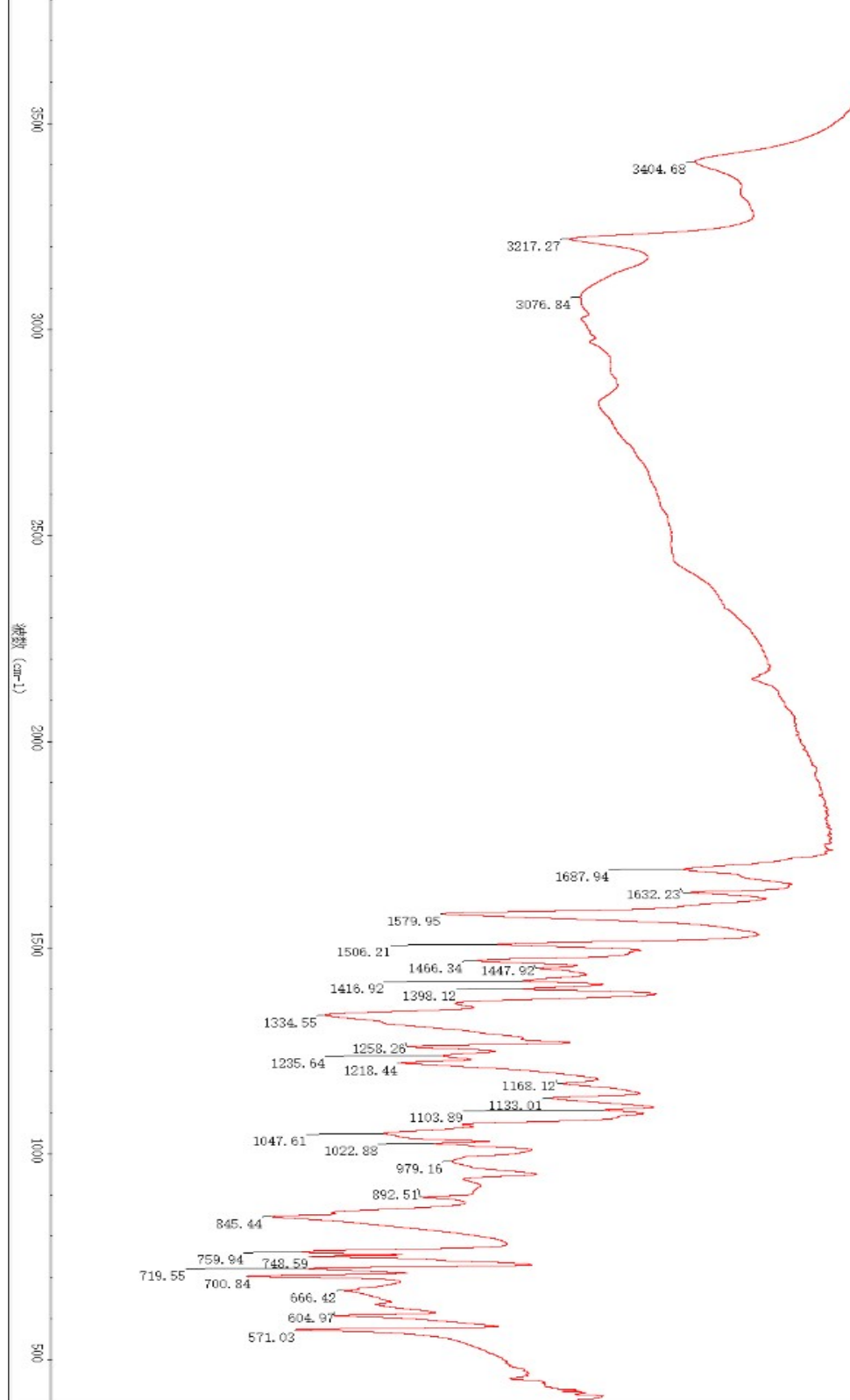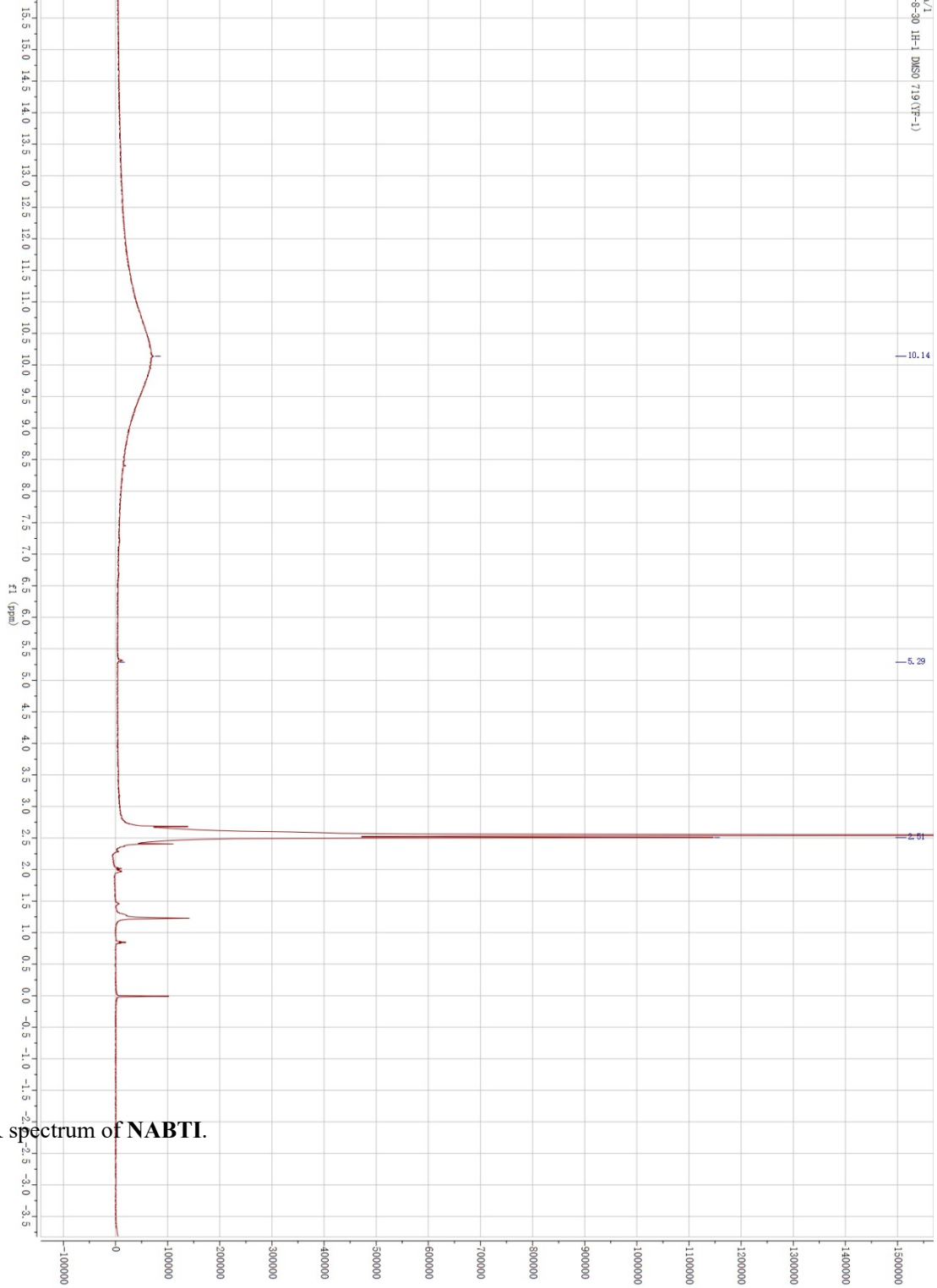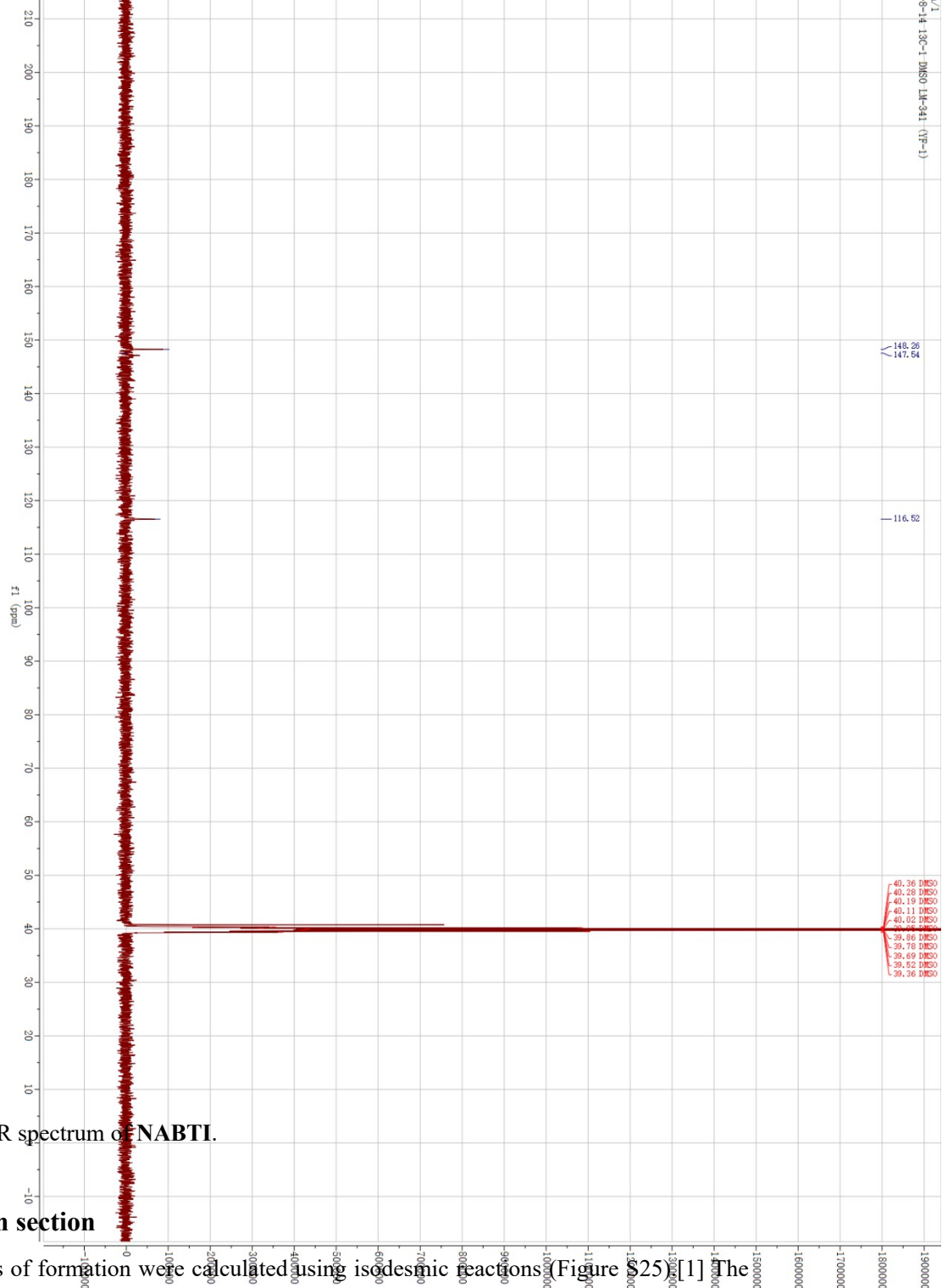## 2 IR and NMR spectrum

Figure S3 IR spectrum of **NABTI**.

Figure S4. IR spectrum of **4**.
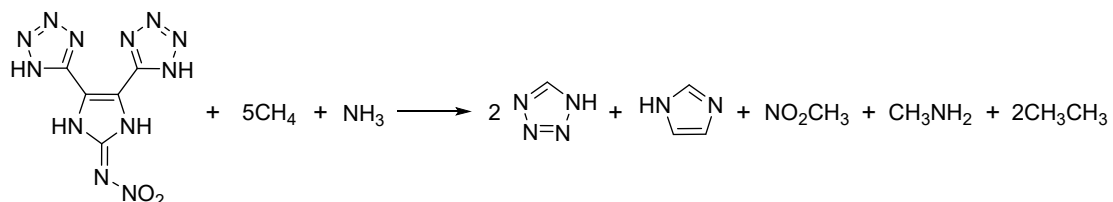
Figure S5. ^{1}H NMR spectrum of **NABTI**.

Figure S6. ^{13}C NMR spectrum of **NABTI**.

3 The calculation section

The gas phase heats of formation were calculated using isodesmic reactions (Figure S25).[1] The calculations were carried out using Gaussian 09 suite of programs,[2] at the B3LYP/6-31 G* level.

And the solid state heats of formation were calculated using the equation 1.[3]
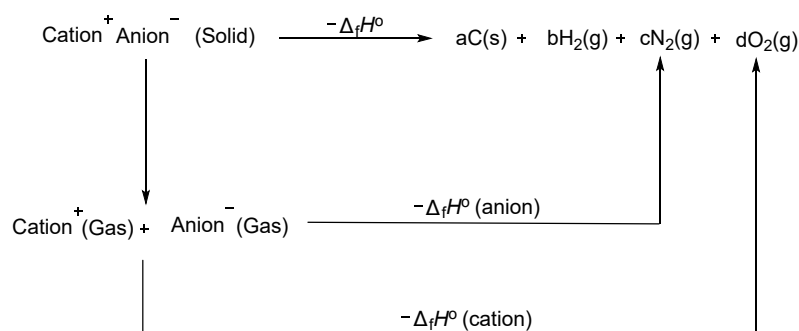

Figure S7 Isodesmic reaction of compound NAIBT.

The enthalpy of sublimation can be represented as eq (1) and on the basis of thepredicted electrostatic potential of a molecule.[4]

$$\Delta H_{sub} = a(SA)^2 + b\sqrt{\upsilon\sigma_{tot}^2} + c \qquad (1)$$

Here SA is the surface area of the 0.001 electrons bohr^{-3} isosurface of the electronic density of the compounds, $\upsilon\sigma_{tot}^2$ is derived from the molecular electrostatic potential calculation, and a, b, c are fitting parameters reported by Politzer et al.[4]

For energetic salts, the solid-phase heats of formation are calculated based on a Born-Haberenergy cycle (Scheme S1).[5]

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

$$\Delta Hf^o \text{ (salt, 298 K)} = \Delta Hf^o \text{ (cation, 298K)} + \Delta Hf^o \text{ (anion, 298K)} - \Delta HL \qquad (2)$$

where ΔHL is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al. [Eq. (3)]

$$\Delta HL = UPOT + [p(nM/2 - 2) + q(nX/2 - 2)]RT \qquad (3)$$

where nM and nX represent the nature of the ions, Mq+and Xp-, and are equal to 3 for monatomic ions, 5 for linear polyatomicions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} is as the follow:
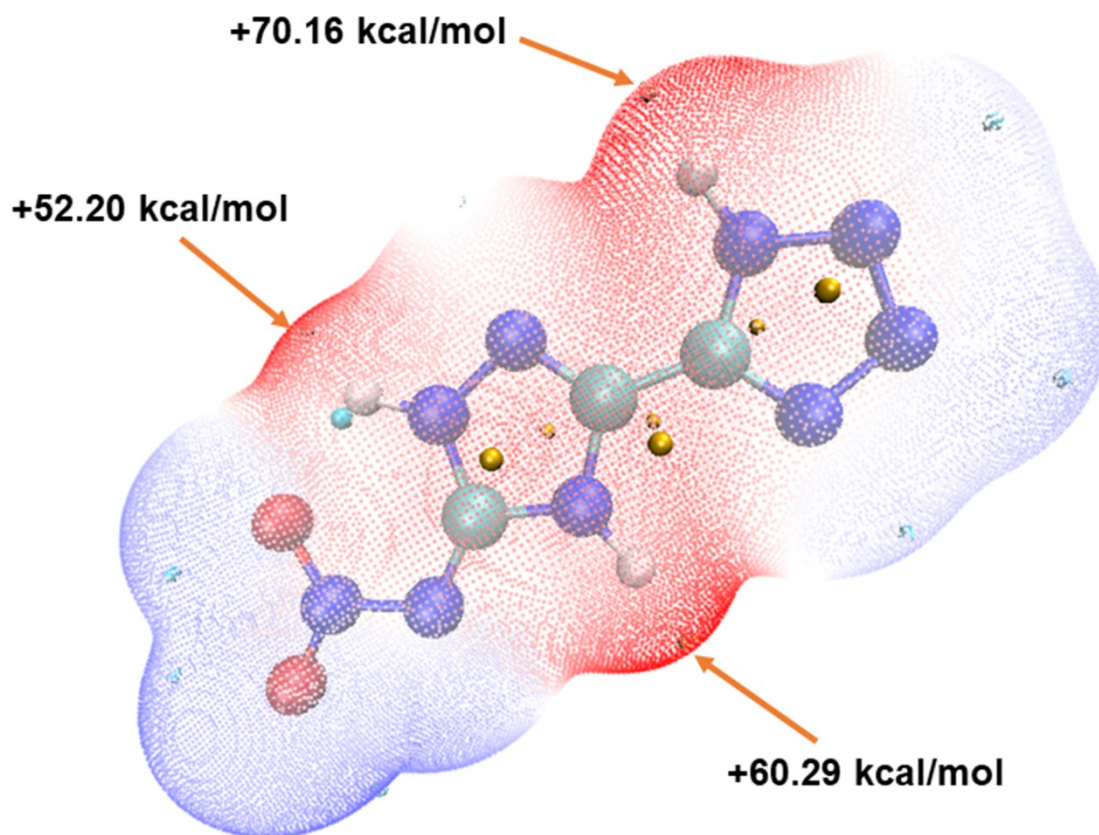
$$U_{POT} \text{ [kJ mol}^{-1}] = \gamma(\rho m/Mm)1/3 + \delta \qquad (4)$$

where ρm (g cm^{-3}) is the density of the salt, Mm is the formula mass of the ionic compound, and values for γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.8

Table S5. Calculated total energy (E_0), zero-point energy (ZPE), thermal correction to enthalpy (ΔH_T), and heats of formation (HOF) in gas state.

Compound	E_0 / a. u.	ZPE / kJ mol^{-1}	ΔH_T / a. u.	HOF/kJ mol^{-1}
NABTI	-1000.1936689	382.636	0.160791	948.61
CH_4	-40.5240195	118.22	0.048836	-74.60
NH_3	-56.5479477	90.67	0.038336	-45.87
NABTI⁻	-999.6875669	346.869	0.146956	712.07
NO_2CH_3	-245.0133749	131.32	0.055294	-74.300
NH_2CH_3	-95.8532042	169.15	0.068745	-23.000
$C_3N_2H_4$	-226.2145594	187.053	0.075969	194.03

CN$_4$H$_2$	-258.250899	123.259	0.051374	364.4
C$_2$NH$_8^+$	-135.5340286	285.179	0.114056	13.92

+70.16 kcal/mol

+52.20 kcal/mol

+60.29 kcal/mol

Figure S8. The molecular electrostatic potential (positive value) distributions of **NATT**.

Reference

(1) J. Zhang, H. D, F. Wang, *et al*. DFT Studies on a High Energy Density Cage Compound 4-Trinitroethyl-2,6,8,10,12-pentanitrohezaazaisowurtzitane. *J. Phys. Chem. A*, 2011, **24**, 6617-6621.

(2) M. J. Frisch, Gaussian 09. Revision a. 02, Gaussian, Inc., Wallingford CT, 2009.

(3) P. W. Atkins, Physical Chemistry. Oxford University Press, Oxford, U. K., 1982.

(4) P. J. Politzer, S. Murray, T. Brinck, P. Lan, Immunoanalysis of agrochemicals. ACS Sympsium Series 586, American Chemical Society, Washington, DC, 1994.

(5) H. D. B. Jenkins, D. Tudela, L. Glasser, Lattice Potential Energy Estimation for Complex Ionic Salts from Density Measurements, *Inorg. Chem.*, 2002, **9**, 2364-2367.