Supporting Information

A safe and scaled up route to inert ammonia oxide hydroxylammonium azide ($H_7N_5O_2$), hydrazinium azide (H_5N_5) and ammonium azide (H_4N_4)

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General Methods

All reagents were purchased from VWR or AK Scientific in analytical grade and were used as supplied. 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. Densities were measured at room temperature using a Micromeritics AccuPyc 1340 gas pycnometer. Elemental analyses were carried out on a Vario Micro cube Elementar Analyser. The sensitivities to impact (IS) and friction (FS) were determined according to BAM standards.

The geometric optimization and frequency analyses of the structures are based on available single-crystal structures using the B3LYP functional with the 6-31+G** basis set. Single-point energies were calculated at the MP2/6-311++G** level.[S1] All of the structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

Experimental Section

Caution

Although no explosions or hazards were observed during the preparation and handling of these compounds, all are potentially explosive materials. Mechanical actions involving scratching or scraping must be avoided. In addition, all of the compounds must be synthesized on a small scale. Manipulations must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn at all times.

$\mathbf{\overset{+}{N}H_4\ \overset{-}{N}_3}$

In one 100 mL flask, trimethylsilyl azide ($TMSN_3$) (1.15 g, 10 mmol) was dissolved in methanol (30 mL), and ammonium fluoride (0.37 g, 10 mmol) was added to the solution at room temperature. After 6 h, the colorless crystalline ammonium azide (0.54 g, 9.0 mmol) was obtained by air drying in a yield of >90%. M.p. 141 °C; IR (KBr): ṽ 3144, 3012, 2834, 2036, 1818, 1418, 663, 651, 626 cm^{-1} (w); Elemental analysis: Calcd (%) for H_4N_4 (75.05): C 0.00, H 6.71, N 93.29; Found: C 0.13, H 6.53, N 92.13.

$\mathbf{\overset{+}{N}_2H_5\ \overset{-}{N}_3}$

Hydrazonium azide (H_5N_5), 2

Hydrazine monohydrate (5 g, 0.1 mol) was dissolved in water (15 mL), and 48% aqueous hydrofluoric acid solution (4.0 g, 0.1 mol) was added to the solution at 0 °C. Then the solution was stirred at 0 °C for 4 h, and warmed to room temperature. The white solid hydrazinium fluoride was obtained by air drying with a yield of 86% (4.5 g). Then trimethylsilyl azide ($TMSN_3$) (1.15 g, 10 mmol) was dissolved in methanol (30 mL), and hydrazinium fluoride (0.5 g, 9.6 mmol) was added to the solution at room temperature. After 8 h, the colorless crystalline hydrazinium azide (0.6 g, 8.6 mmol) was obtained by air drying in a yield of >90%. M.p. 75 °C; IR (KBr): ṽ 3356, 3285, 3053, 2033, 1598, 1508, 1338, 1234, 1094, 953, 649, 643, 460 cm^{-1} (w); Elemental analysis: Calcd (%) for H_5N_5 (75.05): C 0.00, H 6.71, N 93.29; Found: C 0.37, H 6.69, N 93.76.

$\mathbf{NH_3O \cdot \overset{+}{N}H_3OH\ \overset{-}{N}_3}$

Ammonia oxide hydroxylammonium azide ($H_7N_5O_2$), 3

In a round-bottomed flask (100 mL), 48% aqueous hydrofluoric acid solution (4.0 g, 0.1 mol) was dissolved in water (30 mL), and hydroxylamine (6.6 g, 50% solution in water) (1 mL) was added dropwise to the solution. The system was stirred continuously at room temperature for 6 h. The pink solid hydroxylammonium fluoride (4.8 g, 9 mmol) was collected after being dried by air. Then trimethylsilyl azide (1.15 g, 10 mmol) was dissolved in methanol (30 mL), hydroxylammonium fluoride (1.06 g, 20 mmol) was added to the solution at room temperature. After 8 h, the colorless solid, ammonia oxide hydroxylammonium azide (0.92 g, 8.4 mmol) was obtained in 84 % yield. M.p 64 °C; $T_{d(onset)}$ = 114 °C; IR (KBr): ṽ 3063, 2688, 2037, 1595, 1508, 1184, 1084, 846, 624, 450 cm^{-1} (w); Elemental analysis: Calcd (%) for $H_7N_5O_2$ (109.05): C 0.00, H 6.47, N 64.20; Found: C 0.13, H 6.15, N 62.36.

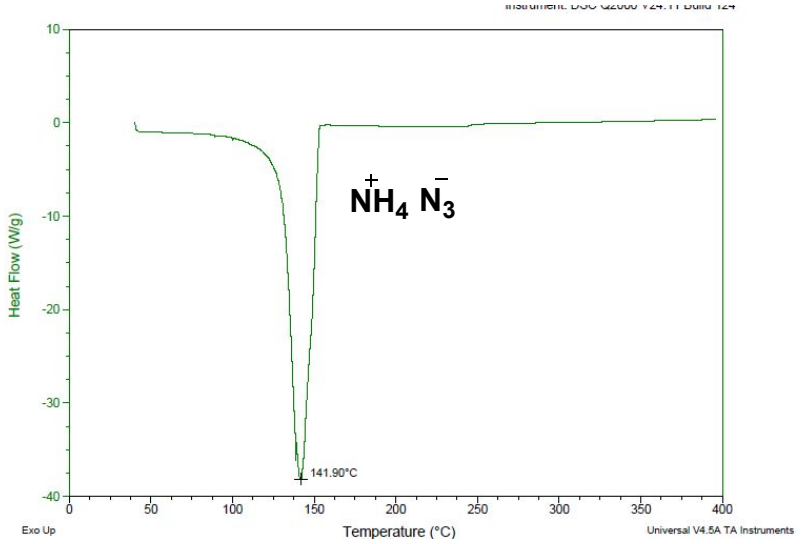
Crystallographic Data

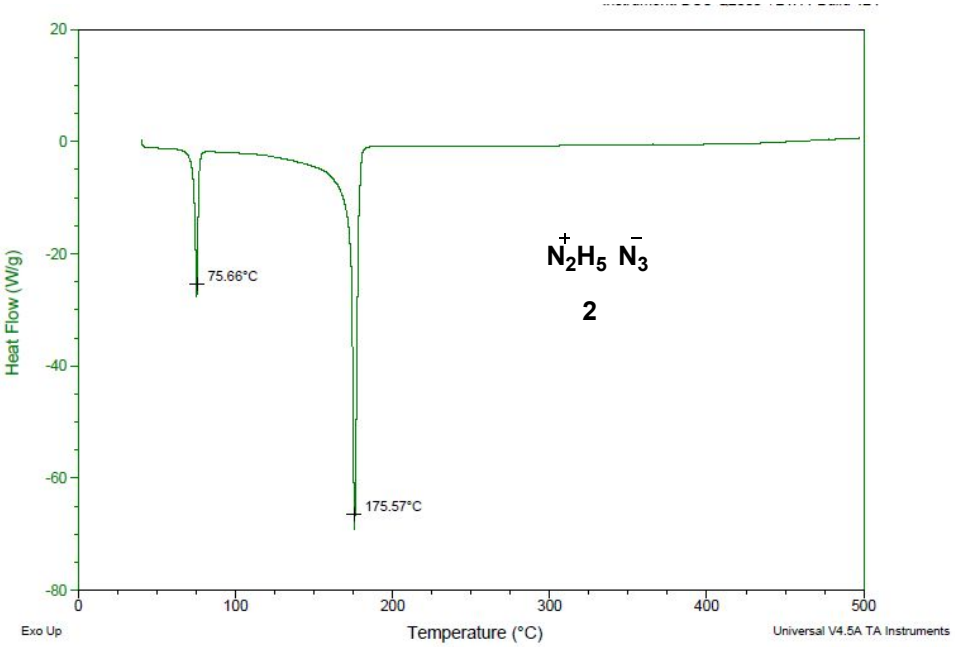
Table S1. Crystal data and structure refinement for **1**, **2** and **3**.

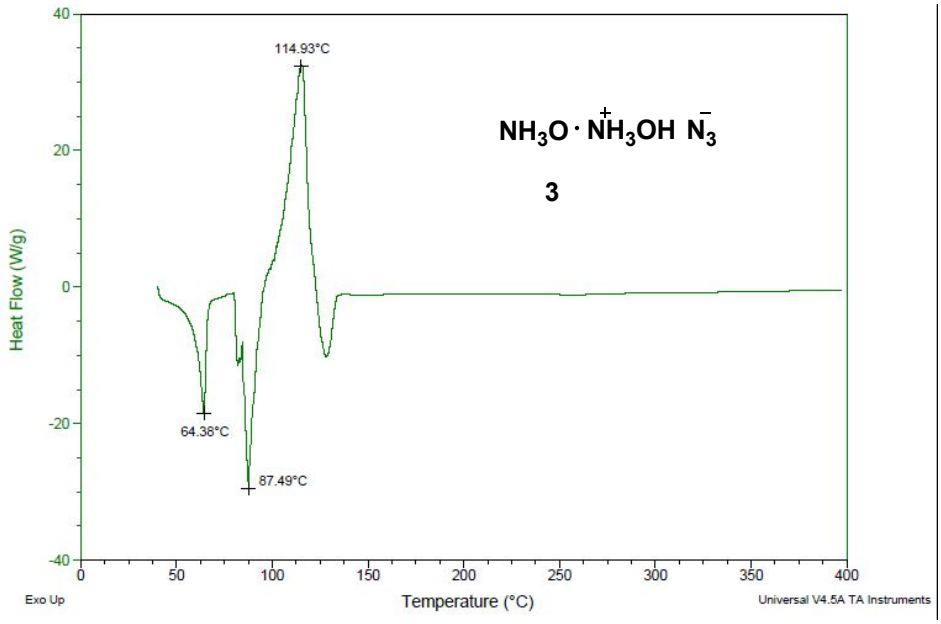
Compound	**1**	**2**	**3**
CCDC	1920046 (1886886)[S2]	1905107	1905108
Formula	H_8N_8	H_5N_5	$H_7N_5O_2$
$D_{calc.}$/ g cm^{-3}	1.365	1.419	1.611
μ/mm^{-1}	0.111	0.115	1.314
Formula Weight	120.14	75.09	109.11
Color	colorless	colorless	colorless
Shape	block	chunk	needle
Size/mm^3	0.27×0.18×0.10	0.20×0.18×0.07	0.29×0.09×0.02
T/K	173(2)	243(2)	173(2)
Crystal System	orthorhombic	monoclinic	orthorhombic
Flack Parameter	-	-	0.4(3)
Hooft Parameter	-	-	0.4(2)
Space Group	$Pmna$	$P2_1/n$	$Pca2_1$
a/Å	8.9331(10)	5.641(2)	19.9594(4)
b/Å	3.7824(4)	5.521(2)	3.55530(10)
c/Å	8.6519(10)	11.306(4)	19.0219(3)
α/°	90	90	90
β/°	90	93.261(4)	90
γ/°	90	90	90
V/Å^3	292.34(6)	351.5(2)	1349.83(5)
Z	2	4	12
Z'	0.25	1	3
Wavelength/Å	0.710730	0.710730	1.541838
Radiation type	MoK_α	MoK_α	CuK_α
Θ_{min}/°	3.278	3.610	4.649
Θ_{max}/°	27.482	27.526	72.127
Measured Refl.	4901	6369	12824

Independent Refl.	357	814	2583
Reflections with I >2(I)	318	604	2035
R_{int}	0.0276	0.0567	0.0715
Parameters	34	67	208
Restraints	0	0	1
Largest Peak	0.202	0.181	0.196
Deepest Hole	-0.171	-0.173	-0.215
GooF	1.179	1.041	0.997
wR_2 (all data)	0.0748	0.1280	0.1025
wR_2	0.0714	0.1145	0.0930
R_1 (all data)	0.0284	0.0636	0.0585
R_1	0.0261	0.0454	0.0402

DSC curves of **1**, **2** and **3**







Reference

S1. R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, **1989**.

S2 This CCDC number are applied by Dr. Ralf Haiges (DOI: 10.5517/ccdc.csd.cc21bg95)S1