Electronic Supplementary Information (ESI)

Denitration of Hydrazinium nitroformate to Form Hydrazinium Dinitromethanide

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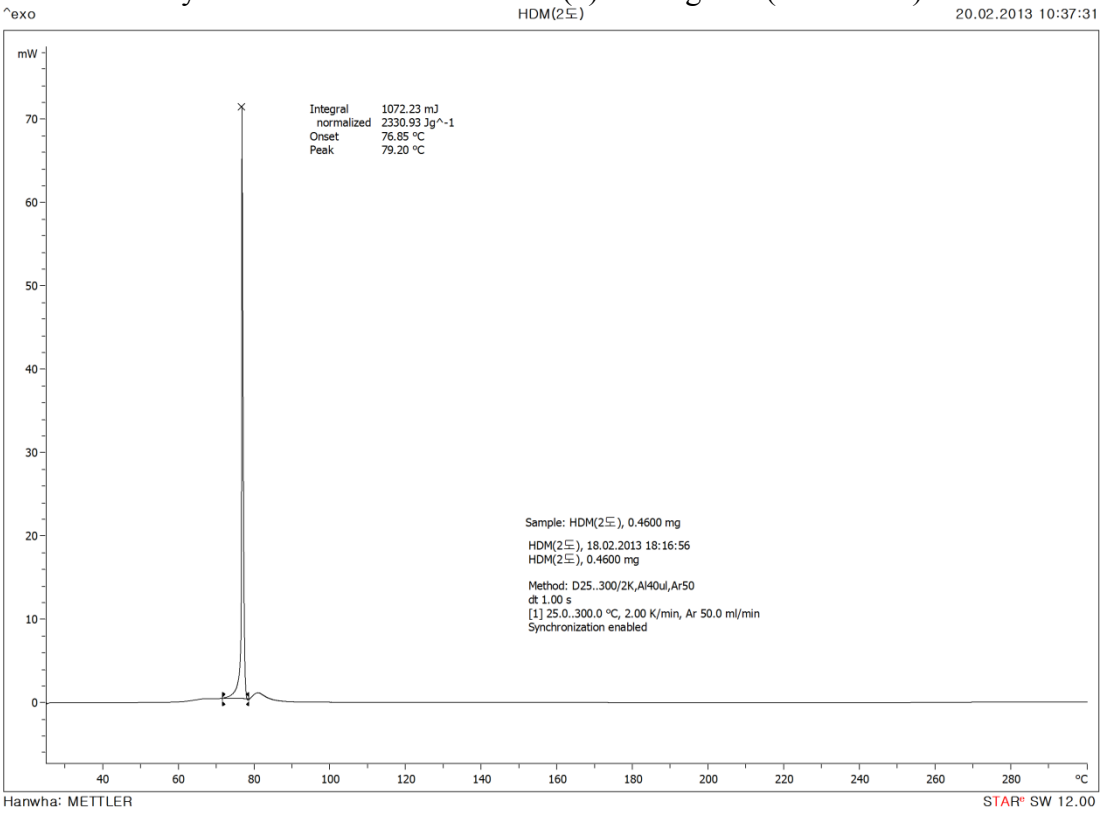
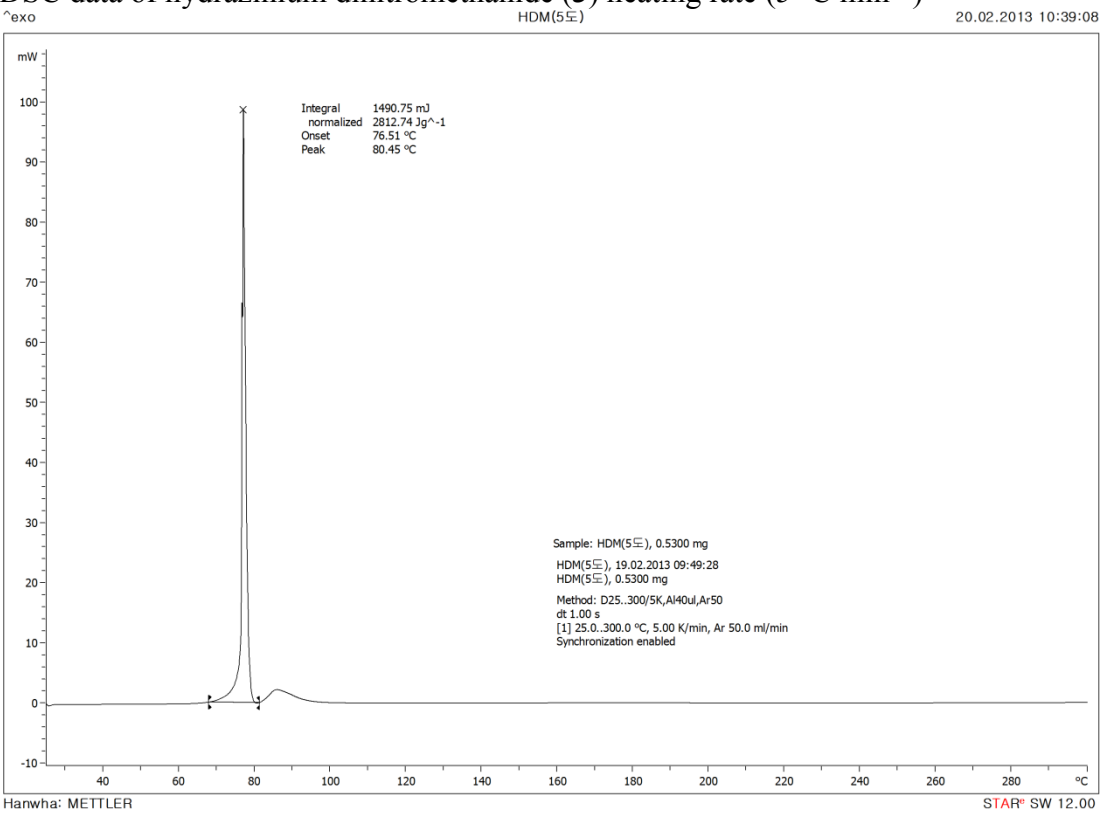
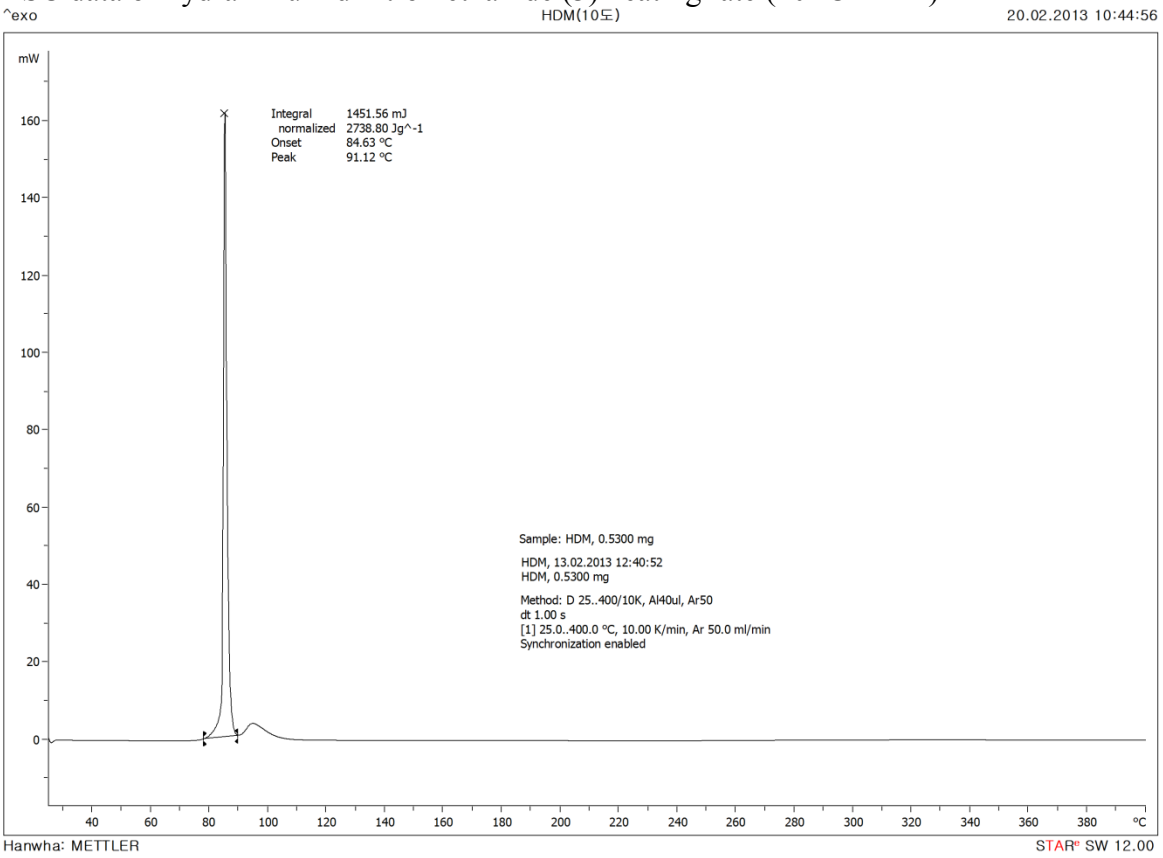


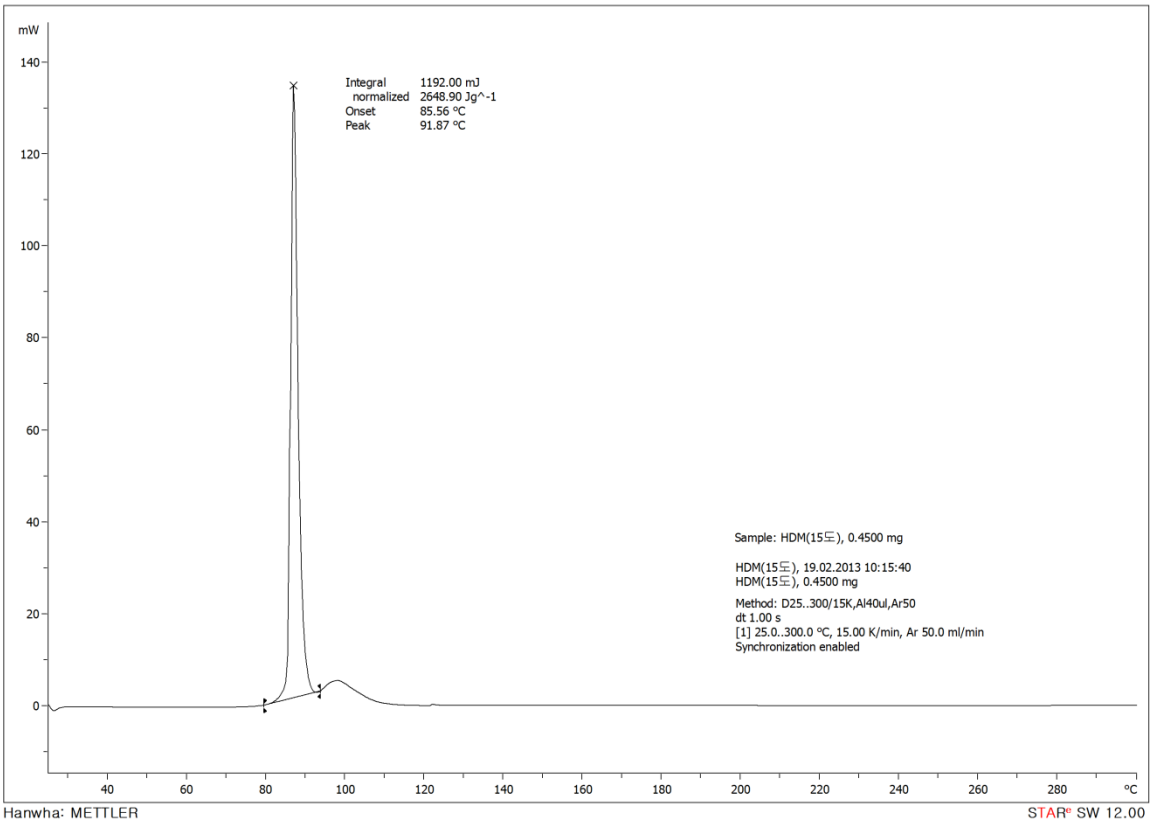
DSC data of hydrazinium dinitromethanide (**3**) heating rate (5 ^{o}C min^{-1})



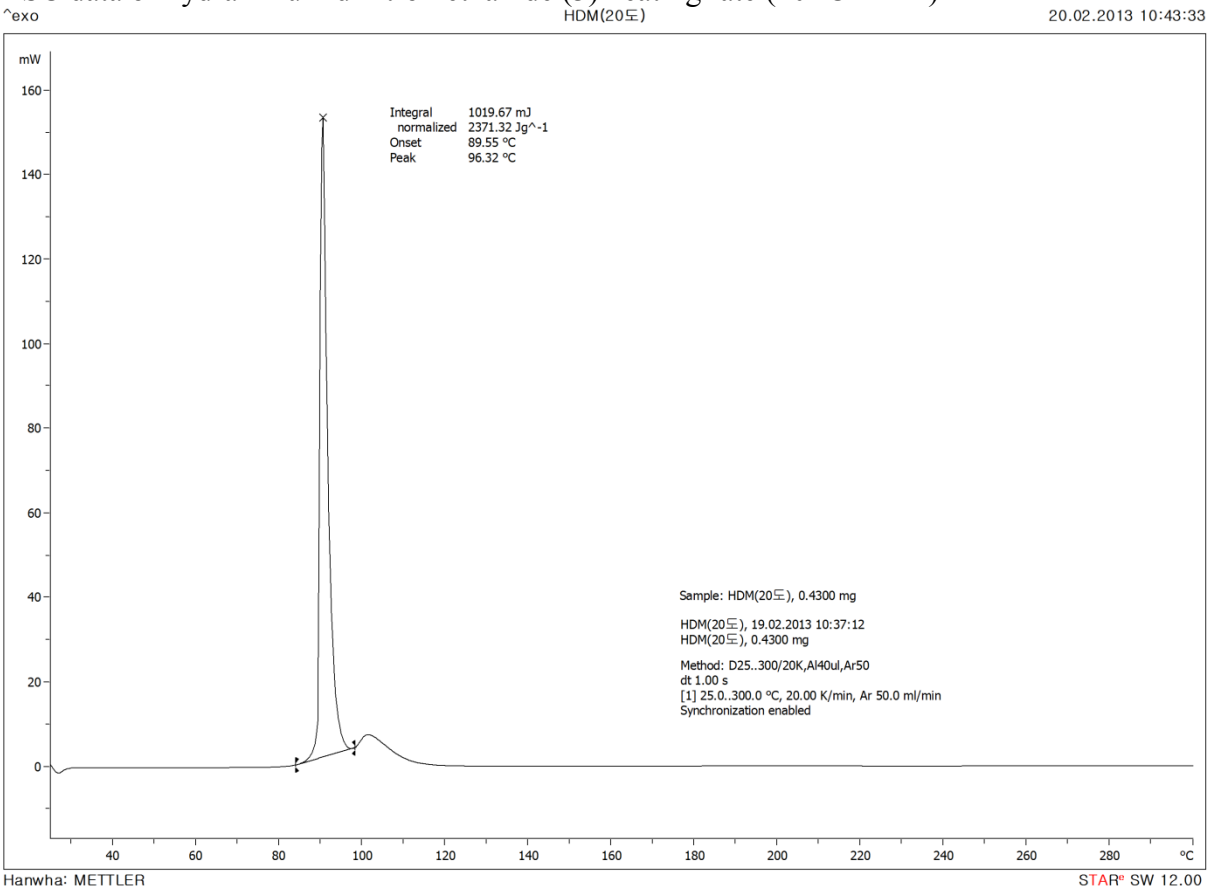
DSC data of hydrazinium dinitromethanide (**3**) heating rate (10 ^{o}C min^{-1})



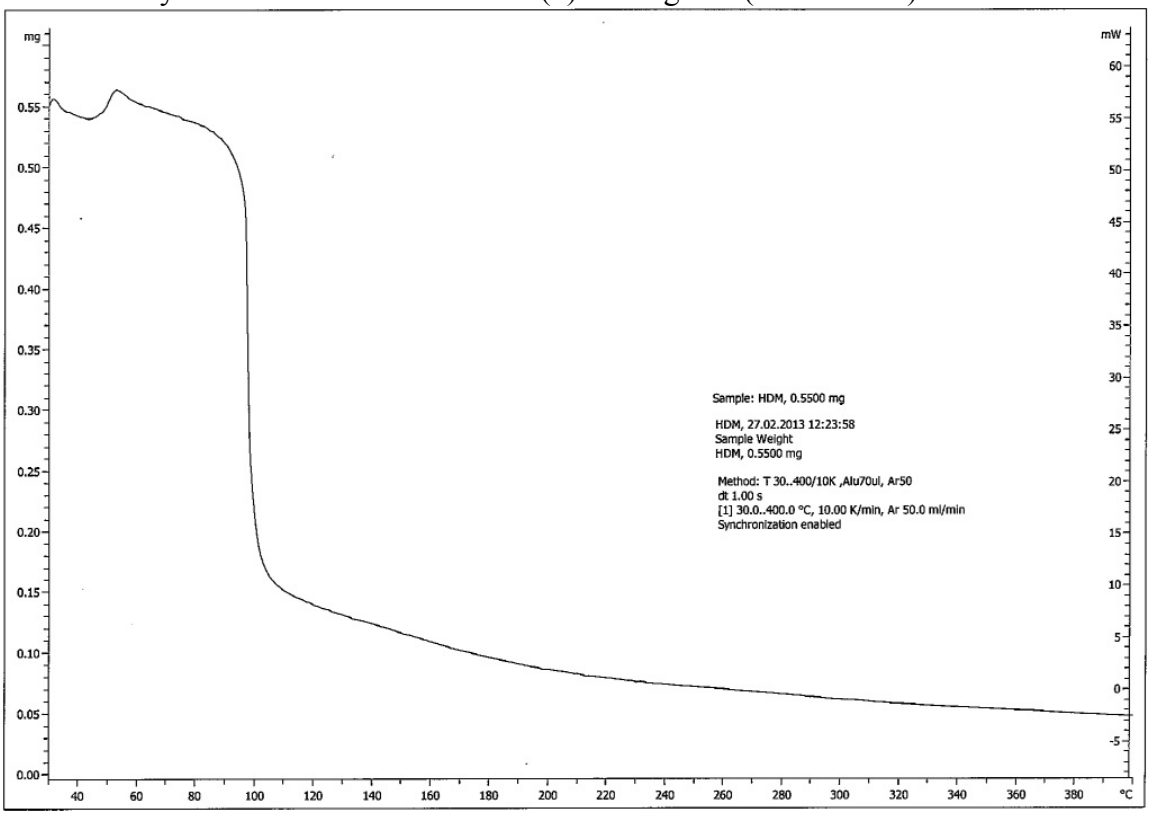
DSC data of hydrazinium dinitromethanide (**3**) heating rate (15 ^{o}C min^{-1})



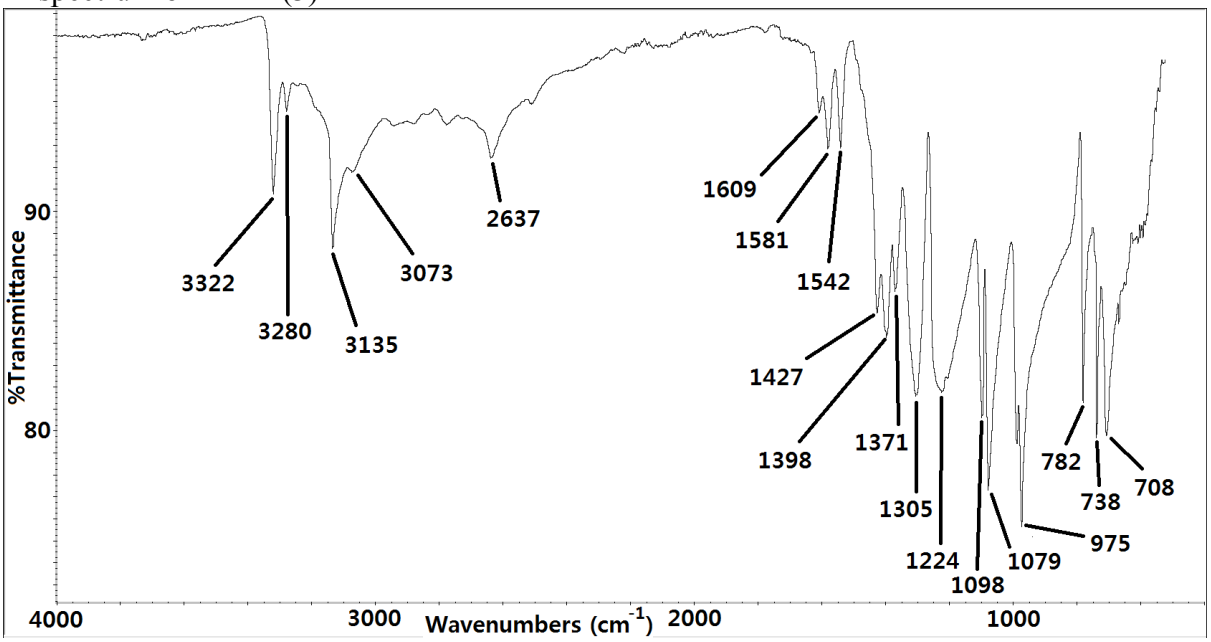
DSC data of hydrazinium dinitromethanide (**3**) heating rate (20 ^{o}C min^{-1})



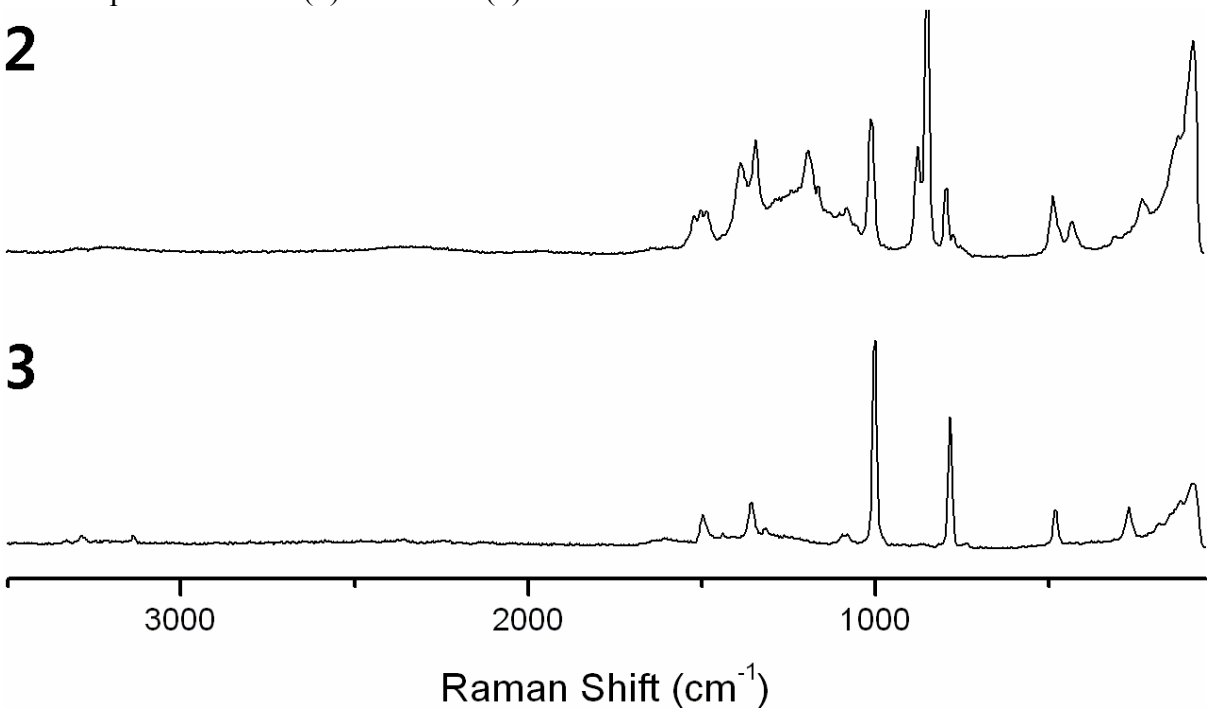
TG data of hydrazinium dinitromethanide (**3**) heating rate (10 ^{o}C min^{-1})



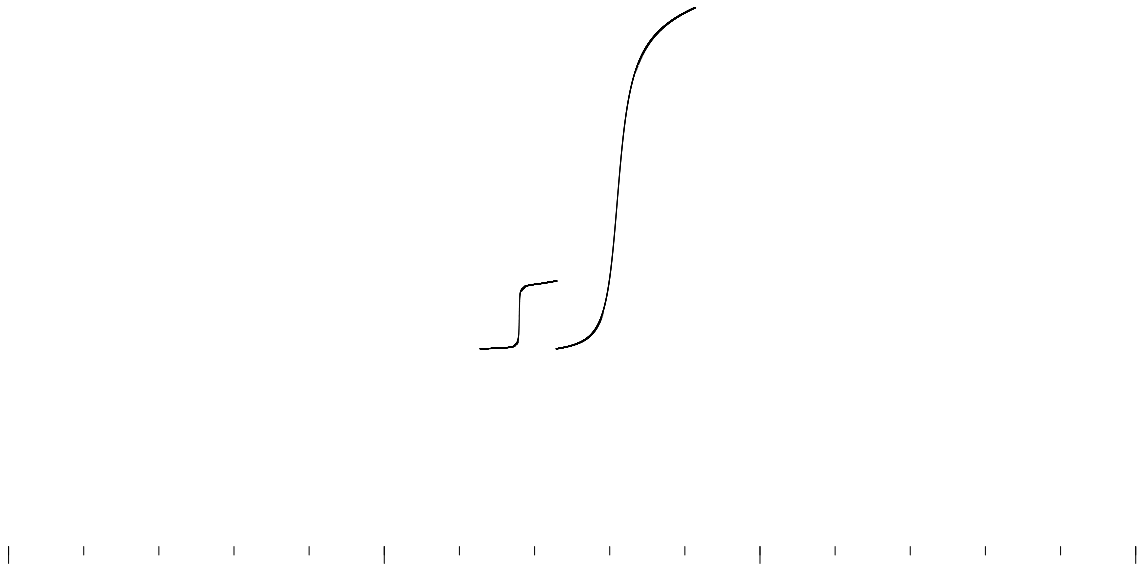
IR spectrum of HDM (**3**)



Raman spectra of HNF (**2**) and HDM (**3**)



^{1}H NMR spectra of HDM (**3**)



^{13}C NMR spectra of HDM (**3**)

Details of the x-ray diffraction analysis of compounds **2** and **3** are provided. Data were collected on a Bruker SMART APEX-II CCD detector using graphite monochromated MoKα radiation (λ = 0.71073). Structures were solved by applying direct methods using SHELXS-97. 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.

Table 1. Crystal data and structure refinement for **3**.

Identification code	HDM (**3**)
Empirical formula	C H6 N4 O4
Formula weight	138.10
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 3.701(3) A alpha = 90 deg. b = 13.875(11) A beta = 98.833(9) deg. c = 10.753(9) A gamma = 90 deg.
Volume	545.6(8) A^3
Z, Calculated density	4, 1.681 Mg/m^3
Absorption coefficient	0.164 mm^-1
F(000)	288
Crystal size	0.25 x 0.24 x 0.22 mm
Theta range for data collection	2.41 to 28.54 deg.
Limiting indices	-4<=h<=4, -18<=k<=18, -13<=l<=14
Reflections collected / unique	9535 / 1360 [R(int) = 0.1425]
Completeness to theta = 28.54	98.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1360 / 0 / 102
Goodness-of-fit on F^2	0.856
Final R indices [I>2sigma(I)]	R1 = 0.0415, wR2 = 0.0843
R indices (all data)	R1 = 0.1428, wR2 = 0.1064
Largest diff. peak and hole	0.177 and -0.233 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	-1088(5)	994(2)	6293(2)	42(1)
C(2)	-1384(6)	55(2)	6581(2)	40(1)
N(3)	350(5)	-385(2)	7640(2)	42(1)
O(4)	-2864(5)	1268(1)	5252(2)	57(1)
O(5)	799(5)	1600(1)	6974(2)	53(1)
O(6)	2486(5)	54(1)	8483(2)	53(1)
O(7)	-216(5)	-1273(2)	7740(2)	54(1)
N(8)	4112(6)	1714(2)	10215(2)	41(1)
N(9)	6351(6)	1969(2)	9273(2)	45(1)

Table 3. Bond lengths [A] and angles [deg] for **3**.

N(1)-O(5)	1.254(2)
N(1)-O(4)	1.266(2)
N(1)-C(2)	1.348(3)
C(2)-N(3)	1.363(3)
C(2)-H(2)	0.93
N(3)-O(7)	1.256(3)
N(3)-O(6)	1.264(2)
N(8)-N(9)	1.448(3)
N(8)-H(8A)	1.05(3)
N(8)-H(8B)	1.04(3)
N(8)-H(8C)	0.85(3)
N(9)-H(9A)	1.06(3)
N(9)-H(9B)	0.76(3)

O(5)-N(1)-O(4)	118.8(2)
O(5)-N(1)-C(2)	124.9(2)
O(4)-N(1)-C(2)	116.4(2)
N(1)-C(2)-N(3)	125.5(2)
N(1)-C(2)-H(2)	117.2
N(3)-C(2)-H(2)	117.2
O(7)-N(3)-O(6)	120.4(2)
O(7)-N(3)-C(2)	116.5(2)
O(6)-N(3)-C(2)	123.0(2)
N(9)-N(8)-H(8A)	103.1(15)
N(9)-N(8)-H(8B)	108.4(17)
H(8A)-N(8)-H(8B)	116(2)
N(9)-N(8)-H(8C)	113.0(19)
H(8A)-N(8)-H(8C)	108(2)
H(8B)-N(8)-H(8C)	109(3)
N(8)-N(9)-H(9A)	101.9(15)
N(8)-N(9)-H(9B)	106(3)
H(9A)-N(9)-H(9B)	116(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **3**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	35(1)	54(2)	33(1)	-2(1)	-4(1)	-2(1)
C(2)	36(1)	47(2)	32(1)	-1(1)	-9(1)	-5(1)
N(3)	35(1)	57(2)	32(1)	-2(1)	1(1)	0(1)
O(4)	60(1)	63(1)	38(1)	9(1)	-20(1)	-6(1)
O(5)	59(1)	54(1)	41(1)	-4(1)	-15(1)	-9(1)
O(6)	54(1)	59(1)	37(1)	-1(1)	-16(1)	-1(1)
O(7)	60(1)	49(1)	48(1)	8(1)	-5(1)	-4(1)
N(8)	28(1)	57(2)	37(1)	-1(1)	0(1)	2(1)
N(9)	36(1)	64(2)	33(1)	-3(1)	1(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3**.

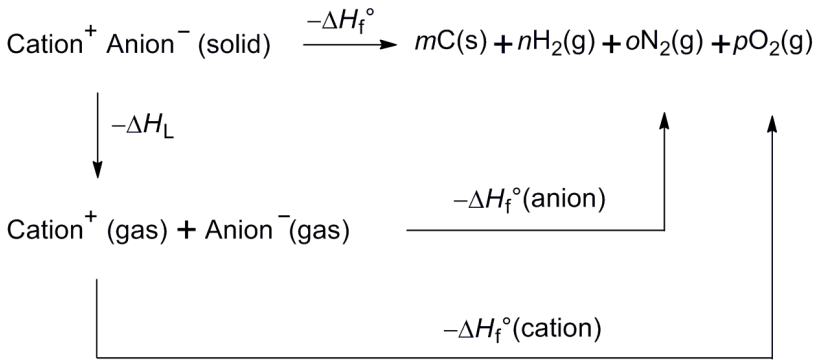
	x	y	z	U(eq)
H(2)	-2899	-325	6009	48
H(8A)	4700(70)	2260(20)	10890(30)	80(10)
H(8B)	4780(80)	1020(20)	10520(30)	89(11)
H(8C)	1840(90)	1740(20)	9940(30)	69(9)
H(9A)	5720(70)	2710(20)	9120(30)	83(11)
H(9B)	5770(80)	1630(20)	8720(30)	71(12)

Table 6. Hydrogen bonds for **3** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(8)-H(8A)...O(5)#1	1.05(3)	1.97(3)	3.012(4)	173(2)
N(8)-H(8A)...O(4)#1	1.05(3)	2.31(3)	2.895(4)	114(2)
N(8)-H(8A)...N(1)#1	1.05(3)	2.49(3)	3.389(4)	144(2)
N(8)-H(8B)...O(6)#2	1.04(3)	2.01(3)	3.004(3)	159(2)
N(8)-H(8B)...N(3)#2	1.04(3)	2.61(3)	3.386(4)	131(2)
N(9)-H(9A)...O(4)#1	1.06(3)	2.39(3)	3.167(4)	129(2)
N(9)-H(9A)...O(7)#3	1.06(3)	2.43(3)	3.245(4)	132(2)
N(9)-H(9B)...O(5)	0.76(3)	2.42(3)	3.006(3)	135(3)
N(9)-H(9B)...O(6)	0.76(3)	2.50(3)	3.075(4)	134(3)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,z+1/2 #2 -x+1,-y,-z+2 #3 -x+1/2,y+1/2,-z+3/2



Born-Haber cycle for the formation of HNF (**2**) or HDM (**3**).