A facile method to prepare energetic materials (EMs)

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Section 1. Materials and instrumentations

The chemicals and reagents were purchased from Beijing Chemical Reagent Company and supplied by the industry without further purification. Solvents were purified according to standard procedures. Elemental analysis was performed with a Vario EL IIIFully-Automatic Trace Element Analyzer. Fourier Transform Infrared Spectroscopy (FT-IR) analysis was obtained from an IRPrestige-21 spectrometer. A mixture containing approximately 1 to 2% of sample, the rest consisting of dried KBr, was ground into a fine powder. The powder was compressed using a stainless steel mold and a pressure device. Transform Infrared Spectroscopy spectra was recorded from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Differential Scanning Calorimetry (DSC) was obtained on a CDR-4 (Shanghai Precision & Scientific Instrument Co., Ltd, China) with an aluminum crucible (5 mm in diameter, 3 mm high). The operation conditions are as follows: sample mass is approximately 0.3 mg; heating rates are 5, 10, 15, 20, and 25 ^{o}C min^{-1}, respectively; temperatures range from 50 to 500 ^{o}C; the atmosphere is a self-generating static atmosphere, Al_2O_3 was used as a reference sample.

Section 2. Synthetic procedures

General Procedure for the prepation of 1,2-bis(hydrazinocarbonyl)hydrazine (BHCH):

Five dialkyl azodicarboxylates including dimethyl azodicarboxylate (DMAD), diethyl azodicarboxylate (DEAD), diisopropyl azodicarboxylate (DIAD), ditert-butyl azodicarboxylate (DTAD) and dibenzyl azodicarboxylate (DBAD) were chosen as the start materials and reacted with hydrazine hydrate to get BHCH with high yield.

To a 100 mL round-bottom flask containing a stir bar, dialkyl azodicarboxylate (20 mmol) and 60% hydrazine hydrate solution (5 g, 60 mmol) was added slowly to 20 mL deionized water at different temperatures. After stirring overnight, the solution was transferred into 200 mL ethanol, then the product was collected by filtration, washed with cold deionized water and ethanol, and dried in a vacuum dryer. Single crystals of BHCH suitable for X-ray analyses were obtained easily by slow crystallization from the filtrate for 7 days. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.70 (s, 2H, NH), 7.30 (s, 2H, NH), 4.01 (s, 4H, NH_2) ppm; Anal. Calcd for BHCH: $C_2H_8N_6O_2$ (%): C 16.22, N 56.74 H 5.44%; found C 16.25, N 56.73, H 5.51%. ESI-MS (M+) Calcd for $C_2H_8N_6O_2$ 148.07, found 149.21. IR (cm^{-1}, KBr): 3312, 3205, 3087, 2936, 1662, 1546, 1481, 1341, 1184, 1038, 942, 905, 748, 613.

Preparation of EM-1:

0.15 g (1 mmol) BHCH was added to a solution of 0.23 g (1 mmol) picric acid (PA) in 20 mL of water. The mixture was continuously stirred for 1 h at 60 °C. The EM-1 was precipitated from water after the solution was cooled to room temperature and obtained by filtration. Even change the ratio of the starting materials (BHCH:PA = 2:1 or 1:2), only EM-1 can be obtained. The single crystals of EM-1 suitable for X-ray analyses were obtained easily by slow crystallization from the filtrate for several days. Anal. Calcd for EM-1: $C_8H_{11}N_9O_9$ (%): C 25.47, N 33.42 H 2.94%; found C 25.53, N 33.57, H 3.01%. IR (cm^{-1}, KBr): 3387, 3344, 3281, 1599, 1198, 1089, 1012, 1655, 1148, 1383, 828. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.89 (s, 4H, NHN*H*$_2$), 9.34(s, 2H, N*H*NH$_2$), 8.97(s, 2H, N*H*CO), 8.59 (s, 2H, ArH); ESI-MS (M+) Calcd for $C_2H_9N_6O_2^+$ 149.08, found 149.11; ESI-MS (M-) Calcd for $C_6H_2N_3O_7^-$ 227.99, found 227.80. Raman (cm^{-1} 200 mW, 25 °C): 1551, 1314, 1148, 943, 817, 707, 344.

Preparation of EM-2:

0.15g (1 mmol) BHCH was added to a solution of 0.49 g (2 mmol) 2, 4, 6-trinitroresorcinol (TNR) in 20 mL of water. The mixture was continuously stirred for 1 h at 60 °C. The EM-2 was precipitated from water after the solution was cooled to room temperature and obtained by filtration. Even change the ratio of the starting materials

(BHCH:TNR = 2:1 or 1:1), only EM-2 can be obtained. The single crystals of EM-2 suitable for X-ray analyses was crystallized after storage at 0 ^{o}C under water for several days. Anal. Calcd for EM-2: $C_{14}H_{24}N_{12}O_{23}$ (%): C 23.08, N 23.08 H 3.32%; found C 23.11, N 23.14, H 3.21%. IR (cm^{-1}, KBr): 3354, 3319, 1692, 1663, 1623, 1508, 1453, 1374, 1307, 1286, 1187, 927, 785, 736. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.29 (s, 4H, $\mathrm{NHN}H_2$), 8.94(s, 2H, $\mathrm{N}H\mathrm{NH}_2$), 8.60(s, 2H, ArH); ESI-MS (M+) Calcd for $C_2H_{10}N_6O_2^+$ 149.08, found 149.11; ESI-MS (M-) Calc'd for $C_6H_2N_3O_8^-$ 243.98, found 243.91. Raman (cm^{-1} 200 mW, 25 °C): 1471, 1322, 1274, 1186, 825, 753, 699, 407, 304, 178.

Section 3. X-ray crystallography

The signal crystal obtained as above were used in the X-ray diffraction study. Data collections were performed on a Rigaku AFC-10/Saturn 724^{+} CCD diffractometer with graphite monochromated Mo-Kα radiation (λ=0.71073A$^{\circ}$) at 153(2) K. The structure of EMs was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares procedures on F^2 with SHELXL-97. All non-hydrogen atoms were obtained from the difference Fourier map and refined anisotropically. Hydrogen atoms were generated geometrically, assigned appropriated isotropic thermal parameters, and included in structure factor calculations. Crystallographic data and experimental details for structure analyses are summarized in table S1.

Table S1 Crystallographic data and structure determination details for BHCH, EM-1 and EM-2

Complex	**BHCH**	**EM-1**	**EM-2**
Empirical formula	C2H8N6O2	C8H11N9O9	C14H24N12O23
Formula mass	148.14	377.26	728.45
Temperature (K)	153(2)	153(2)	153(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pna2(1)*	*P2(1)/c*	*P2(1)/c*
Z	4	4	4
a (Å)	9.280(3)	4.6017(14	10.324(2)
b (Å)	4.5988(16)	25.268(8)	9.2938(19)
c (Å)	14.376(5)	11.950(4)	29.738(6)

α(°)	90.00	90.00	90.00
β(°)	90.00	97.11	99.37(3)
γ(°)	90.00	90.00	90.00
V (Å^3)	613.5(4)	1378.8(7)	2815.4(10)
D_c(g·cm^{-3})	1.604	1.817	1.719
μ(M$_o$$K_\alpha$) (mm^{-1})	0.137	0.165	0.165
F(000)	312	776	1504
θ(°)	5.66~63	5.94～63.08	2.78~54.98
Reflection collected	6776	16876	20334
Independent reflection [R_{int}/	1923 [R_{int}=0.0253]	4588 [R_{int}=0.0457]	6415 [R_{int}=0.0484]
S	1.000	1.058	1.229
R_1, wR_2[$I>2\sigma(I)$]	0.0343, 0.0764	0.0536, 0.1165	0.0733, 0.1976
R_1, wR_2(all)	0.0366, 0.0780	0.0825, 0.1281	0.0844, 0.2154
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e·Å^{-3})	0.24, -0.19	0.37, -0.29	0.89, -0.42

Table S2 Selected bond lengths for BHCH, EM-1 and EM-2

BHCH

Bond	lengths/Å	Bond	lengths/Å
O1-C1	1.2447(16)	N3-H3	0.89(2)
O2-C2	1.2442(16)	N4-C2	1.3670(16)
N1-N2	1.4133(17)	N4-H4	0.87(2)
N1-H1A	0.897(18)	N5-C2	1.3384(17)
N1-H1B	0.90(2)	N5-N6	1.4090(17)
N2-C1	1.3397(17)	N5-H5	0.853(17)
N2-H2	0.838(18)	N6-H6A	0.89(3)
N3-C1	1.3681(17)	N6-H6B	0.87(2)
N3-N4	1.3870(14)		

EM-1

Bond	lengths/Å	Bond	lengths/Å
O1-C1	1.2338(19)	N4-C2	1.374(2)
O2-C2	1.249(2)	N4-H4	0.8600
O3-C3	1.2636(19)	N5-C2	1.342(2)
O4-N7	1.2249(19)	N5-N6	1.413(2)
O5-N7	1.2285(19)	N5-H5	0.8601
O6-N8	1.2342(18)	N6-H6B	0.8599
O7-N8	1.2353(19)	N6-H6A	0.8600
O8-N9	1.2202(19)	N7-C4	1.447(2)
O9-N9	1.214(2)	N8-C6	1.444(2)

N1-N2	1.4182(19)	N9-C8	1.467(2)
N1-H1B	0.8600	C3-C4	1.443(2)
N1-H1C	0.8601	C3-C8	1.448(2)
N1-H1A	0.8601	C4-C5	1.394(2)
N2-C1	1.361(2)	C5-C6	1.374(2)
N2-H2	0.8601	C5-H5	0.9500
N3-C1	1.351(2)	C6-C7	1.402(2)
N3-N4	1.3802(19)	C7-C8	1.363(2)
N3-H3	0.8600	C7-H7	0.9500

EM-2

Bond	lengths/Å	Bond	lengths/Å
O1-N1	1.233(4)	N7-H7C	0.8600
O2-N1	1.222(4)	N8-C13	1.363(4)
O3-C2	1.261(4)	N8-H8A	0.8599
O4-N2	1.232(4)	N9-C13	1.350(4)
O5-N2	1.241(4)	N9-N10	1.378(4)
O6-N3	1.225(4)	N9-H9	0.8601
O7-N3	1.255(4)	N10-C14	1.367(4)
O8-C6	1.341(4)	N10-H10	0.8602
O8-H8B	0.8400	N11-C14	1.385(4)
O9-N4	1.252(3)	N11-N12	1.423(4)
O10-N4	1.234(4)	N11-H11	0.8599
O11-N5	1.223(4)	N12-H12A	0.8601
O12-N5	1.245(9)	N12-H12B	0.8602
O13-C10	1.263(4)	N12-H12C	0.8601
O14-N6	1.216(4)	C1-C6	1.379(5)
O15-N6	1.224(3)	C1-C2	1.434(4)
O16-C12	1.340(4)	C2-C3	1.453(4)
O16-H16	0.8400	C3-C4	1.378(4)
O17-C13	1.231(4)	C4-C5	1.385(4)
O18-C14	1.221(4)	C4-H4	0.9500
O19-H19A	0.8200	C5-C6	1.427(4)
O19-H19B	0.8200	C7-C8	1.398(4)
O20-H20A	0.8400	C7-C12	1.418(4)
O20-H20B	0.8394	C8-C9	1.372(4)
O21-H21A	0.8400	C8-H8	0.9500
O21-H21B	0.8402	C9-C10	1.454(4)
N1-C1	1.464(4)	C10-C11	1.428(4)
N2-C3	1.447(4)	C11-C12	1.376(4)
N3-C5	1.435(4)	O22-H22A	0.8200
N4-C7	1.425(4)	O22-H22B	0.8200
N5-O12A	1.233(16)	O23-H23A	0.8201
N5-C9	1.449(4)	O23-H23B	0.8201

N6-C11	1.470(4)	O24-H24A	0.8398
N7-N8	1.411(4)	O24-H24B	0.8399
N7-H7A	0.8598	N7-H7B	0.8598

Table S3 Selected bond angles for BHCH, EM-1 and EM-2

BHCH

Bond	Angles/°	Bond	Angles/°
N2-N1-H1A	108.0(13)	C2-N5-N6	121.97(11)
N2-N1-H1B	107.3(14)	C2-N5-H5	118.9(12)
H1A-N1-H1B	109.3(17)	N6-N5-H5	119.1(12)
C1-N2-N1	121.34(12)	N5-N6-H6A	107.3(15)
C1-N2-H2	123.2(14)	N5-N6-H6B	109.9(16)
N1-N2-H2	115.4(14)	H6A-N6-H6B	101.7(18)
C1-N3-N4	120.67(10)	O1-C1-N2	123.31(12)
C1-N3-H3	118.5(12)	O1-C1-N3	119.37(11)
N4-N3-H3	118.4(12)	N2-C1-N3	117.32(11)
C2-N4-N3	120.78(10)	O2-C2-N5	123.46(12)
C2-N4-H4	115.2(13)	O2-C2-N4	119.33(11)
N3-N4-H4	119.6(13)	N5-C2-N4	117.19(11)

EM-1

Bond	Angles/°	Bond	Angles/°
H1A-N1-H1B	106.3	O9-N9-O8	123.73(15)
H1A-N1-H1C	114.3	O9-N9-C8	118.19(14)
H1B-N1-H1C	105.5	O8-N9-C8	118.08(14)
N2-N1-H1A	110.3	O1-C1-N3	122.29(15)
N2-N1-H1B	113.5	O1-C1-N2	118.19(14)
N2-N1-H1C	106.9	N3-C1-N2	116.97(14)
N1-N2-H2	117.8	O2-C2-N5	121.74(15)
C1-N2-N1	113.60(13)	O2-C2-N4	122.67(15)
C1-N2-H2	128.0	N5-C2-N4	115.54(14)
N4-N3-H3	116.2	O3-C3-C4	127.20(15)
C1-N3-H3	122.0	O3-C3-C8	121.57(15)
C1-N3-N4	121.81(13)	C4-C3-C8	111.22(14)
N3-N4-H4	118.3	C3-C4-N7	120.50(14)
C2-N4-N3	117.67(14)	C5-C4-N7	115.79(14)
C2-N4-H4	116.9	C5-C4-C3	123.69(15)
N6-N5-H5	120.3	C4-C5-H5A	120.4
C2-N5-H5	119.8	C6-C5-C4	119.26(15)
C2-N5-N6	119.92(14)	C6-C5-H5A	120.4
N5-N6-H6A	108.2	C5-C6-N8	119.37(14)
N5-N6-H6B	109.5	C5-C6-C7	121.52(15)
H6A-N6-H6B	106.9	C7-C6-N8	119.10(14)

O4-N7-O5	121.65(15)	C6-C7-H7	121.2
O4-N7-C4	119.79(14)	C8-C7-C6	117.58(15)
O5-N7-C4	118.53(14)	C6-C7-H7	121.2
O6-N8-O7	123.03(14)	C7-C8-C3	126.05(15)
O6-N8-C6	119.09(14)	C7-C8-N9	118.23(14)
O7-N8-C6	117.84(13)	C3-C8-N9	115.73(14)

EM-2

Bond	Angles/°	Bond	Angles/°
C6-O8-H8B	109.5	C6-C1-C2	126.4(3)
C12-O16- H16	109.5	C6-C1-N1	117.5(3)
H19A-O19-H19B	104.4	C2-C1-N1	116.0(3)
H20A-O20-H20B	115.5	O3-C2-C1	122.2(3)
H21A-O21-H21B	114.5	O3-C2-C3	125.7(3)
O2-N1-O1	124.1(3)	C1-C2-C3	112.1(3)
O2-N1-C1	118.6(3)	C4-C3-N2	117.6(3)
O1-N1-C1	117.4(3)	C4-C3-C2	123.1(3)
O4-N2-O5	121.8(3)	N2-C3-C2	119.3(3)
O4-N2-C3	120.5(3)	C3-C4-C5	121.1(3)
O5-N2-C3	117.6(3)	C3-C4-H4	119.5
O6-N3-O7	121.7(3)	C5-C4-H4	119.5
O6-N3-C5	119.7(3)	C4-C5-C6	120.0(3)
O7-N3-C5	118.6(3)	C4-C5-N3	119.3(3)
O10-N4-O9	121.3(3)	C6-C5-N3	120.5(3)
O10-N4-C7	119.9(3)	O8-C6-C1	119.1(3)
O9-N4-C7	118.8(3)	O8-C6-C5	123.5(3)
O11-N5-O12A	118.7(10)	C1-C6-C5	117.3(3)
O11-N5-O12	120.1(5)	C8-C7-C12	120.4(3)
O12A-N5-O12	30.3(12)	C8-C7-N4	118.7(3)
O11-N5-C9	119.4(3)	C12-C7-N4	120.8(3)
O12A-N5-C9	118.2(8)	C9-C8-C7	120.7(3)
O12-N5-C9	119.2(4)	C9-C8-H8	119.7
O14-N6-O15	124.6(3)	C7-C8-H8	119.7
O14-N6-C11	118.2(3)	C8-C9-N5	117.2(3)
O15-N6-C11	117.2(3)	C8-C9-C10	122.9(3)
N8-N7-H7A	105.5	N5-C9-C10	119.9(3)
N8-N7-H7B	108.5	O13-C10-C11	121.0(3)
H7A-N7-H7B	113.3	O13-C10-C9	126.6(3)
N8-N7-H7C	108.9	C11-C10-C9	112.4(3)
H7A-N7-H7C	110.7	C12-C11-C10	126.8(3)
H7B-N7-H7C	109.8	C12-C11-N6	117.8(3)
C13-N8-N7	115.1(3)	C10-C11-N6	115.4(3)
C13-N8-H8A	128.5	O16-C12-C11	118.6(3)
N7-N8-H8A	105.3	O16-C12-C7	124.5(3)

C13-N9-N10	120.6(3)	C11-C12-C7	116.9(3)
C13-N9-H9	116.1	O17-C13-N9	122.9(3)
N10-N9-H9	123.2	O17-C13-N8	121.6(3)
C14-N10-N9	119.0(3)	N9-C13-N8	115.5(3)
C14-N10-H10	120.4	O18-C14-N10	125.4(3)
N9-N10-H10	120.4	O18-C14-N11	123.3(3)
C14-N11-N12	114.5(3)	N10-C14-N11	111.0(3)
C14-N11-H11	113.3	H22A-O22-H22B	115.2
N12-N11-H11	112.4	H23A-O23-H23B	99.2
N11-N12-H12A	108.1	H24A-O24-H24B	103.9
N11-N12-H12B	108.4		
H12A-N12-H12B	97.4		
N11-N12-H12C	115.5		
H12A-N12-H12C	113.9		
H12B-N12-H12C	111.9		

Table S4 Hydrogen bonds present in EM-1 and EM-2

EM-1

D-H···A	d (D-H)/Å	d (H···A)/Å	d (D-H···A)/Å	∠(D-H···A)/°
N5-H5···O2	0.87	2.08	2.9482(10)	176
N1-H1A···O3	0.95	2.03	2.8625(10)	146
N1-H1A···O4	0.95	2.11	2.8273(9)	131
N1-H1B···O3	0.96	1.88	2.7693(9)	153
N1-H1B···O9	0.96	2.40	2.8131(9)	105
N1-H1C···O7	0.97	2.16	2.9725(10)	140
N2-H2···O2	0.83	2.04	2.8719(10)	174
N3-H3···O6	0.89	2.50	3.0689(10)	122
N3-H3···O1	0.89	2.13	2.9670(10)	156
N4-H4···N6	0.82	2.30	2.6413(9)	105
N4-H4···O6	0.82	2.29	3.0434(10)	153
N6-H6A···O8	0.88	2.50	2.9049(10)	109
N6-H6B···O5	0.90	2.57	3.3065(11)	140
N6-H6B···O8	0.90	2.59	3.3985(11)	150

EM-2

D-H···A	d (D-H)/Å	d (H···A)/Å	d (D-H···A)/Å	∠(D-H···A)/°
N4-H4A···O5	0.89	2.59	3.3919(7)	151
N4-H4A···O1	0.89	2.57	3.2898(7)	138
N4-H4B···O5	0.89	2.45	2.9015(6)	112
N5-H5···O9	0.89	2.05	2.9367(6)	173
N6-H6···N4	0.89	2.23	2.6272(5)	107
N6-H6···O7	0.89	2.26	3.0354(6)	145

N7-H7···O7	0.89	2.50	3.0602(6)	122
N7-H7···O8	0.89	2.13	2.9615(6)	155
N8-H8···O9	0.89	1.99	2.8713(6)	168
N9-H9A···O2	0.89	2.16	2.8228(6)	131
N9-H9A···O3	0.89	2.05	2.8553(6)	149
N9-H9B···O3	0.89	1.94	2.7688(5)	154
N9-H9B···O4	0.89	2.40	2.8078(6)	108
N9-H9C···O6	0.89	2.23	2.9674(6)	140

Section 4. The electrostatic discharge sensitivities of TNT, RDX, HMX and some energetic MOFs

Table S5 The electrostatic discharge sensitivities of some energetic materials

Energetic materials	TNT	RDX	HMX	EM-1	EM-2
EDS (J)	0.57	0.15	0.2	>24.75	> 24.75

Section 5. Crystal density in 298 K.

The densities of EM-1 and EM-2 in 298 K was calculated using the reported method.[1] The density value was calculated by the volume expansion equation $\rho_{298K} = \rho_T / (1 + \alpha_v (298 - T))$; $\alpha_v = 1.5 \times 10^{-4}$ K^{-1}. The densities of EM-1 and EM-2 are 1.78 and 1.68 g cm^{-3}, respectively.

Section 6. The calculation method of formation enthalpy

This property of EMs can be calculated with good accuracy by quantum chemical calculations.[2] We performed the calculation by using the program package Gaussian 03.[3] The geometric optimization of the structures and frequency analyses were carried out using the B3LYP functional with a 6-31+G** basis set, and the single-point energies were calculated at the MP2/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. The remaining task is to determine the heats of formation of anions and cations, which are computed by using the isodesmic reaction method.

On the basis of Born–Haber energy cycles (Fig. S1), the enthalpy of formation (ΔH_f^o) for each salt can be simplified by equations (S1).

$$\Delta H_f^o \text{ (ionic salt, 289 K)} = \Delta H_f^o \text{ (cation, 289 K)} + \Delta H_f^o \text{ (anion, 289 K)} - \Delta H_L \quad \text{(S1)}$$

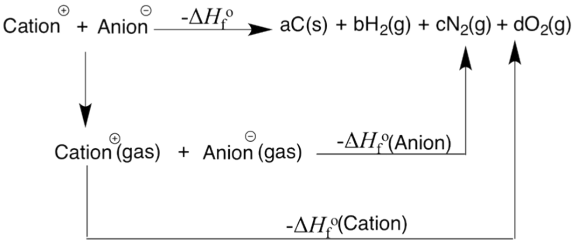

Fig. S1 Born–Haber cycle for the formation of energetic salts.

The lattice energy of the salt (ΔH_L) can be predicted by using equations (S2) provided by Jenkins et al.[4] In the equation, n_M and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

$$\Delta H_L = U_{POT} + [p(n_M / 2 - 2) + q(n_X / 2 - 2)]RT \quad \text{(S2)}$$

The equation for lattice potential energy U_{POT} can be calculated according to equations (S3), in which ρ_m is the density and M_m (g) is the chemical formula mass of the ionic salt, and the coefficients g/kJ mol^{-1} cm and d/kJ mol^{-1} are taken from literature.

$$U_{POT} \text{ (kJ mol}^{-1}) = \gamma (\rho_m / M_m)^{1/3} + \delta \quad \text{(S3)}$$

Table S6 Enthalpy of formation for compounds

Compound	E_0 (a.u.)	ZPE (KJ/mol)	H_T (KJ/mol)	HOF (KJ/mol)
$BHCH^+$	-557.2920123	0.155757	0.0166(7)	643.2
$BHCH^{2+}$	-557.502540532	0.169105	0.181247	2088.1
PA^-	-915.220474	0.098382	0.01395	-108.5
TNR^-	-989.961548	0.102562	0.01467	-318.6

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