Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

A novel stable high-nitrogen energetic material: 4,4'-azobis(1,2,4-triazole)

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Detailed computational information

1. Optimized structure of compound 4

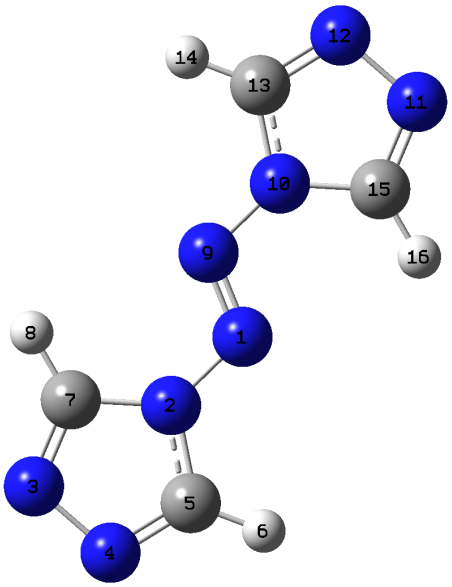

Table S1. Cartesian coordinates of the optimized structure

	X	Y	Z
N	-0.371239	0.503752	0.000125
N	-1.695955	0.162445	0.000579
N	-3.638256	-0.862887	-0.000480
N	-3.867017	0.517889	-0.000143
C	-2.706092	1.103570	0.000169
H	-2.507998	2.165454	0.000469
C	-2.350998	-1.058656	0.000024
H	-1.839530	-2.008248	0.000213
N	0.371200	-0.503871	0.000114
N	1.696002	-0.162685	-0.000309
N	3.638180	0.863039	-0.000104
N	3.867063	-0.517714	0.000194
C	2.706102	-1.103530	0.000066
H	2.508375	-2.165509	0.000134
C	2.351005	1.058694	-0.000264
H	1.839202	2.008070	-0.000625

Table S2. Calculated total energy (E_0), zero-point energy (ZPE), thermal correction (H_T), and enthalpy of formation (HOF) of compound 4 and reference compounds.

Compd.	E_0/a.u.	ZPE/(kJ•mol^{-1})	H_T/(kJ•mol^{-1})	HOF/(kJ•mol^{-1})
4	-592.837151	277.46	26.07	861.38[a]
5	-592.745518	285.18	25.52	679.38
4H-1,2,4-Triazole	-242.309585	154.17	12.08	219.8[b]
N_2H_2	-110.669030	72.19	9.99	211.9[c]
H_2	-1.179572	26.43	8.68	-4.6[b]

[a] The value of solid phase is 878 kJ•mol^{-1}. [b] L.A. Curtiss, K. Raghavanchari, P.C. Redfern, J.A. Pople, J. Chem. Phys. 106 (1997) 1063-1079. [c] L.V. Gurvich, I.V. Veyts, C.B. Alcock, Thermodynamic properties of individual substances[M], Hemisphere Pub. Co., New York, 1989.

2. Detonation performances

Detonation performances of the related compound here were calculated using Kamlet-Jacbos (K-J) equations，

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1+1.30\rho_0)$$

$$P = 1.558\rho^2NM^{1/2}Q^{1/2}$$

where D represents detonation velocity (km•s^{-1}), P is detonation pressure (GPa); N, moles of detonation gases per gram of explosive; M, average molecular weight of these gases; Q, chemical energy of detonation (kJ•g^{-1}); ρ_0, density of explosive (g•cm^{-3}).

Table S3 shows the methods for calculating parameters of the explosive in CaHbOcNd form. All the N atom is converted into N_2, the O atom is considered to form H_2O first and then to be CO_2 with C atom. The remaining C atom will exist in solid state. If there is any O atom left, they will form O_2.

Consequently, the related parameters of 4 and 5 are obtained by the expressions in the third column, since the molecular formula of 4 and 5 is $C_4H_4N_8$, which meets the requirements of the third column in Table S3.

Table S3. Methods for parameters calculation in K-J equations.

	c≥2a+b/2	2a+b/2>c≥b/2	b/2>c
N	(b+2c+2d)/4M’	(b+2c+2d)/4M’	(b+d)/2M’

M	4M'/(b+2c+2d)	(56d+88c−8b)/(b+2c+2d)	(2b+28d+32c)/(b + d)
$Q*10^{-3}$	(28.9b + 94.05a + 0.239□$H°_f$)/M'	[28.9b + 94.05(c/2 − b/4) + 0.239□$H°_f$]/M'	(57.8c + 0.239□$H°_f$)/M'

M' is the molecular weight of the explosive; □$H°_f$ is the heat of formation of the explosive.

Sensitivity

The impact sensitivity was tested on a type 12 tooling according to "up and down" method. A 2.5 kg weight was dropped from a set height onto a 20 mg sample placed on 150 grit garnet sandpaper. An initial height was made by experiences of the testers based on the structure of the tested compound; several trials at different heights, like 40cm, 60cm, 50cm, 55cm, 57cm, were done, and the initial height was set at 55 cm finally since explosion occurred when the height is 57cm, while it did not happen at 55cm. After that, each subsequent test was made at the next lower height if explosion occurred and at the next higher height if no explosion happened. The test height was spaced at log 0.1 intervals. 50 drops were made from different heights based on the method mentioned above, and an explosion or non-explosion was recorded. The H_{50} of 4 is 55.9 cm (14.0 J), while the test result of RDX is 29.7 cm (7.4 J).

Test conditions: 18°C (temperature); 30% (relative humidity).

20 mg sample was placed on a Козπов apparatus. 25 tests were done. An explosion or non-explosion was recorded. RDX was considered as a reference compound, and the friction sensitivity of RDX is 76%. The friction sensitivity of 4 is 92%.

Test conditions: 18°C (temperature); 30% (relative humidity); 90° (swing angle); 474.6MPa (test pressure).

When electrostatic sensitivity was considered, 25 mg sample was placed on a JGY-50(II) Electrostatic test apparatus, while the high voltage was supplied by an EST806F Electrostatic Power Generator. The voltage was increased gradually from 1kV to 45kV. No explosion occurred. Therefore, 25 trials were done when the voltage was 45kV. 4 shows no sensitivity to the voltage of 45kV, which is the limit range of the apparatus.

Test conditions: 28°C (temperature); 36% (relative humidity); Capacitance: 10000PF; Series resistance: 100kΩ.

Spectrometric data

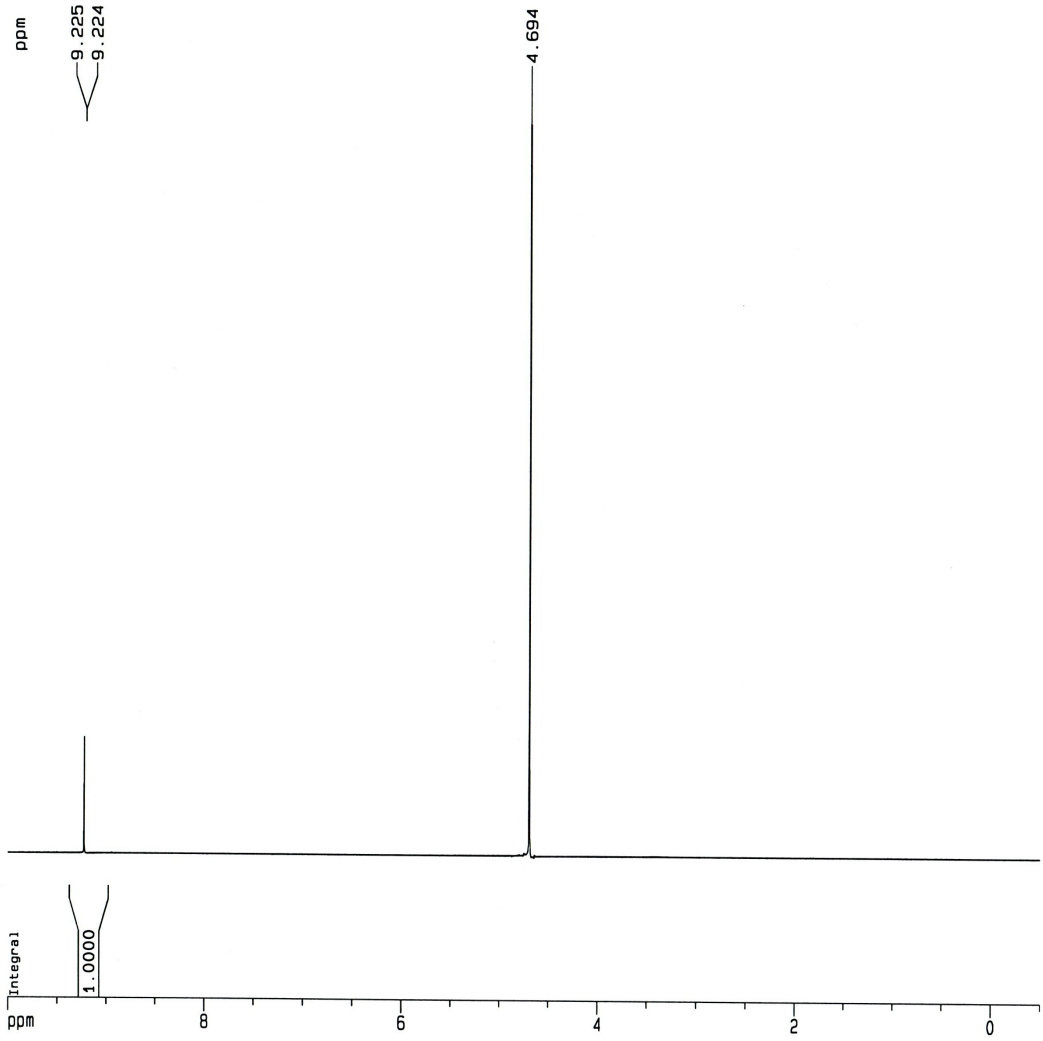

Figure S1. ^{1}H NMR spectrum, 400 MHz, D_2O

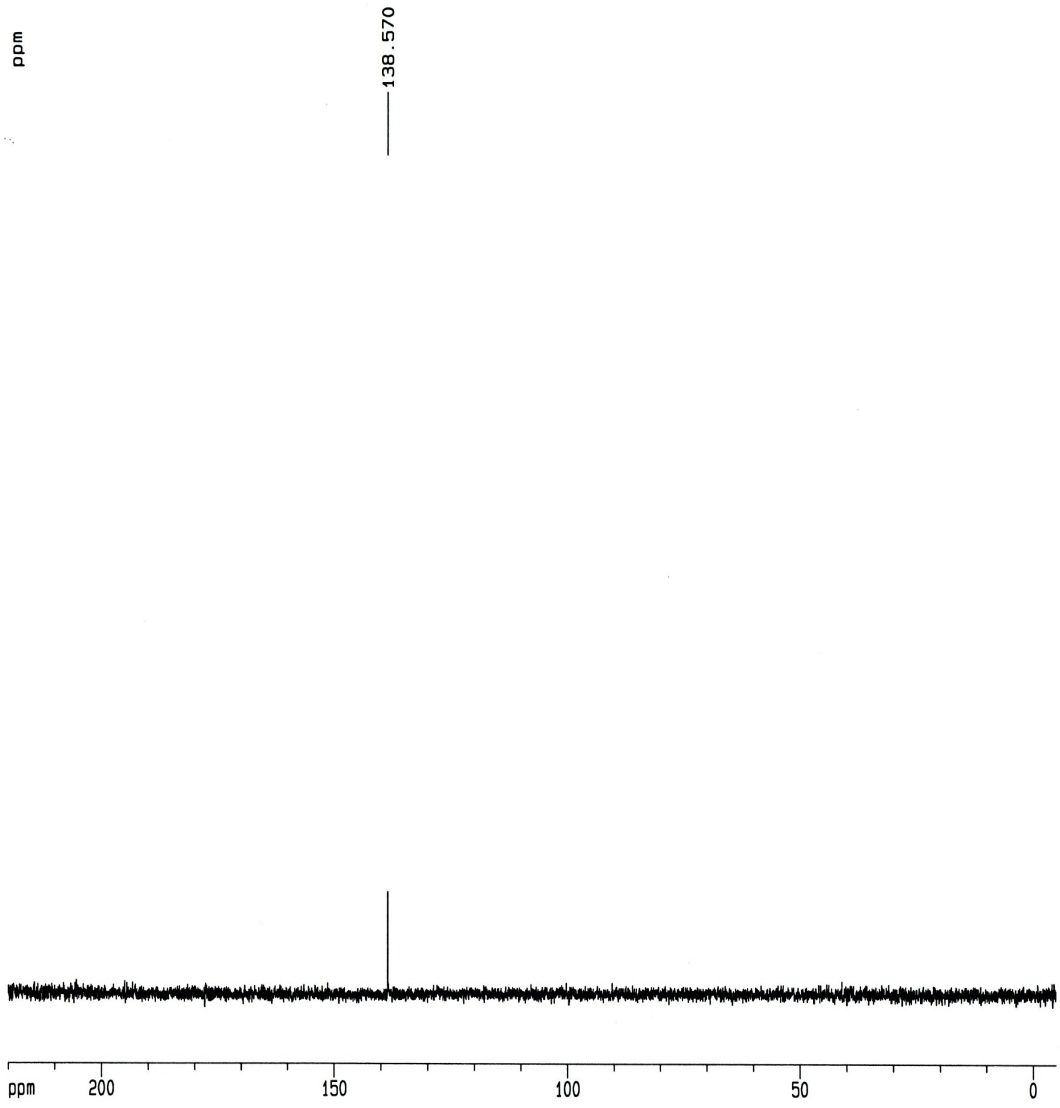

Figure S2. ^{13}C NMR spectrum, 100 MHz, D_2O

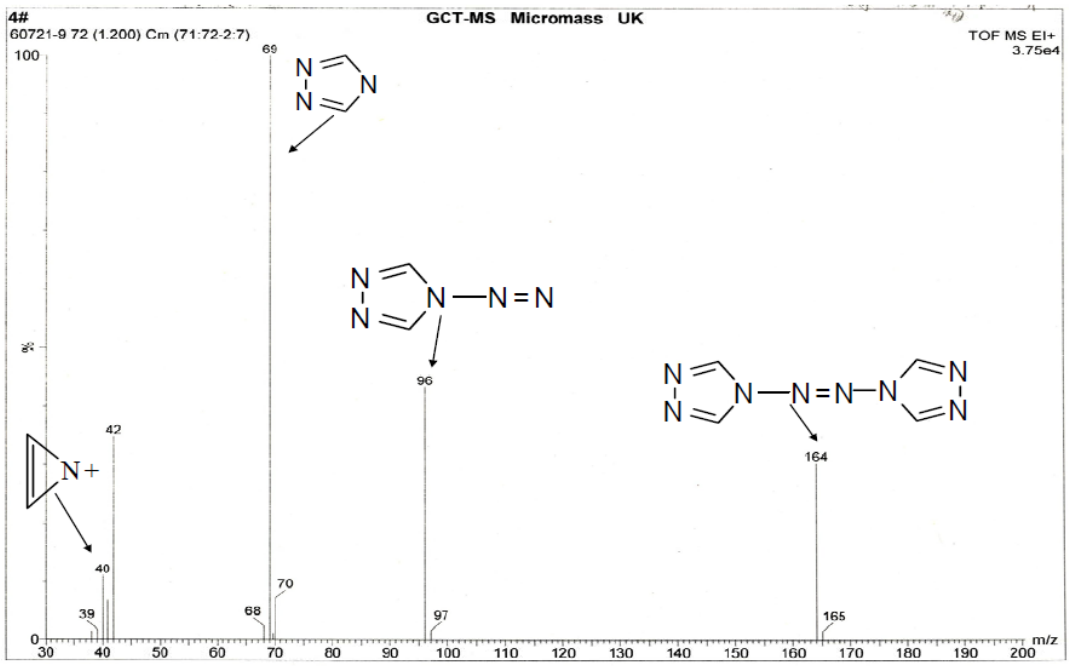

Figure S3. EI-MS spectrum

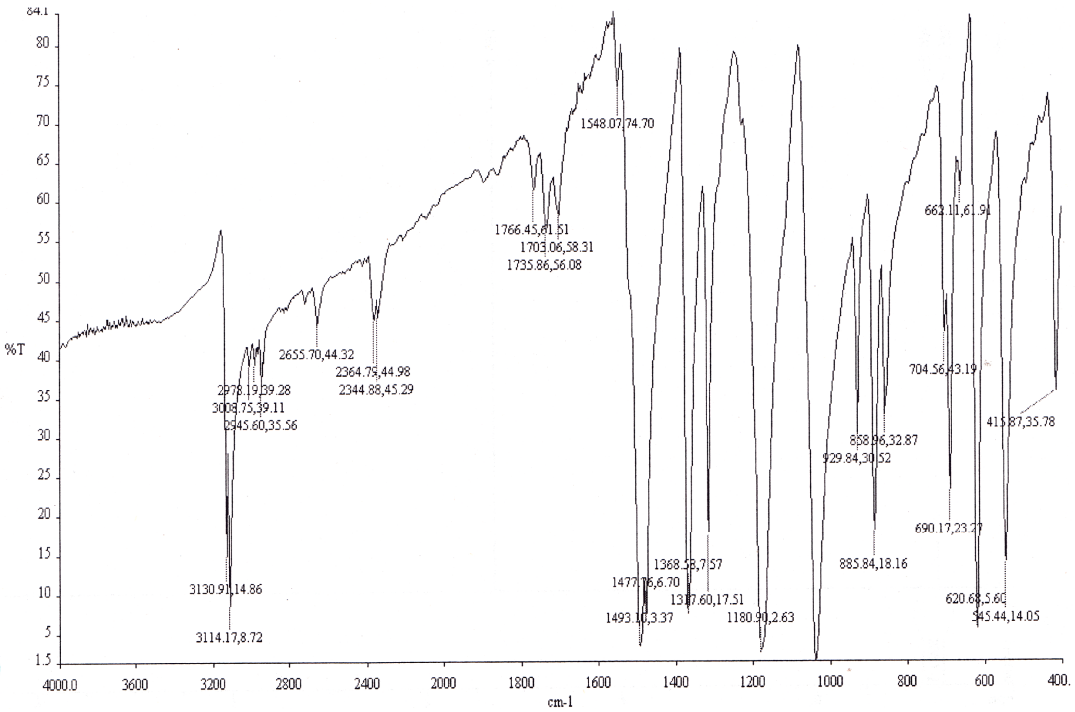

Figure S4. IR spectrum