Electronic Supplementary Information

Synthesis of 1-(2H-tetrazol-5-yl)-5-nitraminotetrazole and its derivatives from 5-aminotetrazole and cyanogen azide: a promising strategy towards development of C-N linked bistetrazolate energetic materials

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Table S1 Crystallographic data and refinement parameters

	1	**3**·H_2O	**4**·H_2O
Empirical formula	$C_2H_2KN_9$	$C_2H_3KN_{10}O_3$	$C_2H_7N_{11}O_3$
Formula weight	191.23	254.24	233.19
Temperature/K	170	170	170
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	7.767(3)	6.3241(9)	6.663(9)
b/Å	11.993(4)	18.197(3)	16.418(17)
c/Å	7.360(3)	7.7647(11)	16.589(17)
α/°	90	90	90
β/°	101.904(14)	95.544(4)	99.96(3)
γ/°	90	90	90
Volume/Å^3	670.8(4)	889.4(2)	1787(3)
Z	4	4	8
ρ_{calc}g/cm^3	1.893	1.899	1.733
μ/mm^{-1}	0.746	0.615	0.152
F(000)	384	512	960
Crystal size/mm^3	0.24 × 0.2 × 0.18	0.24 × 0.2 × 0.18	0.25 × 0.12 × 0.05
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.36 to 54.994	4.476 to 54.816	3.516 to 50.692
Index ranges	-10 ⩽ h ⩽ 10, -15 ⩽ k ⩽ 15, -9 ⩽ l ⩽ 9	-10 ⩽ h ⩽ 10, -15 ⩽ k ⩽ 15, -9 ⩽ l ⩽ 9	-8 ⩽ h ⩽ 5, -19 ⩽ k ⩽ 19, -19 ⩽ l ⩽ 18
Reflections collected	8770	2022	9118
Independent reflections	1516 [R_{int} = 0.0301, R_{sigma} = 0.0241]	2022 [R_{int} = ?, R_{sigma} = 0.0277]	3160 [R_{int} = 0.0421, R_{sigma} = 0.0485]
Data/restraints /parameters	1516/0/117	2022/0/157	3160/23/325
Goodness-of-fit on F^2	1.061	1.182	1
Final R indexes [I>=2σ (I)]	R_1 = 0.0259, wR_2 = 0.0631	R_1 = 0.0547, wR_2 = 0.1672	R_1 = 0.0545, wR_2 = 0.1613
Final R indexes [all data]	R_1 = 0.0308, wR_2 = 0.0657	R_1 = 0.0660, wR_2 = 0.1818	R_1 = 0.0809, wR_2 = 0.1812
Largest diff. peak/hole / e Å^{-3}	0.25/-0.24	0.89/-1.18	0.31/-0.49
CCDC	1534355	1534536	1534406

Table S1 (Continued)

	5·2H_2O	**6**·H_2O	**7**·2H_2O
Empirical formula	$C_3H_{11}N_{15}O_6$	$C_2H_{10}N_{12}O_5$	$C_2H_{14}N_{14}O_4$
Formula weight	353.27	282.22	298.27
Temperature/K	293	170	170
Crystal system	triclinic	triclinic	monoclinic
Space group	P-1	P-1	$P2_1$
a/Å	6.6274(11)	7.7628(8)	3.6735(6)
b/Å	9.3787(14)	8.4720(9)	20.633(4)
c/Å	11.2469(18)	8.6864(9)	7.9016(13)
α/°	102.272(3)	96.566(2)	90
β/°	91.229(3)	99.093(2)	92.690(4)
γ/°	105.997(3)	107.015(2)	90
Volume/Å^3	654.25(18)	531.54(10)	598.23(17)
Z	2	2	2
ρ_{calc}g/cm^3	1.793	1.763	1.656
μ/mm^{-1}	0.162	0.161	0.146
F(000)	364	292	312
Crystal size/mm^3	0.24 × 0.22 × 0.2	0.24 × 0.22 × 0.2	0.24 × 0.22 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.72 to 55.682	4.82 to 54.858	3.948 to 54.934
Index ranges	-8 ≤ h ≤ 8, -12 ≤ k ≤ 12, -14 ≤ l ≤ 12	-9 ≤ h ≤ 10, -10 ≤ k ≤ 10, -10 ≤ l ≤ 11	-4 ≤ h ≤ 4, -26 ≤ k ≤ 26, -10 ≤ l ≤ 10
Reflections collected	5908	5493	10026
Independent reflections	2983 [R_{int} = 0.0215, R_{sigma} = 0.0389]	2363 [R_{int} = 0.0213, R_{sigma} = 0.0304]	2724 [R_{int} = 0.0323, R_{sigma} = 0.0292]
Data/restraints /parameters	2983/0/261	2363/0/199	2724/1/238
Goodness-of-fit on F^2	1.031	1.085	1.105
Final R indexes [I>=2σ (I)]	R_1 = 0.0641, wR_2 = 0.1743	R_1 = 0.0363, wR_2 = 0.1031	R_1 = 0.0282, wR_2 = 0.0668
Final R indexes [all data]	R_1 = 0.0790, wR_2 = 0.1898	R_1 = 0.0410, wR_2 = 0.1108	R_1 = 0.0292, wR_2 = 0.0674
Largest diff. peak/hole / e Å^{-3}	0.51/-0.40	0.21/-0.35	0.18/-0.26
CCDC	1534410	1534412	1534411

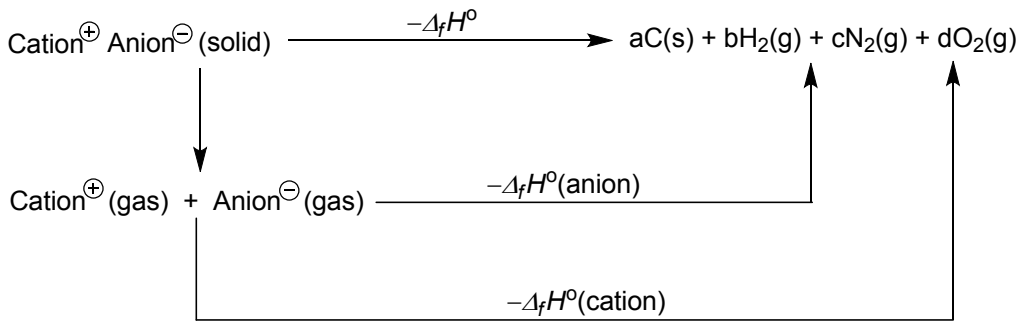
Computational methods for heats of formation

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs.[1] The geometric optimization and frequency analyses were conducted by using the B3LYP functional with the 6-31+G** basis set. Single energy points were calculated at the MP2/6-311++G** level of theory. For all of the compounds, the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. Three explicit appliacations of isodesmic reactions were carried out to obtain the gas-phase heats of formation of the neutral compounds and the anion. The gas-phase enthalpies of the building-block molecules were obtained by using the atomization method with the G2 ab initio calculations. Then the remaining task is to determine the solid-state heats of formation for the synthesized compounds.

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. On the basis of the literature,[2] the heat of sublimation can be estimated with Trouton's rule according to eq 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

$$\Delta H_{sub} = 188/\text{J mol}^{-1}\text{K}^{-1} \times \text{T} \qquad (1)$$

For energetic salts, the heats of formation (HOF, $\Delta_f H°$) were calculated based on a Born–Haber energy cycle (Scheme S1).



Scheme S1 Born–Haber cycle for the formation of ionic salts.

For all the ionic salts, calculation of the HOFs was simplified by using Equation (2).

$$\Delta_f H°\text{ (ionic salts, 298K)} = \Sigma\Delta_f H°\text{(cation, 298K)} + \Sigma\Delta_f H°\text{(anion, 298K)} - \Delta H_L \qquad (2)$$

In eq 2, ΔH_L is the lattice energy of the ionic salts, which could be predicted by using the equation (3) suggested by by Jenkins et al.[3]

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_x/2\text{-}2)]RT \qquad (3)$$

In this equation, n_M and n_X depended on the nature of ions Mp^+ and Xq^-, respectively, and are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

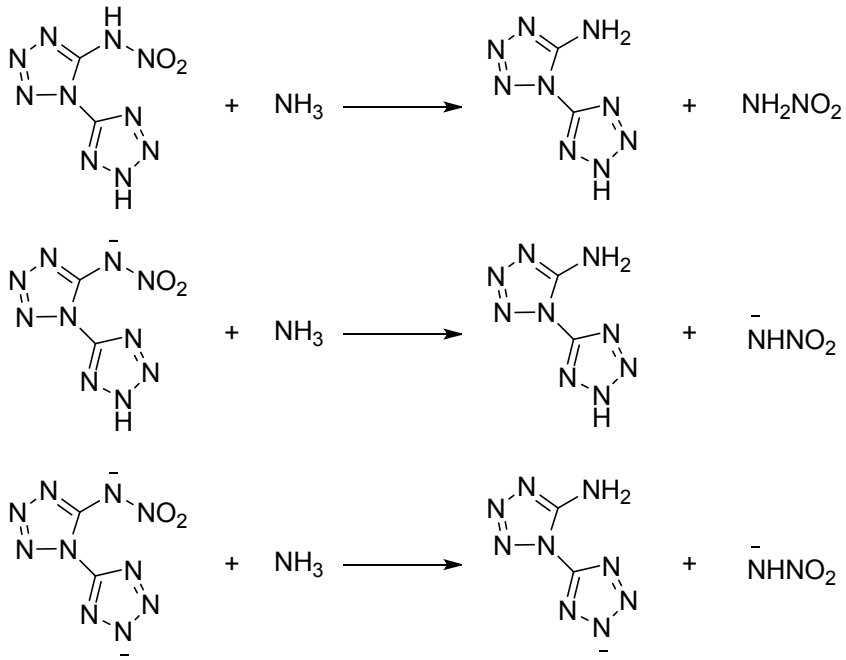
The lattice-potential energy (U_{POT}) was calculated according to Equation (4), in which ρ_m is the density (in g/cm^3) and M_m is the chemical formula mass of the ionic material; the coefficients γ and δ were taken from the literature.[3]

$$U_{POT}\text{ (kJ/mol)} = \gamma\,(\rho_m/M_m)^{1/3} - \delta \qquad (4)$$

$$\Delta_f H°(C^+, g) = \Delta_f H°(C, g) + IE_C \qquad (5)$$

$$\Delta_f H°(A^-, g) = \Delta_f H°(A, g) + EA_A \qquad (6)$$

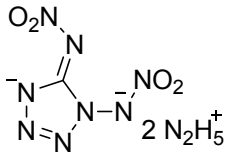
The heats of formation (HOFs) of the ionic salts were obtained by computing the component cations and anions. Specifically, the computation of HOFs for both cations and anions was performed according to literature methods, that is, the gas-phase HOFs of the ions were determined by using Equations (5) and (6) (IE=ionization energy; EA=electron affinity). In Equations (5) and (6), additional calculations for the corresponding neutral molecules ($\Delta_f H°$(C, g) and $\Delta_f H°$(A, g) were performed for the atomization reaction $C_aH_bN_cO_d \rightarrow aC(g) + bH(g) + cN(g) + dO(g)$ by using G2 theory. Based on the results from Equation (5) and (6), the HOFs of the cations and anion were obtained.



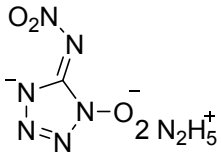
Scheme S2 Isodesmic reactions

Table S2 Comparison of density, heat of formation, detonation velocity of characteristic hydrazinium nitriminotetrazole and bitetrazol compounds

Nitriminotetrazole Compounds:



2-1



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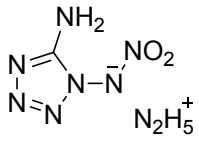

2-3

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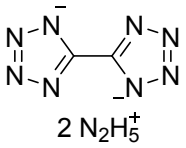

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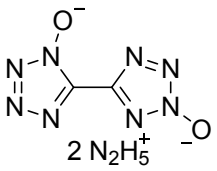


3-2

3-3

	7 in this work	**2-1**[4]	**2-2**[5]	**2-3**[6]	**3-1**[7]	**3-2**[8]	**3-3**[9]
d [g cm^{-3}]	1.70	1.75	1.67	1.68	1.53	1.70	1.73
N [%]	74.79	66.13	66.65	71.17	83.13	71.77	71.77
$\Delta_f H$ [kJ mol^{-1}	852.85	541.3	491.8	516	668.1	591.1	677.7
/kJ g^{-1}]	/3.25	/2.13	/2.34	/2.91	/3.30	/2.52	/2.89
EXPLO5	v6.02	v6.02	v6.03	v5.04	v5.04	v6.01	v5.05
vD [m s^{-1}]	9822	9872	9842	9102	8265	9123	9159

Notes and references

1 M. J. Frisch et al., *Gaussian 09, Revision D. 01*, Gaussian Inc., Wallingford CT, 2009.

2 (a) F. Trouton, *Philos. Mag.*, 1884, **18**, 54; (b) M. S. Westwell, M. S. Searle, D. J. Wales and D. H. Wiliams, *J. Am. Chem. Soc.*, 1995, **117**, 5013.

3 H. D. B. Jenkins, D. Tudela and L. Glasser, *Inorg. Chem.*, 2002, **41**, 2364.

4 D. Fischer, T. M. Klapötke and J. Stierstorfer, *Angew. Chem. Int. Ed.*, 2015, **54**, 10299.

5 D. Fischer, T. M. Klapötke and J. Stierstorfer, *Eur. J. Inorg. Chem.*, 2015, 4628.

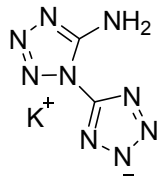
6 T. M. Klapötke, F. A. Martin and J. Stierstorfer, *Chem. Eur. J.*, 2012, **18**, 1487.

7 N. Fischer, D. Izsák, T. M. Klapötke, S. Rappenglück and J. Stierstorfer, *Chem. Eur. J.*, 2012, **18**, 4051.

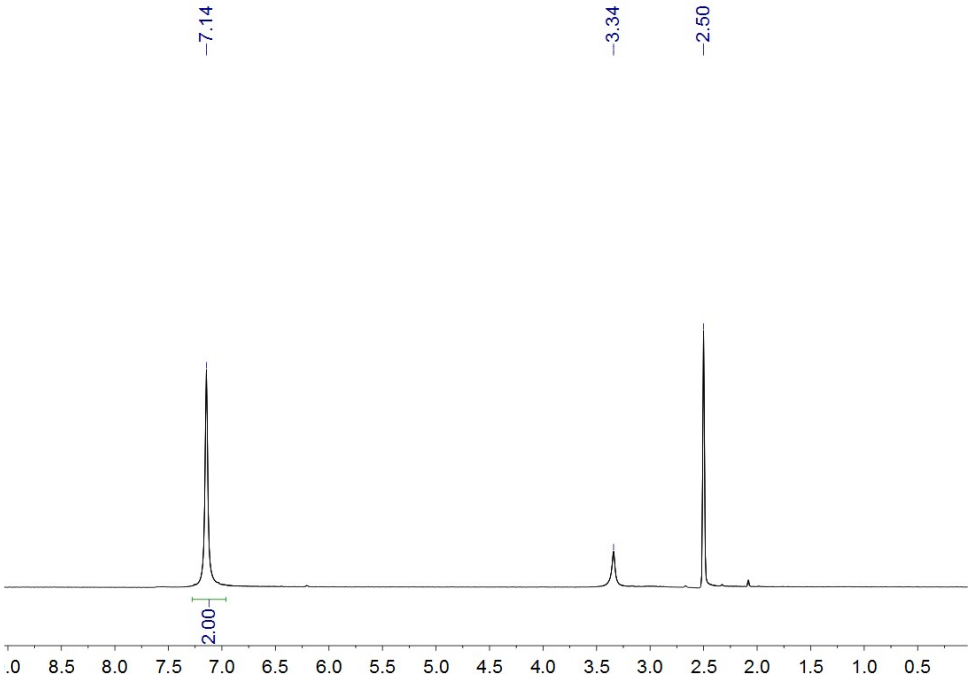
8 K. Hafner, T. M. Klapötke, P. C. Schmid and J. Stierstorfer, *Eur. J. Inorg. Chem.*, 2015, 2794.

9 N. Fischer, T. M. Klapötke, M. Reymann and J. Stierstorfer, *Eur. J. Inorg. Chem.*, 2013, 2167.

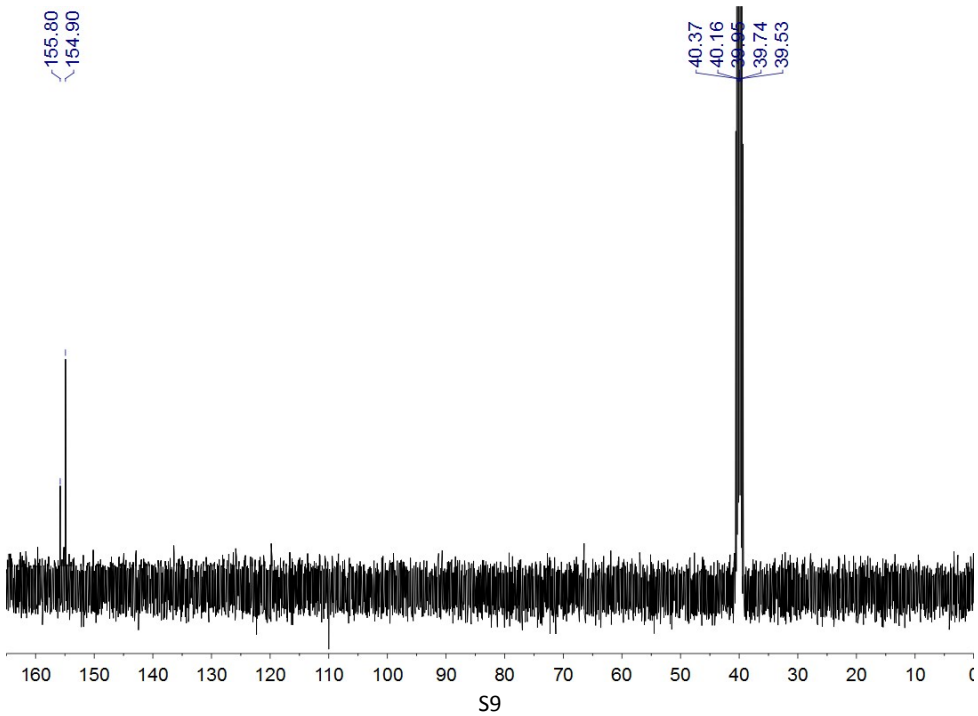
Potassium 2'H-[1,5'-bitetrazol]-5-amine (1)



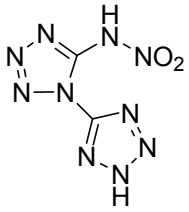
^{1}H NMR, DMSO-d$_6$



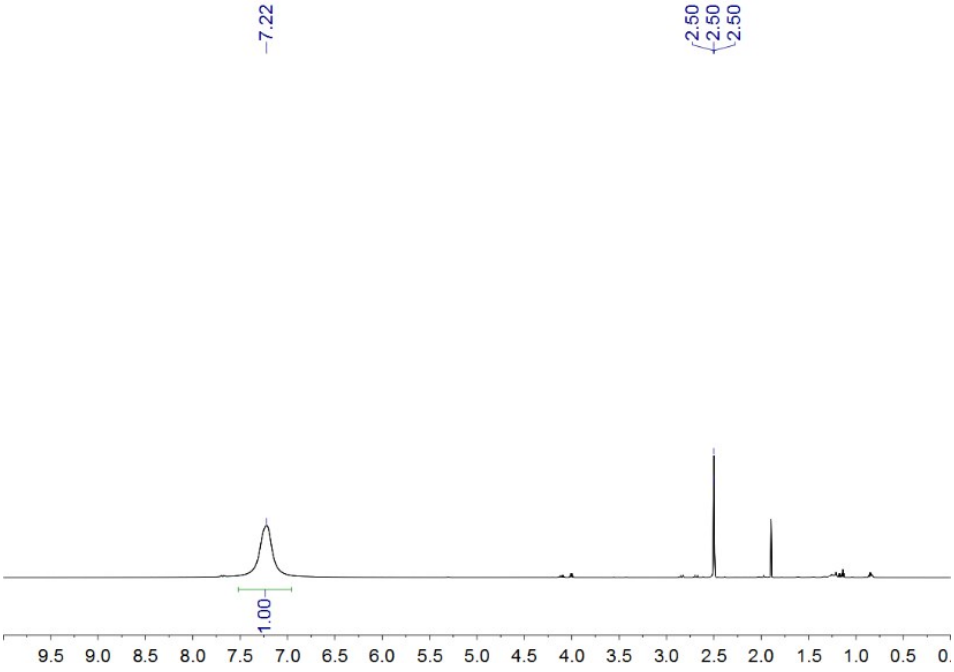
^{13}C NMR, DMSO-d$_6$



1-(2H-Tetrazol-5-yl)-5-nitraminotetrazole (2)



^{1}H NMR, DMSO-d_6



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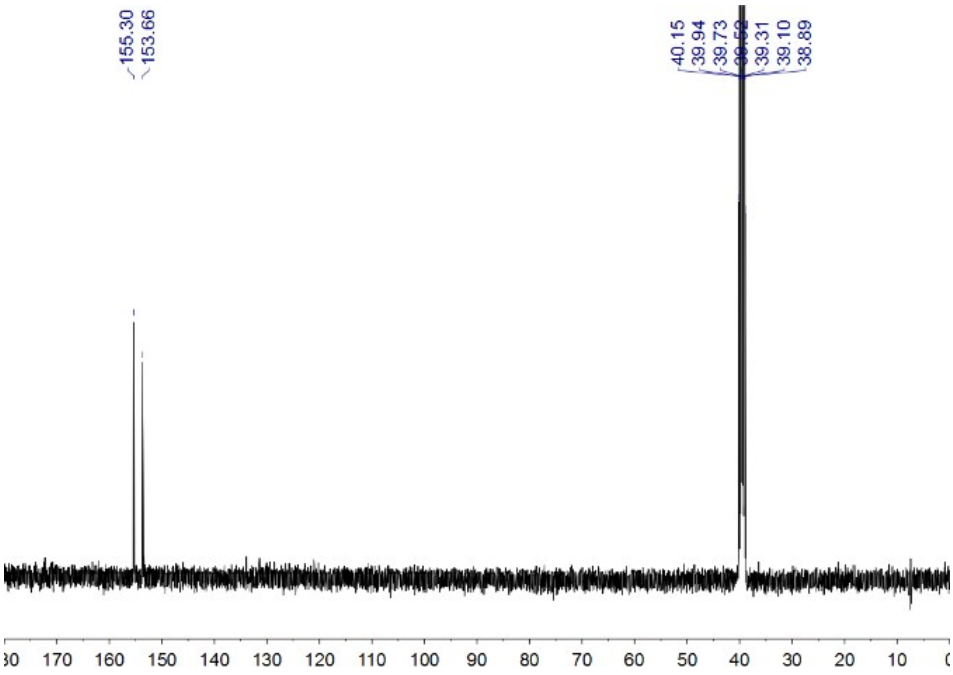
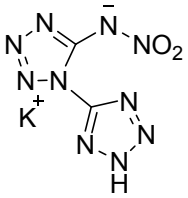
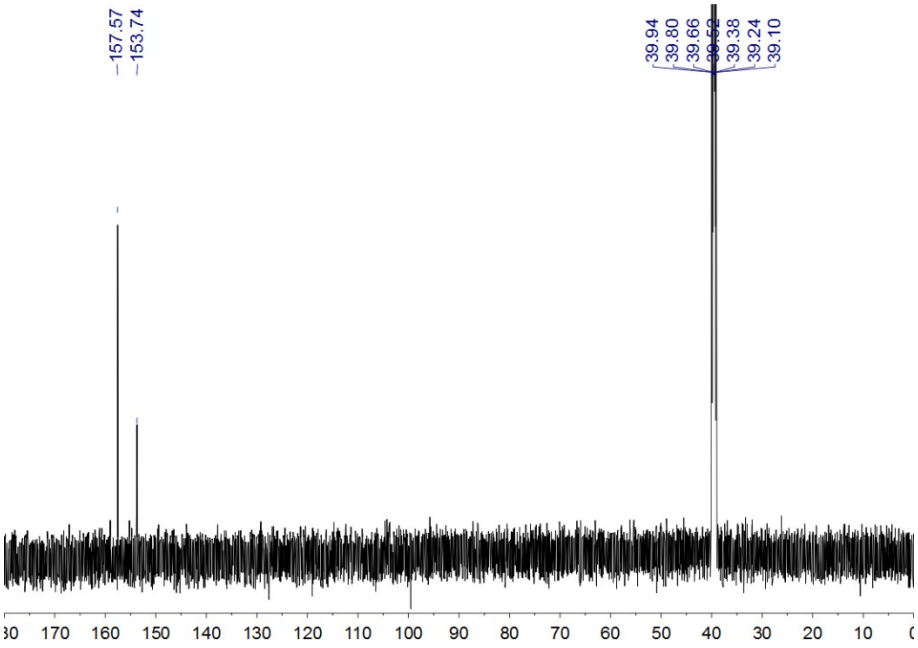


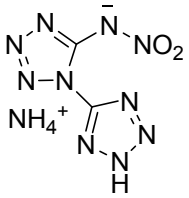
Potassium 1-(2H-tetrazol-5-yl)-5-nitraminotetrazole (3)



^{13}C NMR, DMSO-d_6



Ammonium 1-(2H-tetrazol-5-yl)-5-nitraminotetrazole (4)



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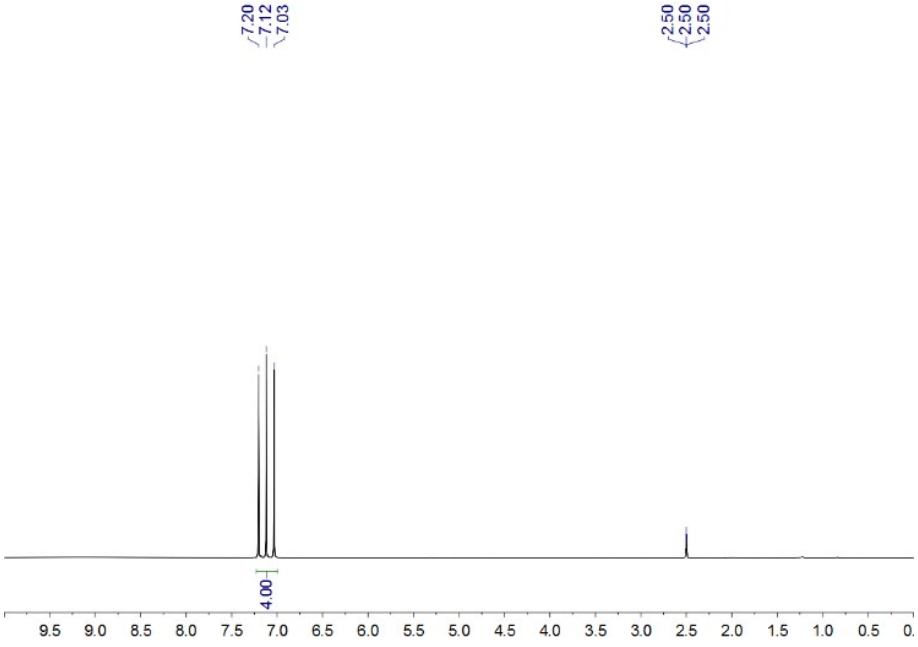

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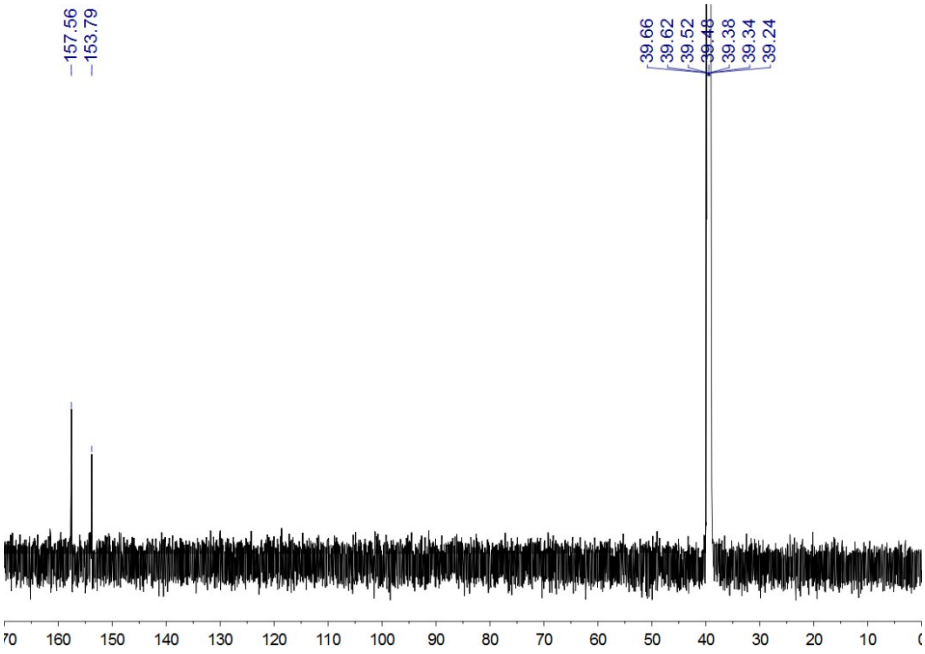
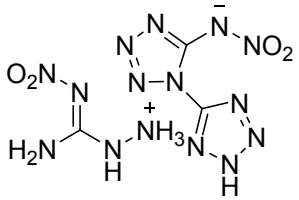


Aminonitroguanidinium 1-(2H-tetrazol-5-yl)-5-nitraminotetrazole (5)



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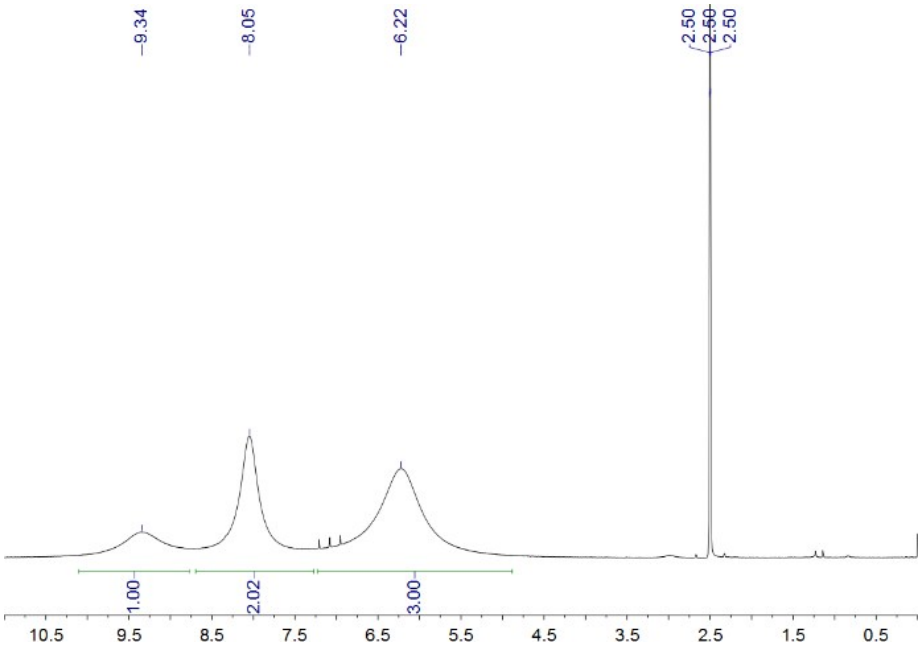

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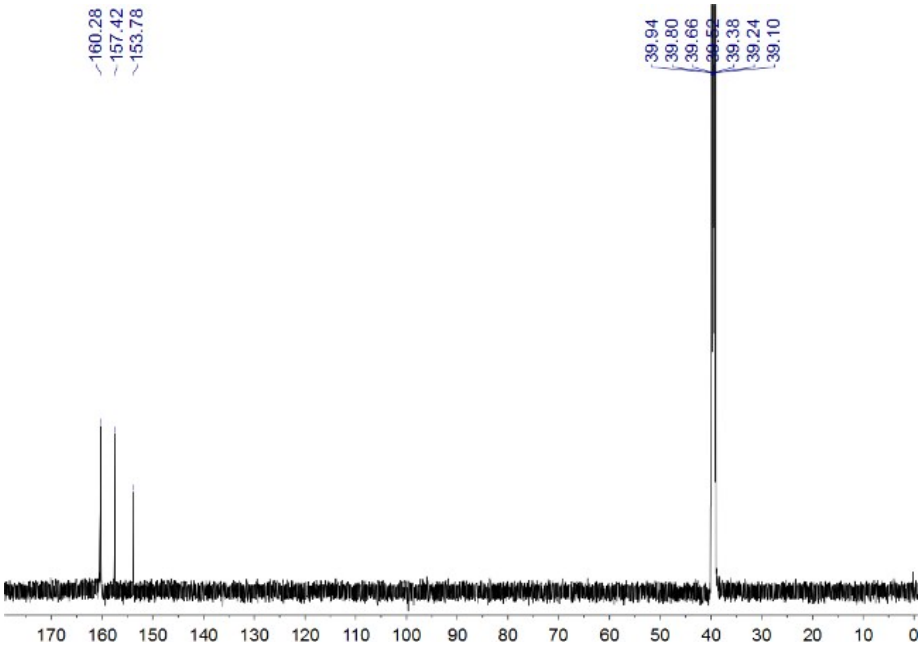
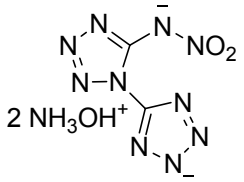


Dihydroxylammonium 1-(2H-tetrazol-5-yl)-5-nitraminotetrazole (6)



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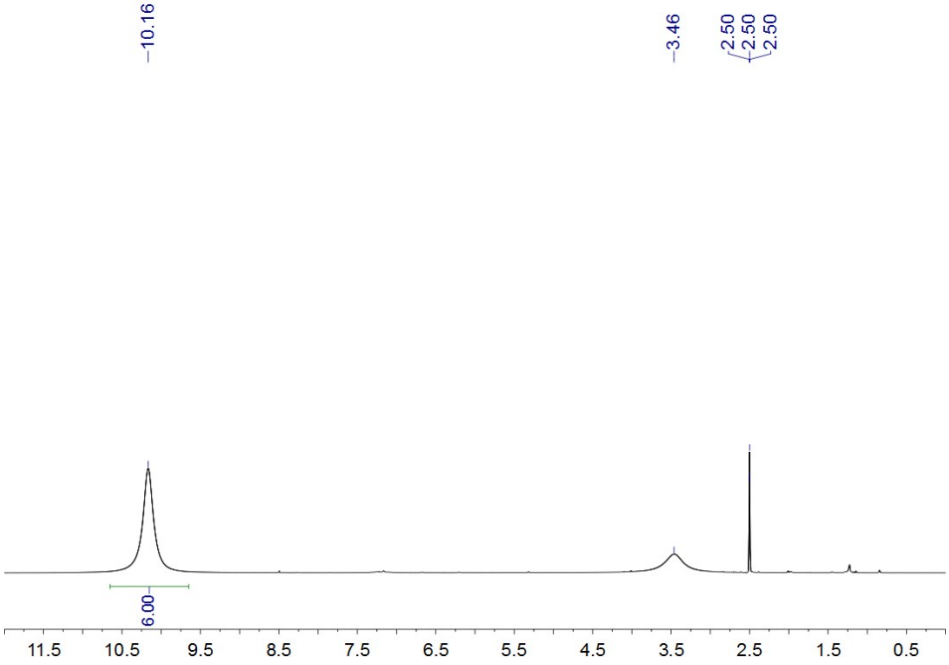

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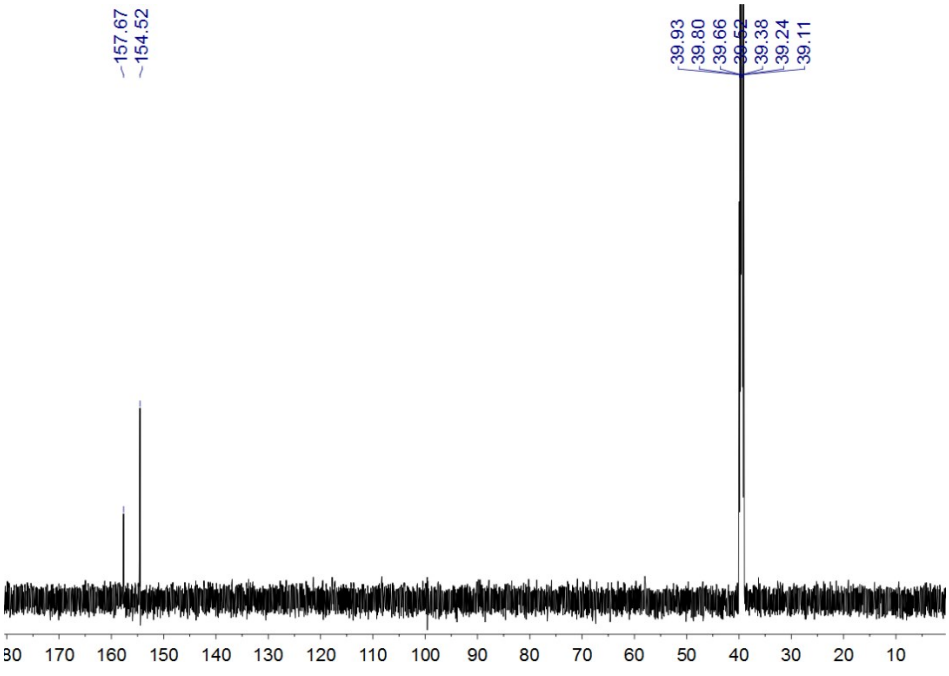
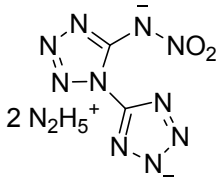


Dihydrazinium 1-(2H-tetrazol-5-yl)-5-nitraminotetrazole (7)



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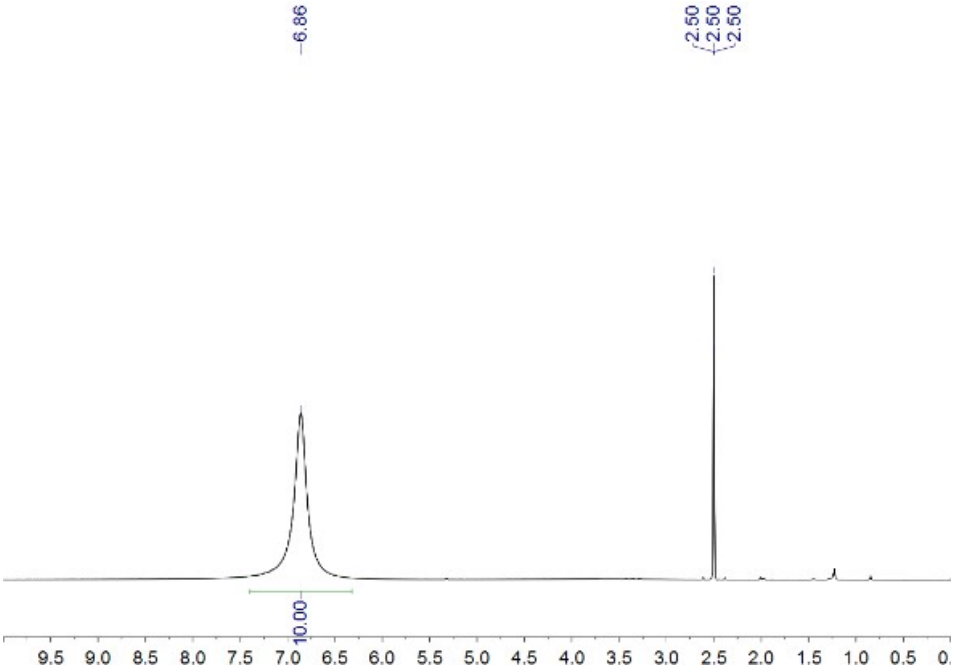

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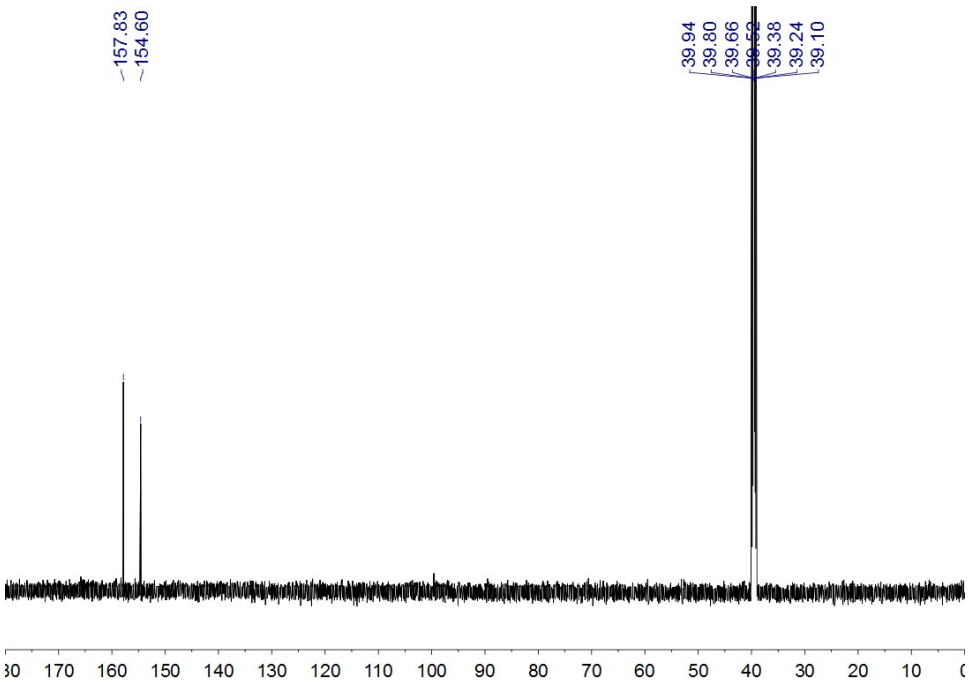
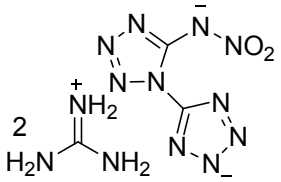


Diguandinium 1-(2H-tetrazol-5-yl)-5-nitraminotetrazole (8)



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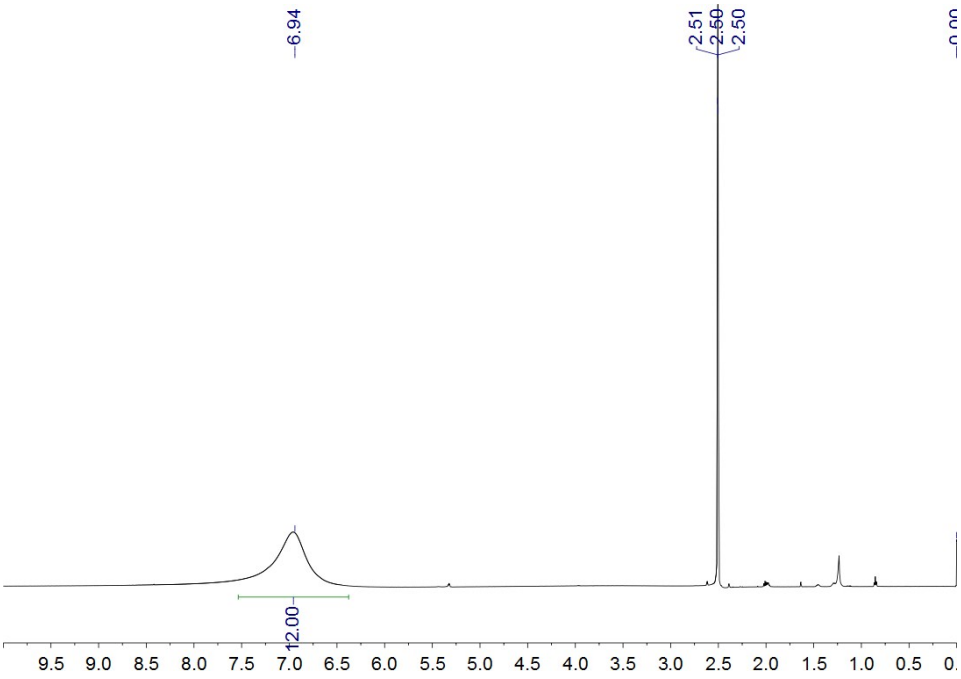

^{13}C NMR, DMSO-d$_6$