Electronic supplementary materials *Mendeleev Commun.*, 2017, **27**, 116–118

Synthesis and structure of 3,4,6-triazidopyridine-2,6-dicarbonitrile possessing the record positive heat of formation

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CONTENT:

I. Instrumentation

TLC analyses were carried out on silica gel 60F254-precoated aluminum sheets with detection by UV light. ^{13}C and ^{15}N NMR spectra were recorded on a Bruker Avance III 500 MHz NMR spectrometer, using TMS (δ_C = 0 ppm) and CD_3NO_2 (δ_N = 0 ppm) as internal standards. IR spectrum was recorded on a Perkin-Elmer Spectrum 100 FT-IR instrument. UV/Vis spectrum was recorded on a Specord M80 UV/Vis spectrometer. Electron impact mass-spectrum (70 eV, direct insertion) was recorded on a Kratos MS-30 mass-spectrometer. Elemental analyses were performed on a CHNS/O Vario Microcube Elemental analyzer.

X-ray data for a single crystal of 3,4,5-triazidopyridine-2,6-dicarbonitrile were collected on a CCD diffractometer Agilent XCalibur with EOS detector (Agilent Technologies UK Ltd, Yarnton, Oxfordshire, England) at 100.0(1) K using graphite-monochromated MoK_α radiation (λ= 0.71073 Å). The structure was solved by direct methods and refined against all F^2 data: SHELXTL [*Sheldrick, G. M. (8/06/2000). SHELXTL v. 6.14, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA*]. All atoms were refined with anisotropic thermal parameters. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1483911) and can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html.

The geometries of the molecules were optimized at B3LYP/6-311+G(d) level of theory. The thermodynamic characteristics of compounds and processes were obtained using isodesmic reaction method in combination with CBS-4M approach [*Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. J. Chem. Phys.* ***2000****, 112, 6532., Goebel, M.; Klapötke, T. M. Adv. Funct. Mater.,* ***2009****, 19, 3, 347-365*]. All calculations were performed with the Gaussian 09 program [*M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr.,*

J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox. Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2013].

The thermal decomposition kinetics of azides and their heat flow properties were recorded by using thermogravimetry (TG) and differential scanning calorimetry (DSC) techniques on a TG-DSC-QMS403C Netzsch STA 409 PC Luxx analyzer (dynamic argon atmosphere under pressure of 0.1 MPa, sample mass of about 3 mg, a heating rate of 5 ºC min^{-1}, temperature range 30–400 ºC).

II. Experimental ^{13}C and ^{15}N NMR spectra of triazide 2

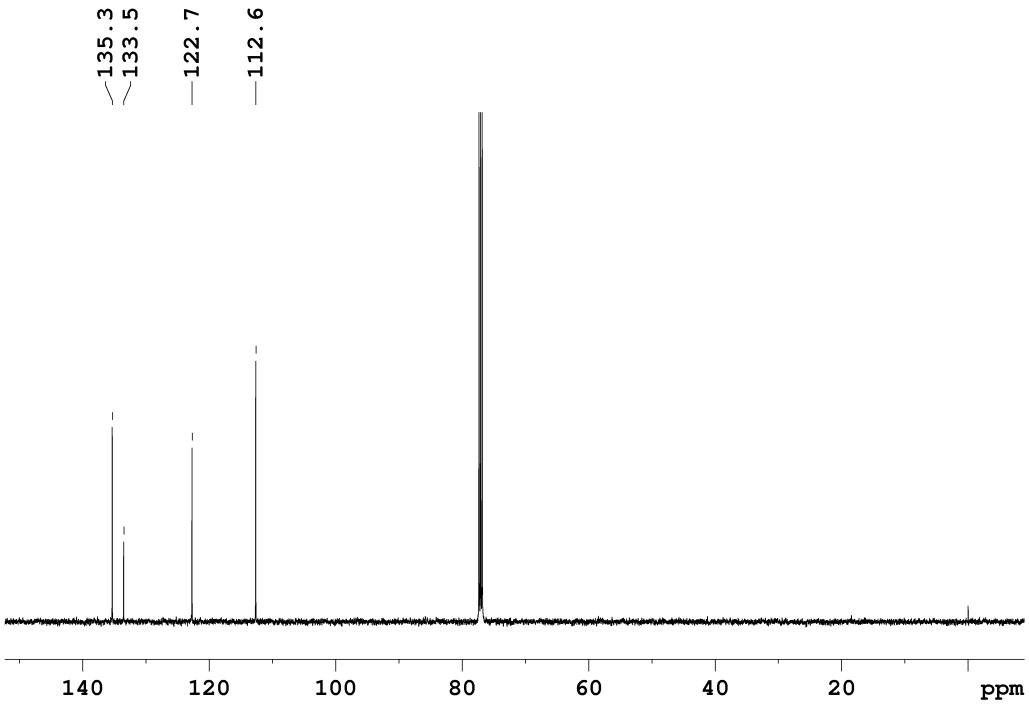


Figure S1 The ^{13}C NMR spectrum of triazide **2** ($CDCl_3$, TMS).

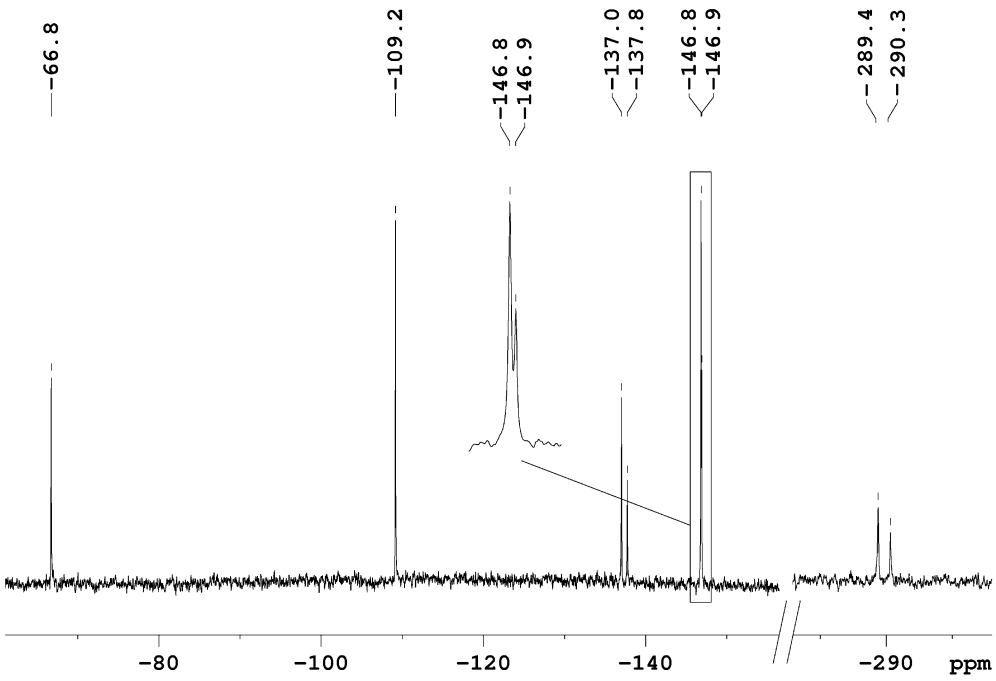
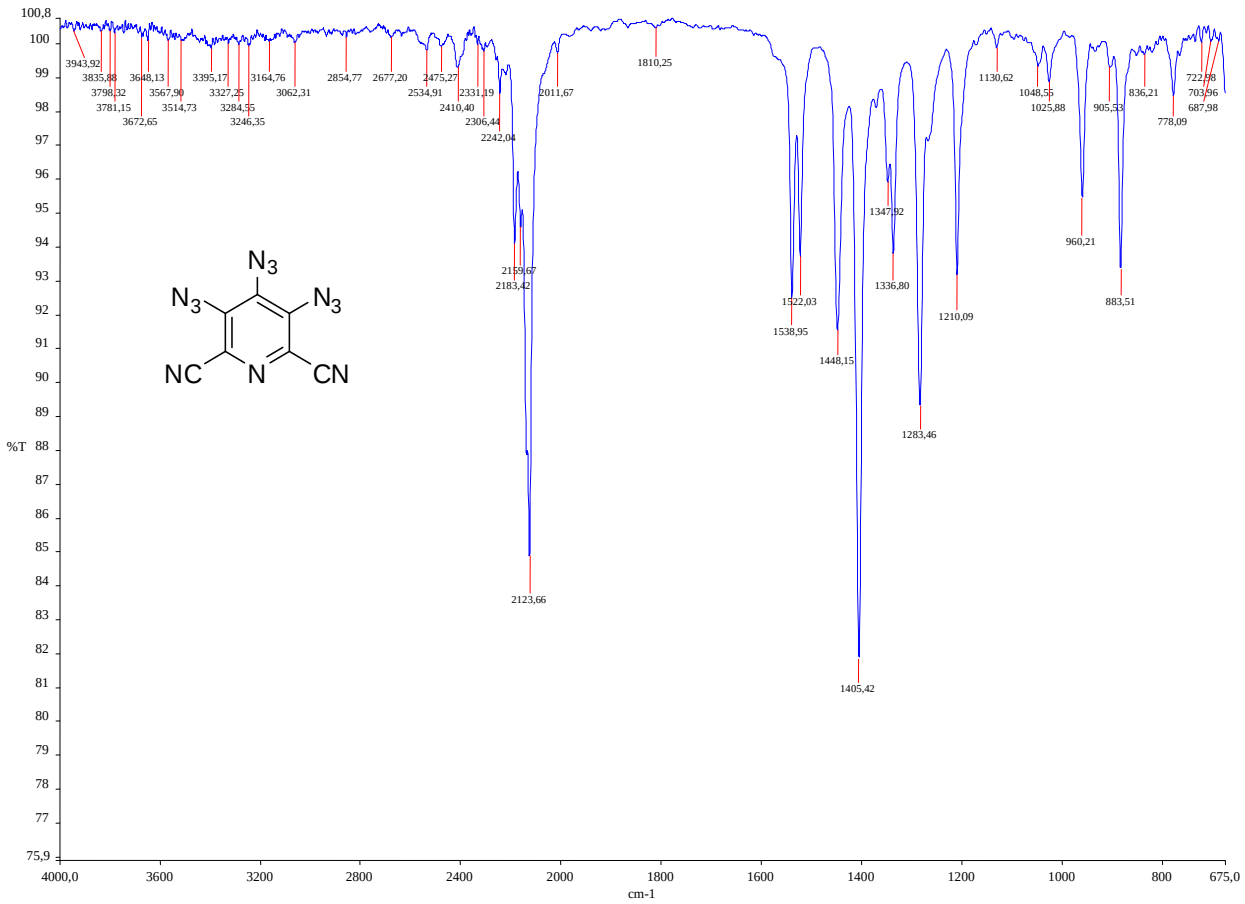
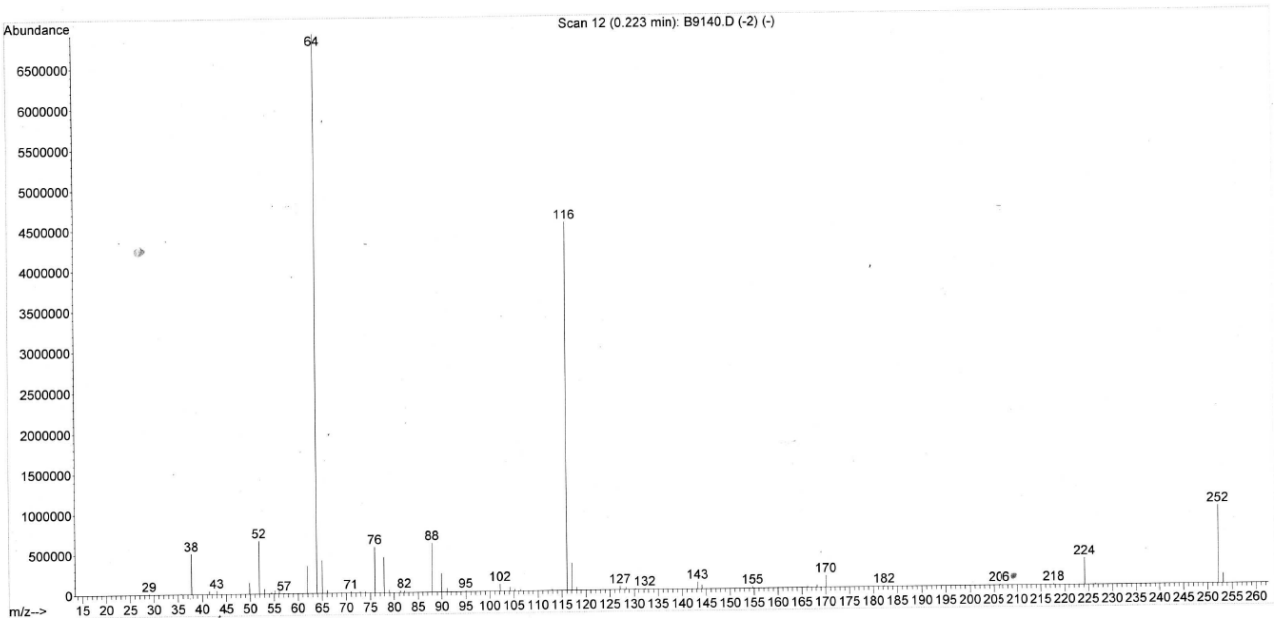


Figure S2 The ^{15}N NMR spectrum of triazide **2** ($CDCl_3$, CD_3NO_2).

III. IR and electron impact mass spectra of triazide 2





IV. Selected crystallographic and geometry parameters of triazide 2

Table S1 Crystal data and structure refinement for compound **2**.

Parameters	Values
Formula (M)	$C_7 N_{12}$ (252.19)
Temperature, K	100.0(2)
Crystal system, space group	orthorhombic, Pca21
Unit cell dimensions	a = 14.7596(11)
	b = 7.0507(5) Å
	c = 9.8837(8) Å
Volume, Å^3	1028.6(1)
Z, density (calculated), g/cm^3	4, 1.629
Absorption coefficient, mm^{-1}	0.123
F(000)	504
Crystal size, mm^3	0.10 x 0.20 x 0.20
θ range for data collection, °	2.76 - 26.99
Index ranges	-18<=h<=16, -9<=k<=8, -10<=l<=12
Reflections collected / unique / I>2σ(I)]	2810 / 1685 [R(int) = 0.029] / 1423
Completeness to θ = 26.99°	0.99
Number of parameters	172
Goodness-of-fit on F^2	1.02
Final R indices [I>2σ(I)]	R_1 = 0.0458, wR_2 = 0.0698
R indices (all data)	R_1 = 0.0614, wR_2 = 0.0761
Largest diff. peak and hole, e·Å^{-3}	0.24 and -0.25

Table S2 Bond lengths (d, Å) in **2**.

Bond	*d, Å*	*Bond*	*d, Å*
N(1)-C(1)	1.335(4)	N(9)-N(10)	1.129(4)
N(1)-C(5)	1.344(4)	N(11)-C(6)	1.142(4)
N(2)-N(3)	1.255(3)	N(12)-C(7)	1.139(4)
N(2)-C(2)	1.404(4)	C(1)-C(2)	1.405(4)
N(3)-N(4)	1.124(4)	C(1)-C(6)	1.455(4)
N(5)-N(6)	1.260(3)	C(2)-C(3)	1.394(4)
N(5)-C(3)	1.401(4)	C(3)-C(4)	1.397(4)
N(6)-N(7)	1.127(3)	C(4)-C(5)	1.406(4)
N(8)-N(9)	1.253(4)	C(5)-C(7)	1.450(4)
N(8)-C(4)	1.407(4)		

Table S3 Bond angles (ω, º) in **2**.

Bond angle	*ω, °.*	*Bond angle*	*ω, °.*
C(1)-N(1)-C(5)	116.4(2)	C(1)-C(2)-C(3)	118.4(3)
N(3)-N(2)-C(2)	119.8(2)	N(5)-C(3)-C(2)	116.2(2)
N(2)-N(3)-N(4)	168.4(3)	N(5)-C(3)-C(4)	125.6(3)
N(6)-N(5)-C(3)	118.4(2)	C(2)-C(3)-C(4)	118.0(2)
N(5)-N(6)-N(7)	170.0(3)	N(8)-C(4)-C(3)	113.6(2)
N(9)-N(8)-C(4)	120.0(2)	N(8)-C(4)-C(5)	127.5(3)
N(8)-N(9)-N(10)	168.7(3)	C(3)-C(4)-C(5)	118.8(3)
N(1)-C(1)-C(2)	124.5(3)	N(1)-C(5)-C(4)	123.7(3)
N(1)-C(1)-C(6)	116.2(2)	N(1)-C(5)-C(7)	114.8(2)
C(2)-C(1)-C(6)	119.2(3)	C(4)-C(5)-C(7)	121.5(3)
N(2)-C(2)-C(1)	114.6(2)	N(11)-C(6)-C(1)	178.0(3)
N(2)-C(2)-C(3)	127.0(2)	N(12)-C(7)-C(5)	178.0(3)

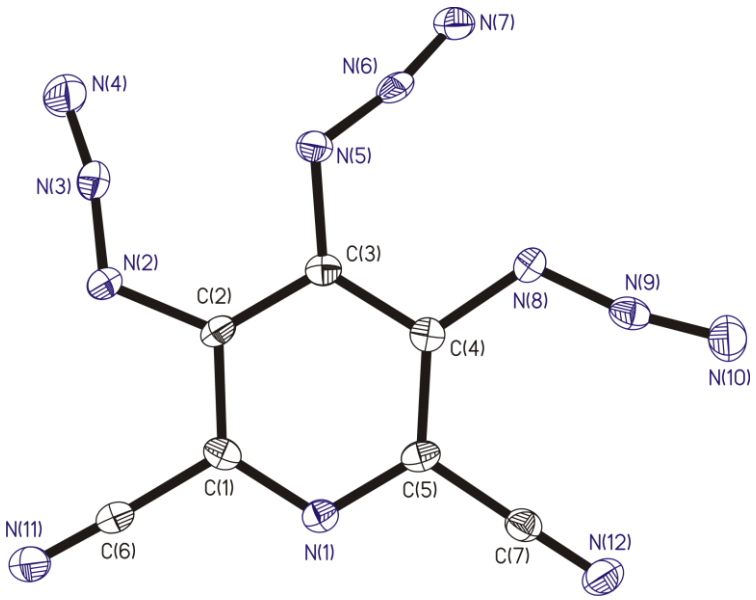
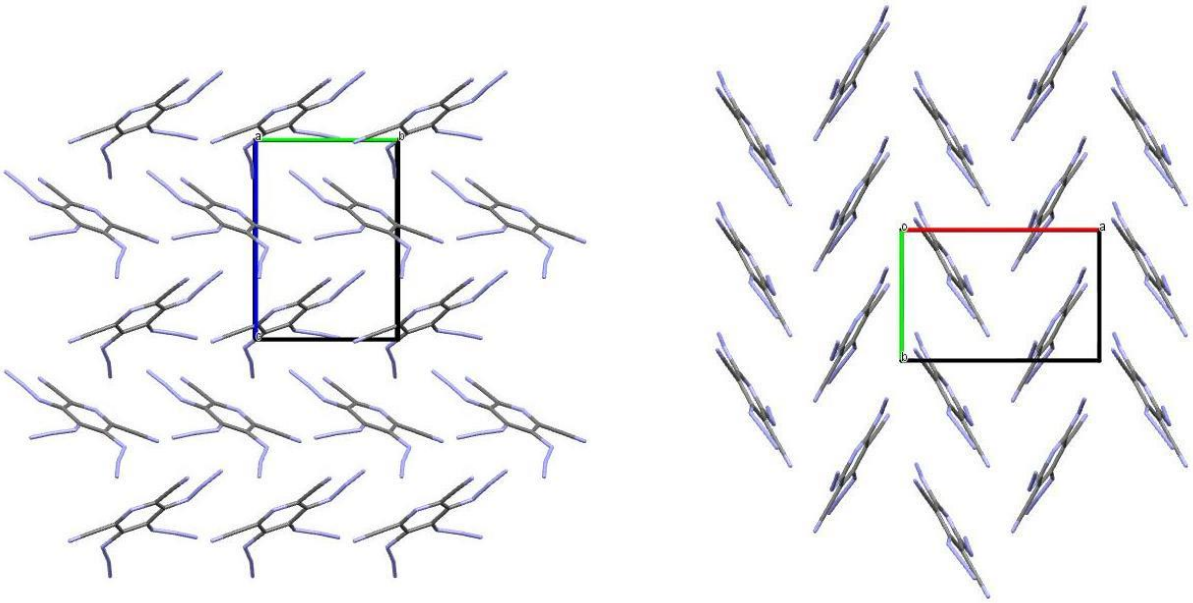


Figure S3 Molecular structure of triazide **2** and atom numbering scheme.

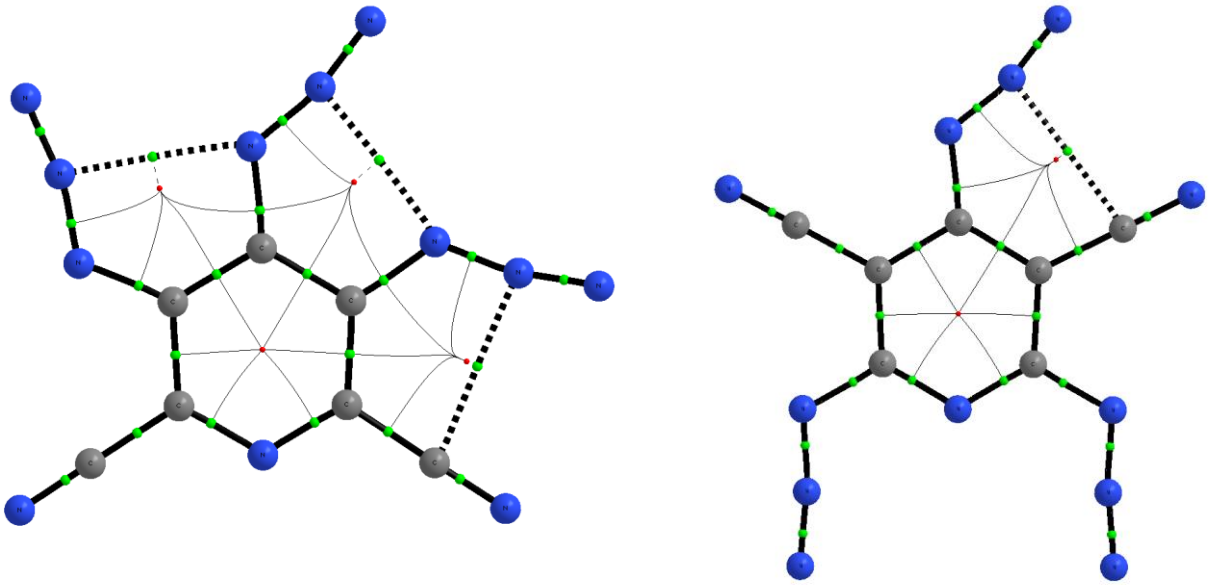


(a) (b)

Figure S4 The *bc* and *ab* projections of crystal structures of triazides **2** (a) and **TAPDN** (b), respectively.

The study of the electron density distribution in the molecules under consideration and estimation of intramolecular interaction energies were performed in the framework of the topological theory R. Bader's "Atoms in Molecules" [*R.F.W. Bader*, «Atoms in Molecules. A Quantum Theory», Clarendron Press, Oxford, 1990] by AIMAll program [AIMAll (Version 16.05.18), *Todd A. Keith*, TK Gristmill Software, Overland Park KS, USA, 2016 (aim.tkgristmill.com)].

The topological analysis of the electron density distribution function shows that, in addition to typical covalent chemical bonds in the molecule of triazide **2**, the intramolecular interactions are present (Figure S5a). Estimations of the energies of these interactions by the Espinosa–Lecomte correlation [*E. Espinosa, E. Molins, C. Lecomte*, Chem. Phys. Lett., **1998**, *285*, 170-173] give values of ~ 3.7-3.8 kcal/mol between the azido groups and ~ 2.2 kcal/mol between the azido and cyano groups. In the case of **TAPDN**, only the γ-azido group is involved in similar intramolecular interactions (Fig.S5b) with energy of ~ 2.2 kcal/mol.



(a) (b)

Figure S5 Molecular graphs of triazides **2** (a) and **TAPDN** (b). Green and red points show critical points (+3,-1) and (+3;+1) types corresponding to bond critical points (chemical bond or van der Waals interactions, for example) and ring critical points, respectively. Dash lines show found intramolecular interactions.

V. Theoretical heats of formation of triazides 2 and TAPDN

The isodesmic reactions used to obtain the heats of formation of triazides **2** and **TAPDN** at 298 K:

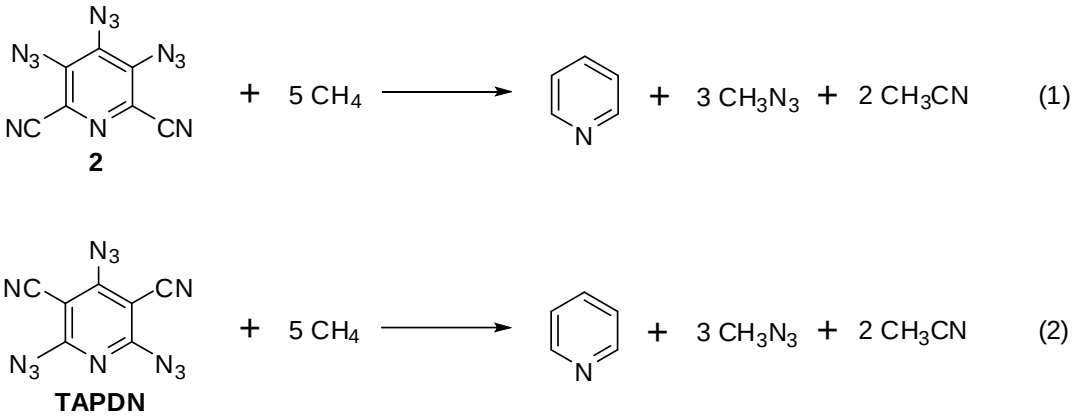


Table S4 Calculated CBS-4 enthalpies (a.u.)* and heats of formation (HOFs, kJ mol^{-1}) for the reference compounds for a gas phase at 298 K.

Compound	CBS-4 enthalpy*	HOF
Triazide **2**	–922.275749	1470.42
TAPDN	–922.300113	1406.45
CH_4	–40.425402	–74.87[a]
CH_3N_3	–203.803562	296.5[b]
C_5H_5N	–247.876035	140.2[c]
CH_3CN	–132.542473	74.04[d]

* Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys*. **2000**, *112*, 6532.

[a] Chase, M. W., Jr., *NIST-JANAF Themochemical Tables, Fourth Edition, J. Phys. Chem. Ref. Data, Monograph 9*, **1998**, 1–1951.

[b] Lide D. R., *Handbook of Chemistry and Physics*, 84ed, CRC Press Boca Raton FL, 2002.

[c] Hubbard, W. N.; Frow, F. R.; Waddington, G., *The heats of combustion and formation of pyridine and hippuric acid, J. Phys. Chem.*, **1961**, *65*, 1326–1328.

[d] An, X.; Mansson, M., *Enthalpies of combustion and formation of acetonitrile, J. Chem. Thermodyn.*, **1983**, *15*, 287–293.

VI. DSC and TGA studies of triazides 2 and TAPDN

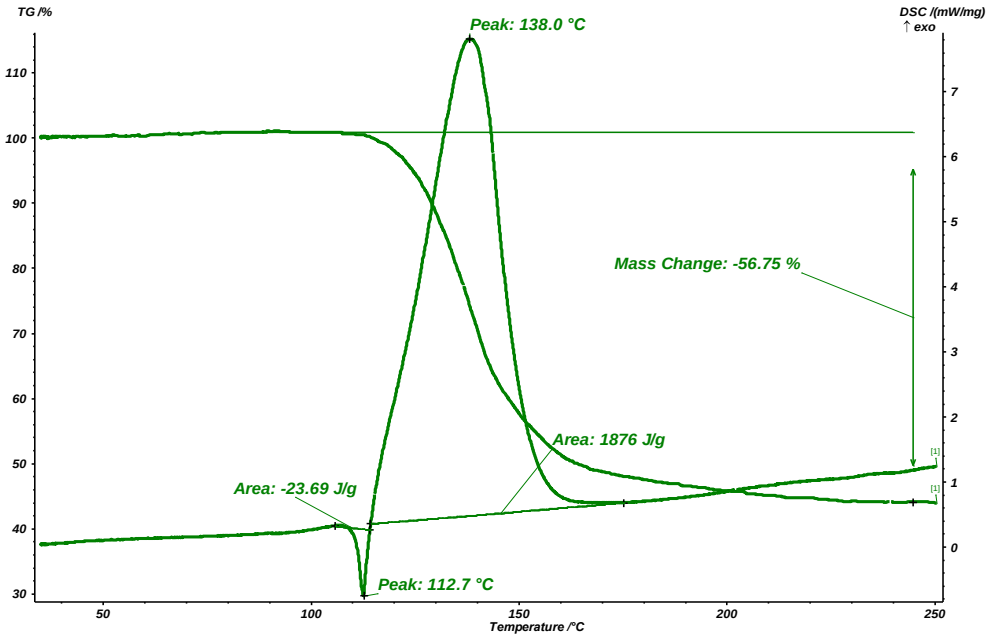


Figure S6 The non-isothermal TG-DSC curve of triazide **2**.

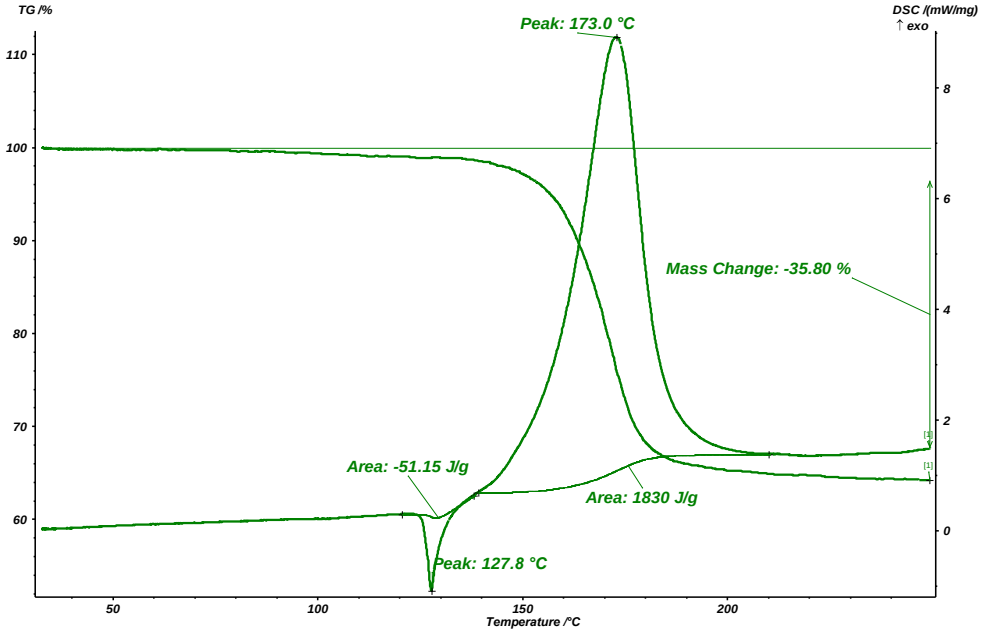
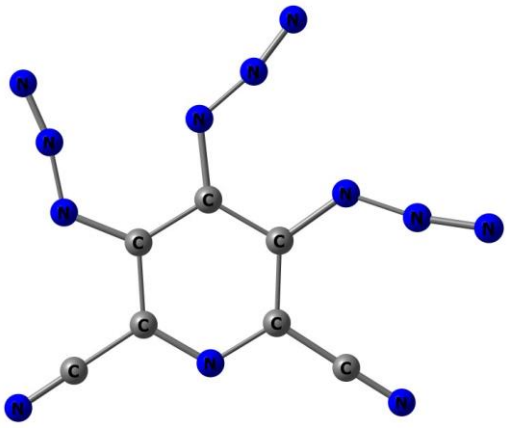


Figure S7 The non-isothermal TG-DSC curve of **TAPDN**.

VII. Absolute energies and Cartesian coordinates for B3LYP/6-311+G(d) optimized molecular geometries of azides 2 and TAPDN

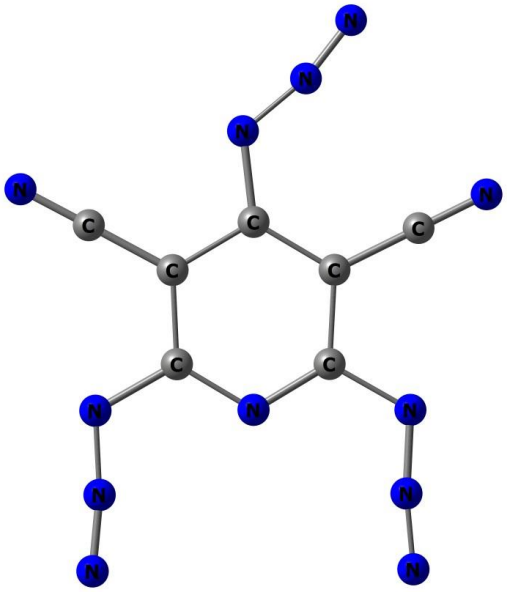
2



Charge : 0
Multiplicity : 1
Total energy: -923.7457346 a.u.

6	7.279203000	0.092670000	0.684880000
6	6.000583000	0.481339000	0.218848000
6	5.519936000	1.752070000	0.599974000
6	6.330951000	2.564204000	1.424352000
6	7.601528000	2.070745000	1.796234000
6	7.803782000	-1.197631000	0.332207000
6	8.509680000	2.872102000	2.565667000
7	8.047922000	0.866180000	1.440664000
7	5.345298000	-0.451753000	-0.568707000
7	4.232150000	-0.268618000	-1.085149000
7	3.252791000	-0.321503000	-1.641228000
7	4.252216000	2.071053000	0.125955000
7	3.674025000	3.149356000	0.328290000
7	2.978432000	4.034726000	0.382065000
7	5.778252000	3.802266000	1.748580000
7	6.203726000	4.524688000	2.664781000
7	6.423477000	5.303627000	3.448498000
7	8.229361000	-2.233141000	0.053090000
7	9.238687000	3.533623000	3.169000000

TAPDN



Charge : 0
Multiplicity : 1
Total energy: -923.7759257 a.u.

6	1.098997000	-0.995443000	-0.000464000
6	-0.230999000	-1.457618000	-0.001156000
6	-1.268281000	-0.497288000	-0.001454000
6	-0.921519000	0.872517000	-0.001502000
6	0.455929000	1.195706000	-0.000729000
6	-0.521895000	-2.849554000	-0.001297000
6	-1.885659000	1.915926000	-0.003270000
7	1.430514000	0.294582000	-0.000233000
7	-2.541337000	-1.037474000	-0.002475000
7	-3.580010000	-0.350475000	0.002876000
7	-4.629029000	0.056805000	0.008175000
7	2.101184000	-1.959951000	-0.000091000
7	3.274907000	-1.543610000	0.000622000
7	4.376710000	-1.321328000	0.001706000
7	0.773899000	2.551033000	-0.000587000
7	1.985966000	2.837560000	0.000350000
7	3.032944000	3.246041000	0.003743000
7	-0.750138000	-3.982023000	-0.000978000
7	-2.669817000	2.765200000	-0.004646000