Supplementary information

2,4,6,8-Tetraazidopyrimido[5,4-*d*]pyrimidine: a novel energetic binary compound

Kristaps Leškovskis,[a] Anatoly Mishnev,[b] Irina Novosjolova,[a] Burkhard Krumm,[c] Thomas M. Klapötke[c] and Māris Turks*[a]

[a] *Institute of Technology of Organic Chemistry, Faculty of Materials Science and Applied Chemistry, Riga Technical University, P. Valdena str. 3, Riga, Latvia*
[b] *Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, Latvia*
[c] *Department of Chemistry, Ludwig Maximilian University, Munich, Butenandtstr. 5-13, 81377 Munich, Germany*

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Experimental

Caution! The title compound is a powerful energetic material with high sensitivities towards shock and friction. Therefore, proper security precautions (safety glass, face shield, earthed equipment and shoes, Kevlar gloves and ear plugs) must be applied while synthesizing and handling the described compound.

Reagents purchased from TCI Chemicals and Acros Organics were used as received.

^{13}C and ^{15}N NMR spectra were recorded on Bruker Avance 500 and Avance 400 instruments. Chemical shifts (δ) are referenced to residual solvents for ^{13}C. ^{15}N NMR shifts were referenced indirectly to the ^{1}H NMR frequency of TMS with the 'xiref'-macro.

Differential thermal analysis (DTA) measurements to determine the decomposition were performed at a heating rate of 5 °C min^{-1} with an OZM Research DTA 552-Ex instrument.

Single-crystal diffraction data were collected on an XtaLAB Synergy-S Dualflex diffractometer (Rigaku Corporation, Tokyo, Japan) equipped with a HyPix6000 detector and micro-focus sealed X-ray tube (Rigaku, Tokyo, Japan) using Cu Kα radiation (λ = 1.54184 Å). Single crystals were fixed with oil in a nylon loop of a magnetic CryoCap and set on a goniometer head. The samples were cooled down to 150 K, and ω-scans were performed with a step size of 0.5°. Data collection and reduction were performed with CrysAlisPro 1.171.40.35a software (Oxford Diffraction Ltd., Abingdon, UK). The structure solution and refinement were performed with SHELXT[1] and SHELXL[2] software, which are part of the CrysAlisPro and Olex2 suites. The H atoms were positioned geometrically and treated as riding on their parent C or N atoms. Molecular graphics were prepared using ORTEP3 for Windows[3] and Mercury[4]. The PLA-TON[5] tool was used for the geometrical calculations.

High-resolution mass (HRMS) (electrospray ionization (ESI)) was recorded with an Agilent 1290 Infinity series ultra-high pressure liquid chromatography connected to an Agilent 6230 time-of-flight mass spectrometer or (atmospheric pressure chemical ionization (APCI)) on a 7 T solaria XR (Bruker Daltonik GmbH) Fourier transform ion cyclotron resonance mass spectrometer equipped with an APCI source.

The IR spectra were recorded in Nujol on KBr glass with a Perkin-Elmer Spectrum BX FTIR spectrometer (4000−450 cm^{-1}).

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[1] Sheldrick, G.M. SHELXT–Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 3–8. https://doi.org/10.1107/S2053273314026370.

[2] Sheldrick, G.M. A Short History of SHELX. *Acta Crystallogr. A* **2008**, *64*, 112–122. https://doi.org/10.1107/S0108767307043930.

[3] Farrugia, L.J. WinGX and ORTEP for Windows : An Update. *J. Appl. Crystallogr.* **2012**, *45*, 849–854. https://doi.org/10.1107/S0021889812029111.

[4] Bruno, I.J.; Cole, J.C.; Edgington, P.R.; Kessler, M.; Macrae, C.F.; McCabe, P.; Pearson, J.; Taylor, R. New Software for Searching the Cambridge Structural Database and Visualizing Crystal Structures. *Acta Crystallogr. B* **2002**, *58*, 389–397. https://doi.org/10.1107/S0108768102003324.

[5] Spek, A.L. Single-Crystal Structure Validation with the Program *PLATON*. *J. Appl. Crystallogr.* **2003**, *36*, 7–13. https://doi.org/10.1107/S0021889802022112.

The impact sensitivity tests were carried out according to STANAG 44897[6] using BAM drophammer applying the 1 out of 6 method. The friction sensitivity tests were carried out according to STANAG 448710[7] using BAM friction tester applying the 1 out of 6 method.

Sensitivity towards electrical discharge using an *Electric Spark Tester ESD 2010 EN* from OZM.

Energetic properties were calculated with the EXPLO5 6.02 computer code[8] using the room temperature converted X-ray density and GAUSSIAN16[9] calculated solid state heats of formation.

[6] NATO Standardization Agreement (STANAG) on Explosives, Impact Sensitivity Tests, no. 4489, 1st Edn., September 17, 1999

[7] NATO Standardization Agreement (STANAG) on Explosives, Friction Sensitivity Tests, no. 4487, 1st Edn., August 22, 2002

[8] Sućeska, M., *EXPLO5 V6.02* program, Brodarski Institute, Zagreb, Croatia, **2014**

[9] Gaussian 16, Revision A.03, M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria; M. A. Robb; J. R. Cheeseman; G. Scalmani; V. Barone; G. A. Petersson; H. Nakatsuji; X. Li; M. Caricato; A. V. Marenich; J. Bloino; B. G. Janesko; R. Gomperts; B. Mennucci; H. P. Hratchian; J. V. Ortiz; A. F. Izmaylov; J. L. Sonnenberg; D. Williams-Young; F. Ding; F. Lipparini; F. Egidi; J. Goings; B. Peng; A. Petrone; T. Henderson; D. Ranasinghe; V. G. Zakrzewski; J. Gao; N. Rega; G. Zheng; W. Liang; M. Hada; M. Ehara; K. Toyota; R. Fukuda; J. Hasegawa; M. Ishida; T. Nakajima; Y. Honda; O. Kitao; H. Nakai; T. Vreven; K. Throssell;, J. A. Montgomery; Jr. J. E. Peralta; F. Ogliaro; M. J. Bearpark; J. J. Heyd; E. N. Brothers; K. N. Kudin; V. N. Staroverov; T. A. Keith; R. Kobayashi; J. Normand; K. Raghavachari; A. P. Rendell; J. C. Burant; S. S. Iyengar; J. Tomasi; M. Cossi; J. M. Millam; M. Klene; C. Adamo; R. Cammi; J. W. Ochterski; R. L. Martin; K. Morokuma; O. Farkas; J. B. Foresman; D. J. Fox, *Gaussian, Inc*., Wallingford CT, **2016**.

Crystallography

Table S1. Single crystal X-ray analysis data and refinement details for **TAPP** in its **2T** form (the only tautomer in solid state)

Crystal data for TAPP in its 2T form; CCDC deposition number 2257695	
Chemical formula	C_6N_{16}
M_r	296.22
Crystal system, space group	Orthorhombic, $Pca2_1$
Temperature (K)	150
a, b, c (Å)	12.0754 (3), 10.5591 (3), 8.8651 (3)
V (Å^3)	1130.35 (6)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.17
Crystal size (mm)	0.4 × 0.06 × 0.03
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.41.123a (Rigaku Oxford Diffraction, 2022) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.644, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5814, 1983, 1820
R_{int}	0.036
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.630
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.102, 1.06
No. of reflections	1983
No. of parameters	199
No. of restraints	1
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, -0.34
Absolute structure	Flack x determined using 666 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	0.1 (4)

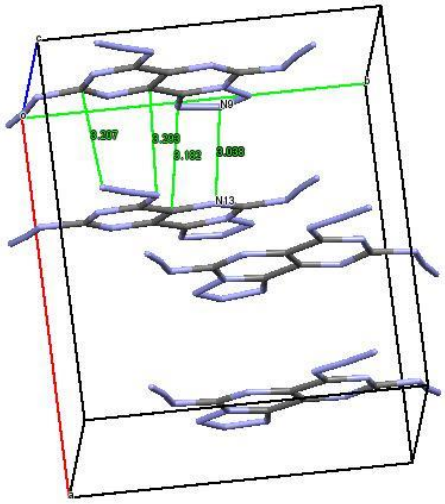
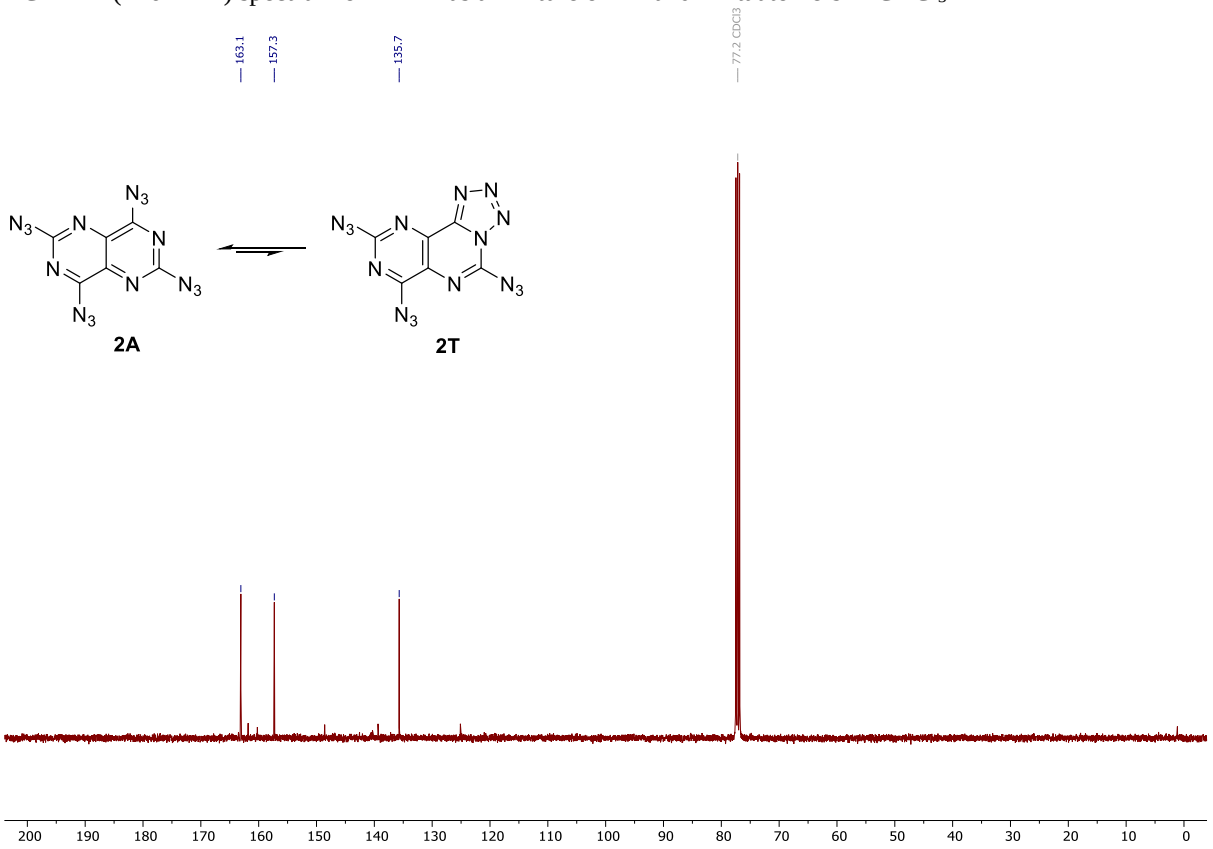


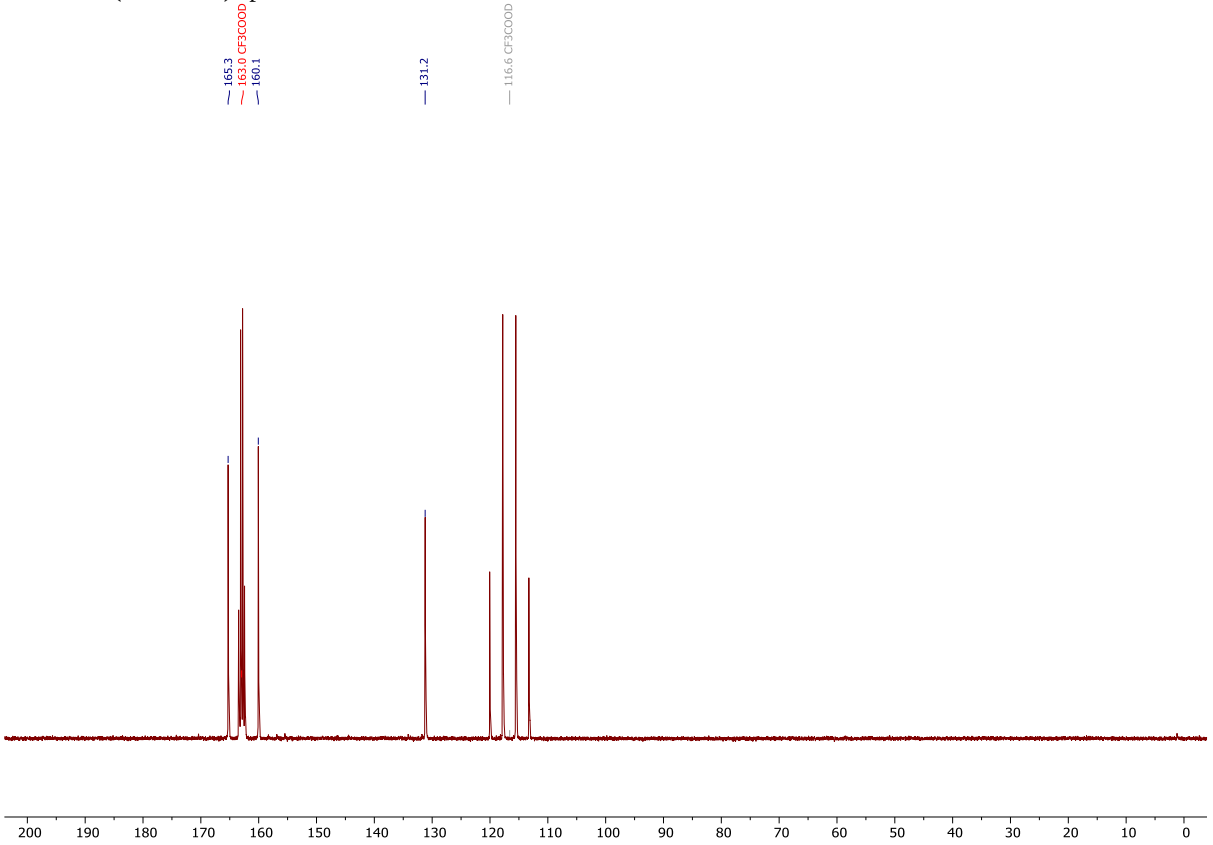
Figure S1. Packing fragment of **TAPP** in its tetrazolo-form **2T** (the only tautomer in solid state) and the shortest interatomic distances between the stacks.

NMR spectra

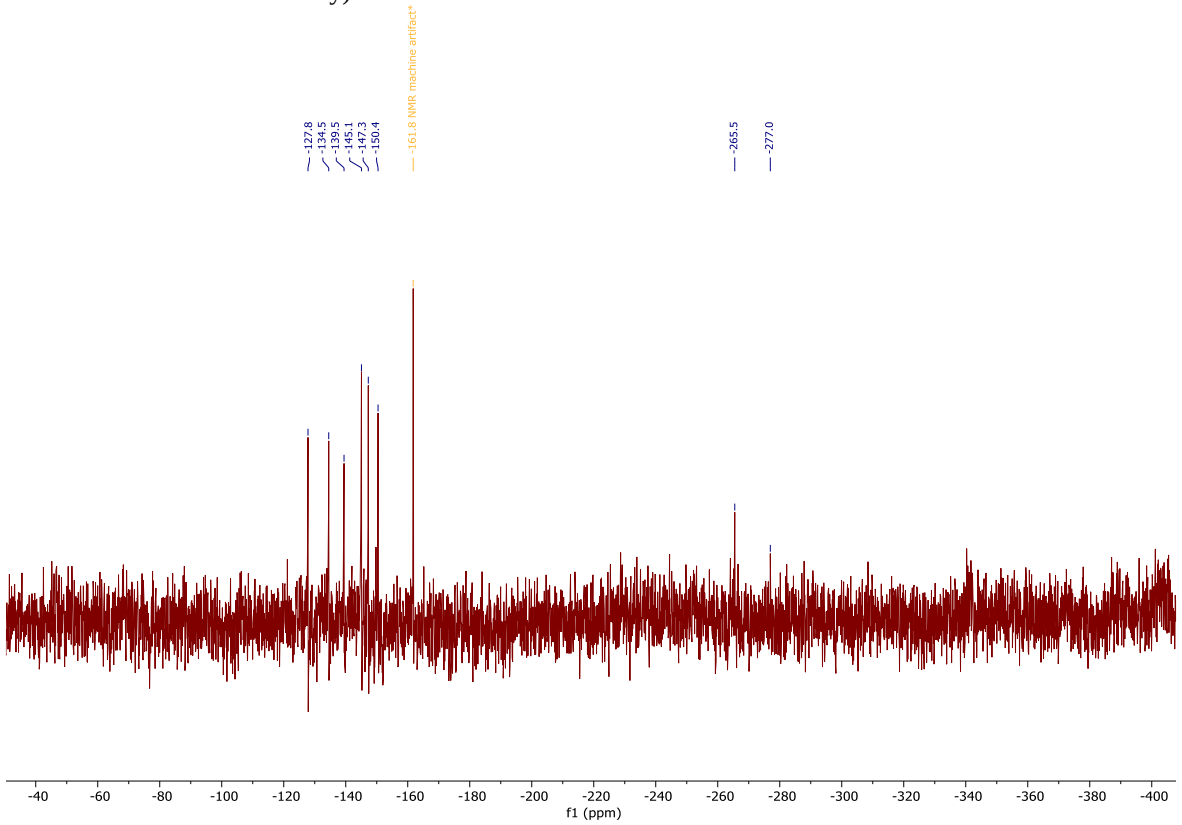
^{13}C NMR (126 MHz) spectrum of **TAPP** as a mixture of **2A** and **2T** tautomers in $CDCl_3$



^{13}C NMR (126 MHz) spectrum of **[D$_2$2A]$^{2+}$ [TFA$^-$]$_2$** in TFA-d_1

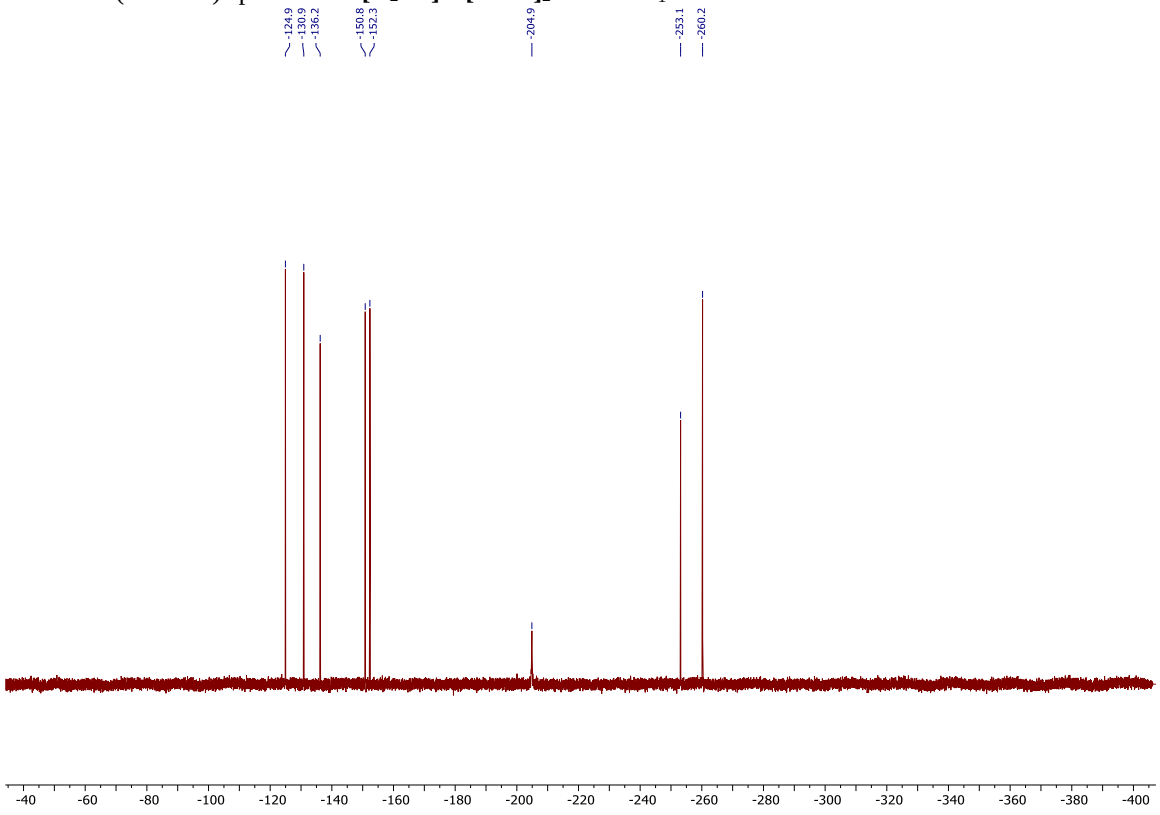


^{15}N NMR (40.5 MHz) spectrum of **TAPP** as a mixture of **2A** and **2T** tautomers in $CDCl_3$ (only **2A** form detected because of low intensity)

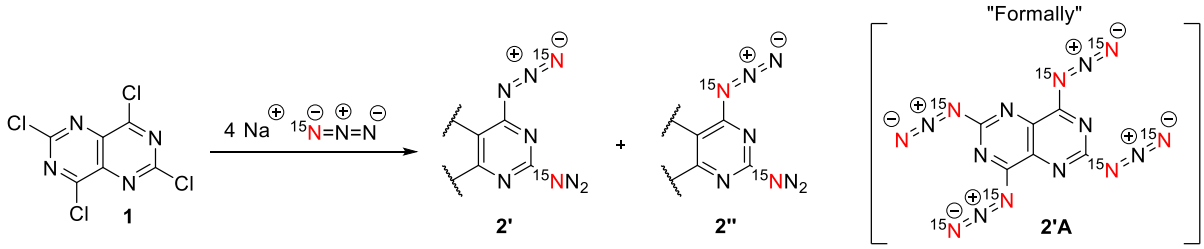


** Artefact signal at -161.8 ppm determined by running blank ^{15}N NMR of $CDCl_3$*

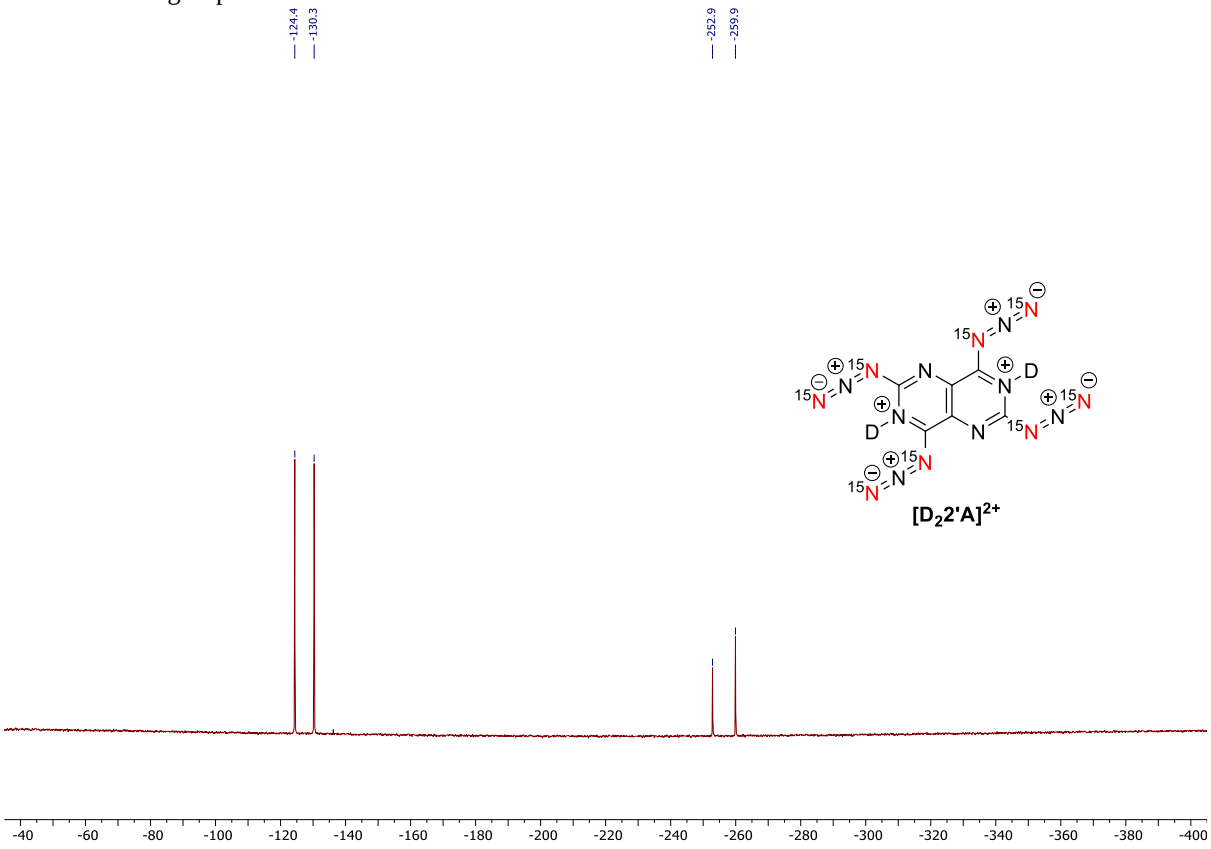
^{15}N NMR (51 MHz) spectrum of **$[D_2 2A]^{2+}$ $[TFA^-]_2$** in TFA-d_1



A mixture of ^{15}N labelled systems as in **2'** and **2''** are obtained with $Na^{15}NN_2$. However, summed up they provide a ^{15}N spectrum as in **2'A.**

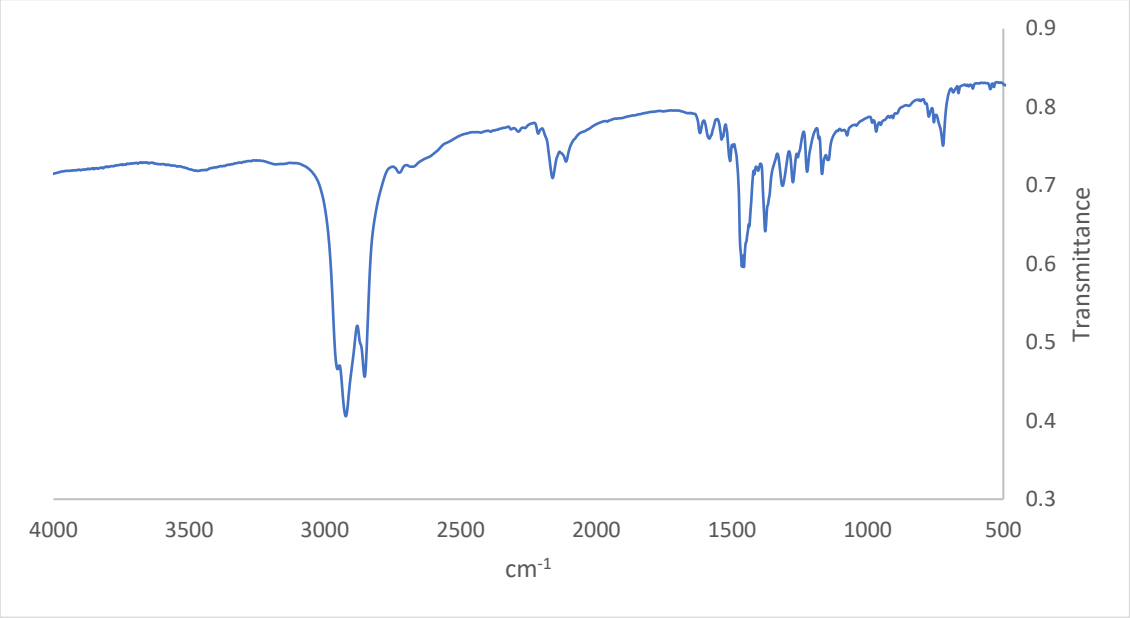


^{15}N NMR (51 MHz) spectrum of **[D$_2$2'A]$^{2+}$ [TFA$^-$]$_2$** in TFA-d_1 with $Na^{15}NN_2$ labelling of α and γ nitrogen atoms of azido groups



FT-IR

FT-IR spectra (Nujol) of **TAPP** in its **2T** form (the only tautomer in solid state)



Heat of Formation Computation

The experimental density of **TAPP** in its **2T** form (X-ray diffraction) at 150 K was determined to be $\rho_{(150K)} = 1.741$ g cm^{-3}. This value was converted into the room temperature (298 K) density to $\rho_{(298K)} = 1.703$ g cm^{-3}.[10]

The enthalpy of formation for the gas phase was calculated at CBS-4M and CBS-QB3 level of theory to[11]:

$\Delta H°_f$(g, CBS-4M) = 1639.5 kJ mol^{-1}

$\Delta H°_f$(g, CBS-QB3) = 1610.0 kJ mol^{-1}.

The enthalpy of sublimation was calculated using the RoseBoom2.3 code[12] to $\Delta H_{sub.} = 101.0$ kJ mol^{-1}.

With the enthalpy of sublimation these values were converted into the enthalpies of formation in the solid state:

$\Delta H°_f$(s, CBS-4M) = 1538.5 kJ mol^{-1}

$\Delta H°_f$(s, CBS-QB3) = 1509.0 kJ mol^{-1}.

The detonation parameters were calculated using the EXPLO5 code (version V7.01.01)[13] and are summarized in Table S2.

Table S2. Detonation parameters of **TAPP** in its **2T** form (the only tautomer in solid state)

density, ρ / g cm^{-3}	1.703
$\Delta H°_f$(s, CBS-QB3) / kJ mol^{-1}	1509.0
$\Omega(CO_2)$ / %	-64.8
$\Delta H°_f$(s) / kJ kg^{-1}	5094.7
Q_{ex} / kJ kg^{-1}	-4590.4
T_{ex} / K	3787
p_{C-J} / GPa	20.8
VoD / m s^{-1}	7477
TNT equivalent (from Q_{ex})	1.04
TNT equivalent (from E°)	1.12

[10] Chemistry of High Energy Materials, 6th edn., T. M. Klapötke, Walter de Gruyter, Berlin/Boston, **2022**, p. 149.
[11] Chemistry of High Energy Materials, 6th edn., T. M. Klapötke, Walter de Gruyter, Berlin/Boston, **2022**, pp 164 – 167.
[12] S. Wahler, RoseBoom, version 2.3, **2022**.
[13] M. Suceska, EXPLO5, version V7.01, **2022**.