

Synthesis, structure and properties of 2,4,6-triazidopyrimidine-5-carbonitrile

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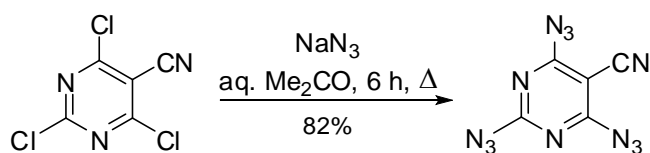
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Abstract

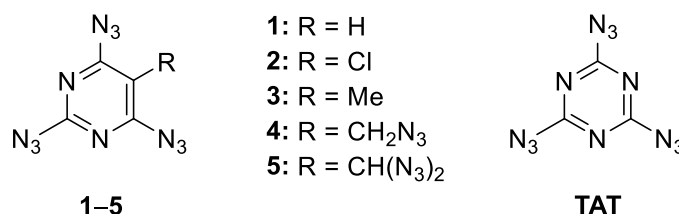
2,4,6-Triazidopyrimidine-5-carbonitrile was obtained in 82% yield by the reaction of 2,4,6-trichloropyrimidine-5-carbonitrile with sodium azide in aqueous acetone and characterized with X-ray diffraction, UV, IR, ^{13}C and ^{15}N NMR spectroscopy, electron impact mass-spectrometry and quantum-chemical calculations. Compared to known 2,4,6-triazidopyrimidines, the triazide obtained has an unusual crystal structure, high melting point, high positive heat of formation and moderate sensitivity to impact and friction.



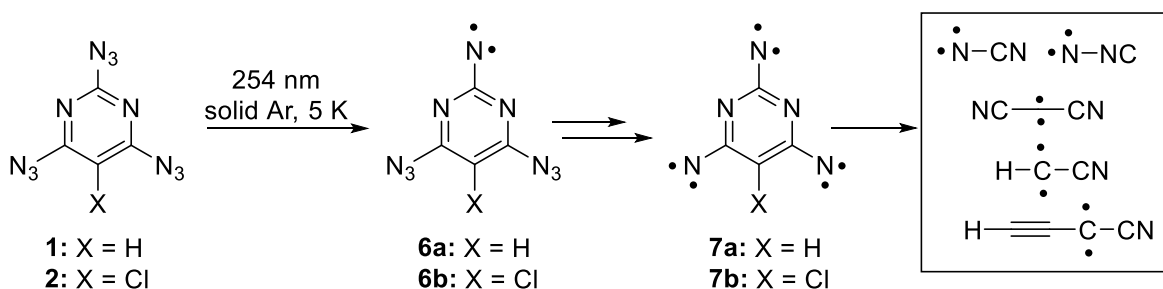
Keywords: Azides, pyrimidines, energetic materials, heat of formation, sensitivity, X-ray diffraction

Introduction

To date, there are only five known 2,4,6-triazidopyrimidines. The first, triazide **1**, was obtained by the reaction of 2,4,6-trichloropyrimidine with sodium azide in DMSO and characterized with UV, IR and ^1H NMR spectroscopy in 1979.¹ The crystal structure,² ^{13}C and ^{15}N NMR spectra,^{3,4} and thermal stability⁵ of this triazide were studied only recently. Triazide **1** is widely used as a photoactive cross-linking agent in lithography⁶ and as starting material for photochemical studies.⁷⁻⁹ Triazide **1** also shows high anticancer activity against Sarcoma 180, Pliss lymphosarcoma and Guerin carcinoma.¹⁰ Moreover, the detonation of triazide **1** under high pressure was used in preparation of carbon nanotubes.³ Before that, similar carbon nanotubes were obtained by detonation of very explosive 2,4,6-triazido-1,3,5-triazine (**TAT**).¹¹ In 2006, four new pyrimidyl azides **2–5** were synthesized.³ According to quantum-chemical calculations,³ tetraazide **4** and pentaazide **5** have very high positive heats of formation and may be of interest as components of high-energy organic materials.



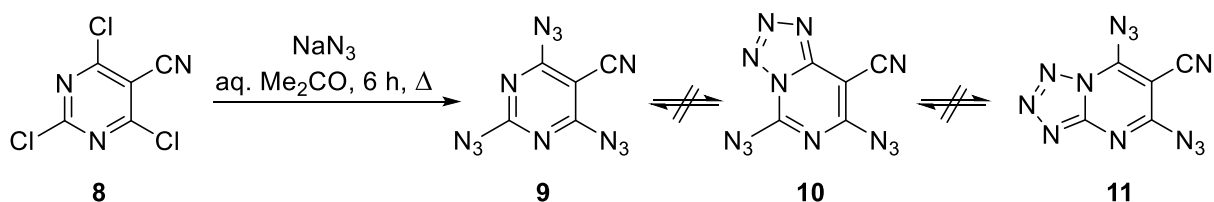
In the last two decades, aryl triazides are widely used as starting materials for photochemical preparation of high-spin nitrenes and other unusual molecules.¹² As a rule, the photolysis of 1,3,5-triazidobenzenes¹³⁻¹⁵ and 2,4,6-triazidopyrimidines¹⁶⁻¹⁸ in cryogenic matrices gives the corresponding septet trinitrenes as the final products. In contrast, the photolysis of **TAT** leads to photochemically unstable 2,4,6-trinitreno-1,3,5-triazine that undergoes further decomposition to form triplet nitrenes NCN and CNN as well as triplet carbene NCCCN.¹⁹ However, the photochemistry of triazides **1** and **2** is the most intriguing. First of all, these triazides undergo selective photolysis of the azido groups in position 2 to form only triplet nitrenes **6a,b** as primary products (Scheme 1).²⁰ Secondly, septet trinitrene **7a**, formed at the late stages of the photolysis of triazide **1**, undergoes partial photodecomposition to form triplet carbenes HCCN and HCCCCN along with NCN, CNN and NCCCN.²⁰ Of all these products, carbene HCCCCN has never before been generated in a laboratory, but was spectrally detected as a component of interstellar matter.²¹



Scheme 1. Photochemistry of triazides **1** and **2**.

As part of our ongoing work on the photochemistry of aromatic triazides,²⁰ we were interested in the synthesis of new 2,4,6-triazidopyrimidines that can possess interesting photochemistry and be readily prepared from commercially available precursors. Herein, we report the synthesis, structure and properties of

2,4,6-triazidopyrimidine-5-carbonitrile (**9**), obtained by boiling of trichloride **8** with sodium azide in aqueous acetone (Scheme 2). This method has never before been used for preparation of 2,4,6-triazidopyrimidines.



Scheme 2. Synthesis of 2,4,6-triazidopyrimidine-5-carbonitrile (**9**).

Results and Discussion

To avoid the undesirable reaction of nitriles with sodium azide that may occur in DMSO to give the corresponding tetrazoles,²² the reaction of trichloride **8** with sodium azide was carried out in aqueous acetone (Scheme 2). As a rule, the azidation of 2,4,6-trihalopyrimidines with sodium azide in such solvents as acetone and acetonitrile results in the formation of the respective 4,6-diazo-2-halopyrimidines as the major products.^{20,23} However, it was reported that triazide **2** can be prepared in 55% yield if the azidation of the starting tetrachloride with sodium azide in acetone is carried out for several days at room temperature in the presence of tetrabutylammonium bromide (TBAB).³ The second product of the reaction, obtained in 21% yield, was 4-amino-2,6-diazo-5-chloropyrimidine. In our work, we did not add TBAB to the reaction mixture. The TLC monitoring showed that the azidation of trichloride **8** with sodium azide in acetone at room temperature led to the formation of two compounds, presumably, 4,6-diazo-2-chloropyrimidine-5-carbonitrile as the major product and small amount of triazide **9**. After boiling for 6 h, the reaction completed to give only one product identified as triazide **9** (Scheme 2).

On comparison with 2-azidopyrazines and 3-azidopyridazines, 2- and 4-azidopyrimidines are less prone to azido-tetrazolo tautomerization.²⁴⁻²⁸ As a rule, the equilibrium between the azide and tetrazole tautomers is strongly shifted to the tetrazoles when electron-releasing substituents are present on the pyrimidine ring.^{27,28} However, the use of DMSO as a solvent sometimes allows the formation of tetrazoles even from azidoazines existing in the solid state exclusively in the azide form.²⁹ In the case of triazide **9**, the azido-tetrazolo tautomerization may theoretically lead to the formation of tetrazoles **10** and **11** (Scheme 2). Meanwhile, none of these tetrazoles was detected during our NMR spectroscopic studies of triazide **9**. Similar to previously studied triazides **1–5**,^{3,4} triazide **9** is present in the solid state as well as in chloroform and DMSO solutions exclusively in the azide form.

Thiazide **9** was obtained as a colorless solid melting at 118–120 °C. This melting point is substantially higher than that reported³ for triazides **1** (98 °C), **2** (90 °C), **3** (103 °C), **4** (22.5 °C), and **5** (–48 °C), which is important for some applications of 2,4,6-triazidopyrimidines as high-energy organic compounds.

Triazide **9** crystallizes from ethanol in the form of colorless prisms with space group $P2_1/c$. The bond lengths and valence angles in the azido groups as well as the spatial orientations of these groups in triazide **9** (Figure 1a) are very close to that reported for triazides **1–3**.^{2,3} At the same time, the crystal structure of triazide **9** has a number of specific features. Firstly, the asymmetric unit of the crystal structure of this triazide consists of two molecules with slightly differing geometries (Figure 1b). Previously, the presence of two symmetry independent molecules in the crystal structure of aromatic triazides was reported only for 2,4,6-

triazidopyridine-3,5-dicarbonitrile.³⁰ Secondly, in contrast to the lamellar and herringbone types of packing characteristic for all aromatic triazides,^{31,32} the crystal structure of triazide **9** is formed from centrosymmetric *A* and *B* dimers, with the energy of pair interactions of 17.0 and 15.9 kcal/mol, respectively (Figure 2). So far, this type of packing has been known only for tetraazidopyridine-4-carbonitrile.³³ These data show that the presence of the cyano groups in tri- and tetraazido-substituted azines favors the dimerization of such azines during the crystallization process, leading to the formation of rather unusual crystal structures. Moreover, the cyano groups of such compounds also control the spatial orientations of *A* and *B* dimers in crystals by means of the $\text{NC}^{\delta+} \cdots \delta^- \text{N}_{\alpha} \text{N}_2$ and $\text{CN}^{\delta-} \cdots \delta^+ \text{CN}_3$ intermolecular interactions (Figure 2).

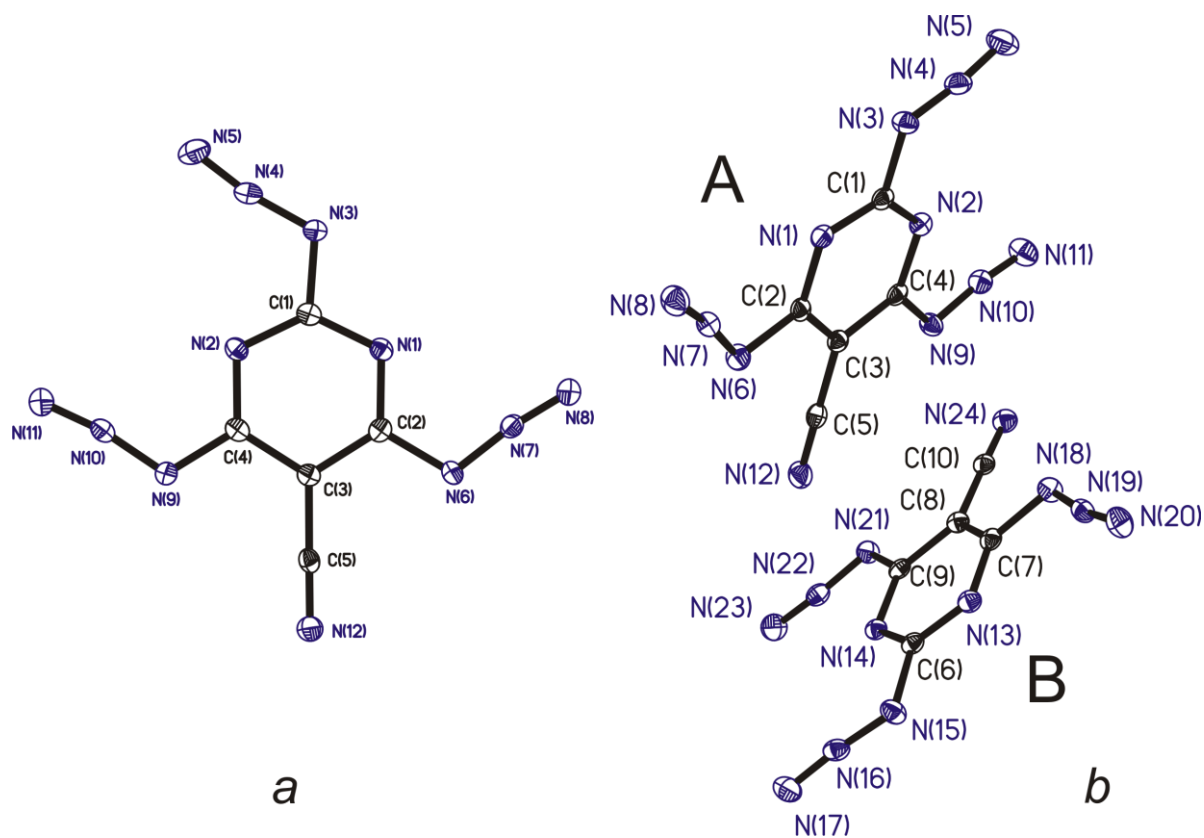


Figure 1. Molecular structure (a) and the asymmetric unit of crystal structure (b) of triazide **9**.

Due to the presence of the electron-withdrawing cyano group, the signals of the carbon atoms in positions 2, 4, and 6 of triazide **9** are manifested in the ^{13}C NMR spectrum at higher magnetic fields, on comparison with similar signals of triazides **1** and **2** (Table 1). The chemical shifts of the nitrogen atoms in the azido groups of triazide **9** are very close to those reported for **TAT**, thus indicating a rather high electron-deficiency of these groups (Table 2). Furthermore, substantial difference in the chemical shifts for the N_{α} atoms of nonequivalent azido groups of triazide **9** suggests⁴ that these groups should notably differ in reactivity toward electron-rich dipolarophiles, phosphines, and reducing agents.

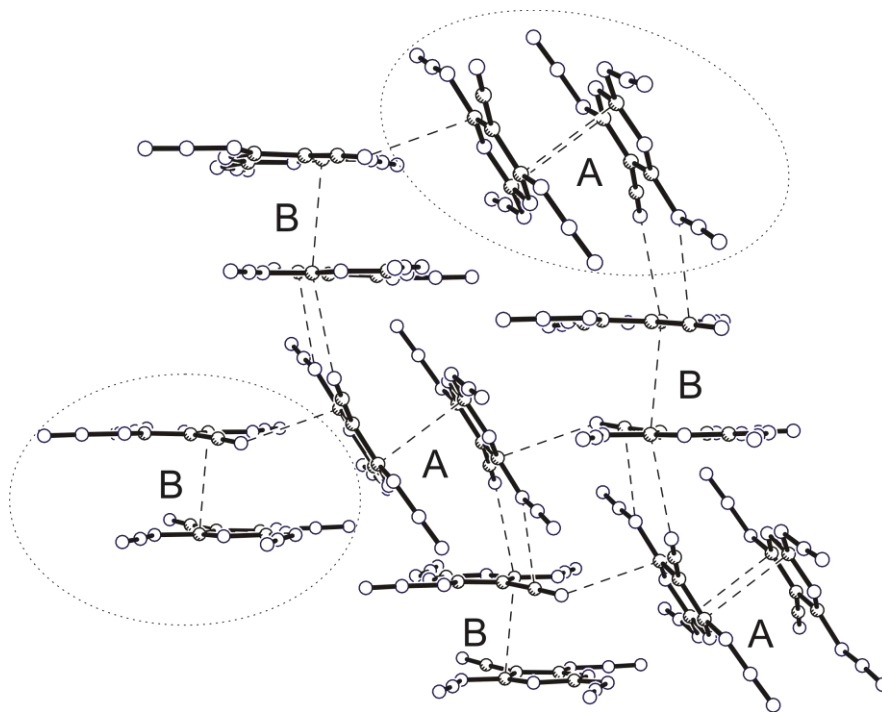


Figure 2. Fragment of crystal structure of triazide **9**.

Table 1. Chemical shifts in ^{13}C NMR spectra (CDCl_3) of triazides **1**, **2**, and **9**

Azide	C-2 ppm	C-4,6 ppm	C-5 ppm	CN ppm
1 ³	161.5	164.9	94.3	—
2 ³	157.5	160.3	100.6	—
9	162.7	166.9	80.9	110.4

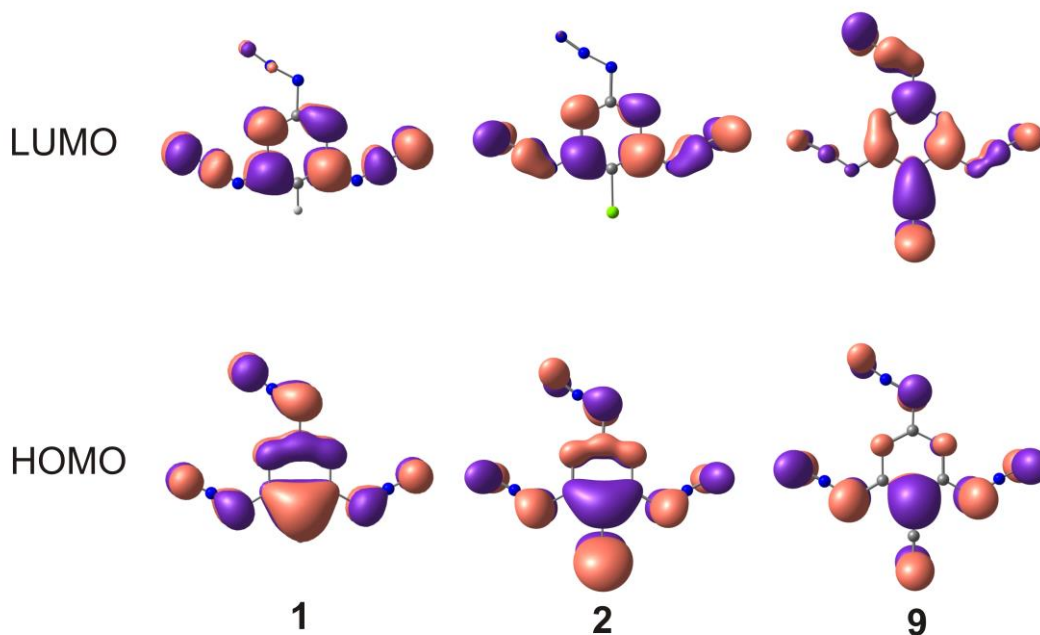
The UV spectrum of triazide **9** displays the absorption band with $\lambda_{\text{max}} = 275$ nm that is absent in the UV spectra of triazides **1** and **2** (Table 3). Beside this, the most intense absorption band of triazide **9** with $\lambda_{\text{max}} = 249$ nm is red shifted by approximately 14 nm on comparison with similar absorption bands of triazides **1** and **2**. These effects suggest that photochemistry of triazide **9** may significantly differ from photochemical transformations of triazides **1** and **2**. Indeed, quantum-chemical calculations at the B3LYP/6-311+G(d) level of theory reveal considerable difference in the LUMO and HOMO of triazides **1** and **2**, from one side, and triazide **9**, from another side (Figure 3). The most photolabile²⁰ azido groups in position 2 of triazides **1** and **2** are distinguished by a very low localization of the LUMO orbital density. In contrast, a similar azido group of triazide **9** bears the high LUMO orbital density. Therefore, it is not excluded that the order of the photolysis of the azido groups of triazide **9** may dramatically differ from that reported²⁰ for triazides **1** and **2**.

Table 2. Chemical shifts in ^{15}N NMR spectra of triazides **1**, **2**, **9**, and **TAT**

Azide	Group	N_α ppm	N_β ppm	N_γ ppm	N_{Ring} ppm	CN ppm
1 ⁴	4,6- N_3	-264.8	-141.0	-134.5	-145.6	–
	2- N_3	-262.7	-140.0	-135.1		
2 ²	4,6- N_3	-263.7	-141.0	-134.5	-144.0	–
	2- N_3	-263.3	-140.3	-132.2		
9	4,6- N_3	-259.7	-144.2	-130.2	-148.6	-99.8
	2- N_3	-257.0	-142.3	-132.4		
TAT ⁴	2,4,6- N_3	-257.3	-142.6	-131.3	-160.2	–

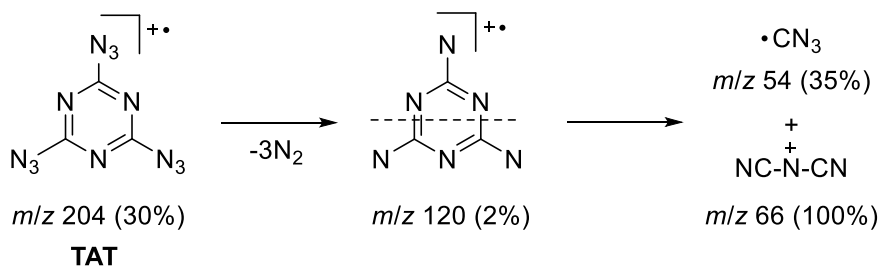
Table 3. UV spectra of triazides **1**, **2**, and **9** in MeCN

Azide	λ_{max} / nm (log ϵ)
1 ²⁸	237 (4.03), 294 (3.67), 303 (3.68)
2 ²⁸	234 (4.01), 300 (3.66), 309 (3.70)
9	249 (4.03), 275 (3.55), 295 (3.46), 304 (3.42)

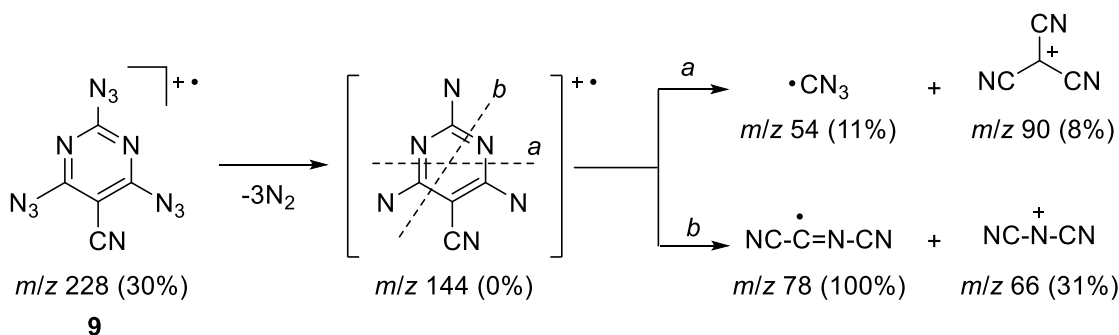
**Figure 3.** The HOMO and LUMO of triazides **1**, **2**, and **9**.

Currently, nothing is known about the stability and fragmentation of 2,4,6-triazidopyrimidines under high-energy electron impact (EI). Our study shows that fragmentation of triazide **9** resembles the fragmentation of the very explosive **TAT**.³⁴ In both cases the intensities of the molecular ions are equal to 30%, indicating on the same stability of triazide **9** and **TAT** under EI. In the case of fragmentation of **TAT**, the main reaction pathway involves the generation of very unstable ion $[\text{M}^+ - 3\text{N}_2]$ that undergoes the break-up of the triazine ring to form intense C_2N_3^+ and CN_3^+ ions (Scheme 3).³⁴ Similar fragmentations are also observed for triazide **9** to give intense C_4N_3^+ , C_3N_3^+ , and C_2N_3^+ ions (Scheme 4). Overall, the fragmentations of triazide **9** and **TAT** result in the formation of eight identical ions with m/z 92 (C_3N_4^+), 90 (C_4N_3^+), 80 (C_2N_4^+), 78 (C_3N_3^+), 66 (C_2N_3^+), 64 (C_3N_2^+),

54 (CN_3^+), and 52 (C_2N_2^+). One of these ions with m/z 64 (C_3N_2^+) may be assigned to the ion of carbene NCCCN. This carbene was previously identified as one of the major products of the photolysis of **TAT** and triazide **1**.^{19,20} Again, the ion with m/z 52 (C_2N_2^+) corresponds to the ion of cyanogen that is the major product of the thermolysis of **TAT**.³⁴ All these data show that many products of thermal, photochemical, and EI-induced decomposition of azides **1**, **9**, and **TAT** are similar, thus explaining the formation of the same carbon nitride nanomaterials³⁴ and carbon nanotubes¹¹ from azides **1** and **TAT**. It is reasonable to assume that triazide **9** may also be used as a precursor of carbon nitride nanomaterials and carbon nanotubes.



Scheme 3. Fragmentation of triazide **TAT** under EI mass spectrometry conditions.



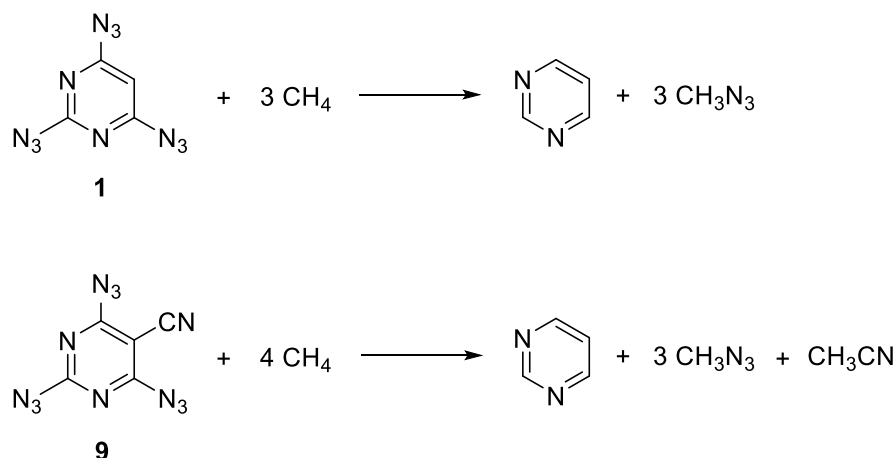
Scheme 4. Fragmentation of triazide **9** under EI mass spectrometry conditions.

To evaluate the heats of formation of triazides **1** and **9**, we applied the CBS-4M method for calculations of isodesmic reactions, widely used in the research of energetic compounds.^{35,36} For this purpose, we considered the isodesmic reactions shown in Scheme 5. The heats of formation for azides in the solid state were calculated following published³⁵ method according to equation (1):

$$\Delta H_f^{\text{solid}} = \Delta H_f^{\text{gas}} - 188 \times \text{mp}, \quad (1)$$

where $\Delta H_f^{\text{solid}}$ is the heat of formation in the solid state, expressed in kJ/mol, ΔH_f^{gas} – the heat of formation in the gas phase in kJ/mol, mp – melting point in K.

According to these calculations (Table 4), the positive heats of formation of triazides **1** and **9** are equal to 5192 and 5276 kJ/kg, respectively. In other words, compound **9** is slightly more energetic than triazide **1**. Previous experimental studies have shown that the positive heat of formation of **TAT** equals to 1053 kJ/mol (5162 kJ/kg).³⁴ Thus, all three triazide **1**, **9** and **TAT** have nearly the same positive heats of formation.



Scheme 5. Isodesmic reactions for triazides **1** and **9**.

Table 4. Total energies (E) and heats of formation (ΔH_f) for the studied compounds, calculated by the CBS-4M method

Compound	$E = E_e + ZPE + E_{298}^0$, a.u.	ΔH_f , kJ/mol
Triazide 1	−754.120917	1123.61 ^a /1053.83 ^b
Triazide 9	−846.236379	1276.71 ^a /1203.17 ^b
Pyrimidine	−263.915156	196.65
CH ₃ N ₃	−203.803562	296.5
CH ₃ CN	−132.542473	74.04
CH ₄	−40.425402	−74.87

^aGas phase. ^bSolid state.

To evaluate the explosive risk of triazide **9**, its sensitivity to impact and friction, in comparison with that of triazide **1** and **TAT**, were tested. The energies and pressures at which these azides do not explode are presented in Table 5.

Table 5. Insensibility levels to impact and friction of triazides **1**, **9** and **TAT**

Azide	Weight / Height h_0 <i>kg / cm</i>	Impact Energy <i>J</i>	Friction Pressure <i>MPa</i>
TAT	0.2/2	0.04	29.42
9	2/10	1.96	58.84
1	2/20	3.92	98.06

Compared to **TAT**, azides **1** and **9** are much less sensitive to impact and friction and only formally may be assigned as primary explosives. At the same time, our testing shows that cyano-substituted triazide **9** is nearly two times more sensitive to impact and by 40% more sensitive to friction on comparison with triazide **1**.

Conclusions

Novel high-energy nitrogen-rich 2,4,6-triazidopyrimidine-5-carbonitrile (**9**) is readily obtained in 82% yield by triazidation of commercially available 2,4,6-trichloropyrimidine-5-carbonitrile (**8**) with sodium azide on boiling in aqueous acetone. Compared to known 2,4,6-triazidopyrimidines, triazide **9** has an unusual crystal structure, high melting point, high positive heat of formation, moderate sensitivity to impact and friction and may be of interest as high-energy compound, photoactive cross-linking agent for lithography and polymer chemistry, and as starting material in synthetic chemistry and photochemistry.

Experimental Section

General. ^{13}C and ^{15}N NMR spectra were recorded in CDCl_3 solutions on a Bruker Avance III 500 MHz spectrometer, using TMS ($\delta_{\text{C}} = 0$ ppm) and CD_3NO_2 ($\delta_{\text{N}} = 0$ ppm) as internal standards. Infra-Red (IR) spectra of crystalline samples were recorded on a Perkin-Elmer Spectrum 100 FT-IR instrument. Ultra-Violet (UV) spectra were recorded in acetonitrile solutions on a Specord M400 instrument. Electron impact mass-spectra (EIMS, 70 eV, direct insertion) were recorded on a Finnigan MAT Incos 50 mass-spectrometer. Elemental analyses were performed on a CHNS/O Vario Microcube Elemental analyzer. Melting points were determined on a Boethius apparatus and are uncorrected. The TLC analyses were carried out on Merck Kieselgel 60F₂₅₄ plates with detection by UV light. All reagents and starting materials were directly used as obtained commercially.

The lower limit of impact sensitivity of azides was evaluated on a K-44-2 impact machine. The lower limit of sensitivity of azides to friction at impact shift was evaluated on a K-44-3 impact machine by measuring the maximum pressure of 0.01 g sample occlusion between steel rolls with diameter of 10 mm at impact shift of one of the rolls with respect to the other that did not lead to explosion of the sample.

All computations were performed with the Gaussian 09 program.³⁷ The geometries of the molecules were optimized at the B3LYP/6-311+G(d) level of theory. The thermodynamic characteristics of compounds and processes were obtained using the isodesmic reaction method in combination with the CBS-4M approach.³⁵

Caution. *The prepared azide is explosive with sensitivity toward various stimuli. Although we had no problems during synthesis, proper protective equipment (Kevlar gloves and wrist protectors, face shield, ear protection, and thick leather coat) should be worn.*

2,4,6-Triazidopyrimidine-5-carbonitrile (9). The mixture of trichloride **8** (4.17 g, 20 mmol) and sodium azide (5.2 g, 80 mmol) in 150 mL of aq. Acetone (5% of water) was boiled for 6 h, then the solvent was removed under vacuum, and a solid residue was washed with water (200 mL), dried on air and recrystallized. Triazide **9** was obtained as a colorless solid (3.74 g, 82%). mp 118–120 °C (EtOH). IR (microcrystals, $\nu_{\text{max}}/\text{cm}^{-1}$): 2235m, 2213m, 2160vs, 2133s, 2096m, 1562s, 1530vs, 1421s, 1371vs, 1280w, 1239s, 1209vs, 1156m, 1136m, 1083w, 1030w, 1006m, 969w, 811m, 782vs, 742s, 696w. UV-vis, $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 249 (4.03), 275 (3.55), 295 (3.46), 304 (3.42). ^{13}C -NMR: δ 80.9, 110.4, 162.7, 166.9. ^{15}N -NMR: δ -99.8, -130.2, -132.4, -142.3, -144.2, -148.6, -257.0, -259.7. EIMS, 70 eV, m/z (rel.int.): 229 (4, $\text{M}^+ + 1$), 228 (30, M^+), 92 (7, C_3N_4^+), 90 (8, C_4N_3^+), 78 (100, C_3N_3^+), 68 (5, CN_4^+), 66 (31, C_2N_3^+), 64 (70, C_3N_2^+), 54 (11, CN_3^+), 52 (35, C_2N_2^+), 50 (12, C_3N^+), 42 (12, N_3^+), 40 (18, CN_2^+), 38 (46, C_2N^+), 26 (9, CN^+). Anal. Calcd. for C_5N_{12} (228.13): C, 26.32; N, 73.68. Found: C, 26.55; N, 73.45%.

X-ray structural studies of compound 9. The X-ray diffraction measurements were performed on a Xcalibur diffractometer with EOS CCD detector (Agilent Technologies UK Ltd.). The recording of reflections, determination and refinement of unit cell parameters were performed at 100(1) K with monochromatic MoK α radiation at λ 0.71073 Å, using the CrysAlis PRO software.³⁸ All calculations were performed with the SHELXTL software suite.³⁹ Molecular formula C₅N₁₂, M 228.17, monocrystal size 0.4 × 0.2 × 0.05 mm; monoclinic syngony; space group *P*2₁/*c*; *a* 11.3672(6), *b* 10.6484(6), *c* 15.2093(8) Å; *V* 1819.1(2) Å³; *Z* 8; *d*_{calc} 1.666 g/cm³; μ (MoK α) 0.129 mm⁻¹. The intensities of 9321 reflections were measured ($2\theta < 58.14^\circ$), and 4871 independent reflections (*R*_{int} 0.0291) were used for further refinement. The final values of structure probability factors: *R*₁ 0.0447 (*wR*₂ 0.0891) for 3536 observed reflections with *I* > 2 σ (*I*), *R*₁ 0.0743 (*wR*₂ 0.1008) for all independent reflections, the number of refinement parameters was 307, *GOF* 0.995. The complete crystallographic dataset for compound **9** was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1588853).

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Supplementary Material

Supplementary material features ¹³C and ¹⁵N NMR, IR, EIMS, and UV spectra of triazide **9**, CBS-4M calculations on isodesmic reactions for **1** and **9**, and Cartesian coordinates for the B3LYP/6-311+G(d) optimized geometries of **1** and **9**.

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