# Synthesis and structure of 3,4,5-triazidopyridine-2,6-dicarbonitrile possessing the record positive heat of formation

Sergei V. Chapyshev,*[a] Denis V. Korchagin,[a,b] Alexander V. Chernyak[a] and Sergei M. Aldoshin[a]

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka,
Moscow Region, Russian Federation. Fax: +7 496 515 3588; e-mail: chap@icp.ac.ru*
[b] *Peoples' Friendship University of Russia, 117198 Moscow, Russian Federation*

**3,4,5-Triazidopyridine-2,6-dicarbonitrile, the first aromatic triazide with three adjacent azido groups in the ring, possessing the record positive heat of formation, was synthesized by azidation of 3,4,5-trichloropyridine-2,6-dicarbonitrile and characterized with X-ray analysis, thermogravimetry, differential scanning calorimetry and spectroscopic methods.**
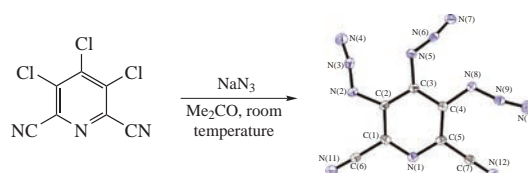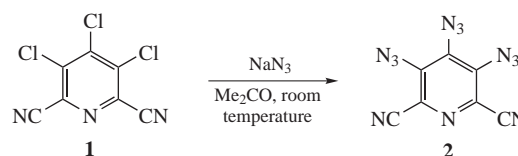
To the moment, 26 six-membered aromatic triazides are known, and, in all of them, the azido groups are located in *meta*-positions relative to each other.[1] The first representative of these compounds, 2,4,6-triazido-1,3,5-triazine (TAT), synthesized by Finger[2] in 1907, has played an important role in the development of chemistry. The X-ray diffraction studies of this triazide for the first time proved a linear structure of the azido groups in organic azides.[3] This finding stimulated the elaboration of such important reactions as the 1,3-dipolar cycloadditions of olefins and acetylenes to azides and the copper-catalyzed azide-alkyne cycloadditions or so-called click-reactions.[4] Furthermore, the detonative decomposition of TAT allowed one to accomplish the first preparation of the $C_3N_4$ carbon nitride nanomaterials[5] and nanotubes[6] possessing unique physical and chemical properties, and the photolysis of TAT made it possible to generate septet 2,4,6-trinitreno-1,3,5-triazine possessing the strongest magnetic properties among all organic hexaradicals.[7] It is worth to note that the first septet organic hexaradical was generated also from an aromatic triazide, namely, from 1,3,5-triazidobenzene-2,4,6-tricarbonitrile.[8] Currently, the photolysis of 2,4,6-tri-azidopyrimidines,[9] 2,4,6-triazidopyridines[10] and 1,3,5-triazido-benzenes[11] is widely used for preparation of various high-spin nitrenes utilized in spin chemistry and investigations of the molecular magnetism. However, the main interest to the synthesis of new aromatic triazides is caused, first of all, by the use of these compounds as green primary explosives and promising components of high-energy organic materials.[12] For a long time, TAT with the positive heat of formation of $\Delta H_\mathrm{f} = 5162$ J g$^{-1}$ was the most energetic representative of aromatic triazides.[13] Unfortunately, this triazide has a low thermal stability (mp 94 °C), high volatility and extremely high sensitivity to mechanical stimuli and electrostatic discharge. Only recently, 2,4,6-triazidopyridine-3,5-dicarbonitrile (TAPDN) has been synthesized, possessing the higher positive heat of formation of $\Delta H_\mathrm{f} = 5740$ J g$^{-1}$, a relatively high thermal stability (mp 127–129 °C), low volatility and low risk to explode on handling.[14] This finding has stimulated us to investigate the structural isomers of TAPDN.

In this work we report on the synthesis, structure and properties of 3,4,5-triazidopyridine-2,6-dicarbonitrile **2** representing the first aromatic triazide with three adjacent azido groups in the

ring and possessing the record positive heat of formation among aromatic triazides.

To synthesize triazide **2**, we used commercially available trichloropyridine **1** as a starting material. It was reported that this trichloride reacts almost instantly with sodium methanethiolate in methanol at room temperature to form the corresponding 3,4,5-trimethylthiopyridine-2,6-dicarbonitrile in nearly quantitative yield.[15] The reaction between compound **1** and excess sodium azide was carried out in aqueous acetone at room temperature.[†] The TLC monitoring indicated almost instant formation of a single product that, according to analytical and spectroscopic studies as well as X-ray analysis, was triazide **2** (Scheme 1).
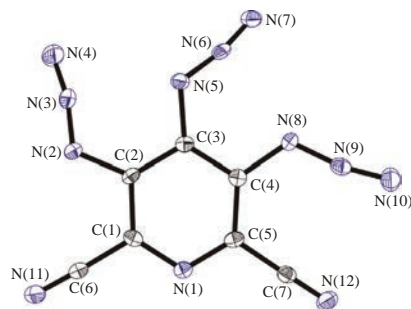


**Scheme 1**

**Figure 1** Molecular structure of triazide **2**.

The X-ray diffraction studies (Figure 1)$^‡$ show that all three azido groups in the molecule of **2** are structurally almost identical ($C–N_\alpha–N_\beta \sim 119°$, $N_\alpha–N_\beta–N_\gamma \sim 169°$, $C–N_\alpha \sim 1.40$ Å, $N_\alpha–N_\beta \sim 1.26$ Å and $N_\beta–N_\gamma \sim 1.13$ Å). Moreover, these groups display also very close signals in the $^{15}$N NMR spectrum.$^§$ All these data drastically contrast with the results of the X-ray diffraction[16] and $^{15}$N NMR spectroscopic[17] studies of isomeric TAPDN, whose α- and γ-azido groups considerably differ in the $C–N_\alpha$, $N_\alpha–N_\beta$, $N_\beta–N_\gamma$ bond lengths, the $C–N_\alpha–N_\beta$ and $N_\alpha–N_\beta–N_\gamma$ bond angles and $^{15}$N NMR spectroscopic characteristics. Note also that the molecule of **2** is characterized by the presence of three intramolecular interactions, namely, two $N_\alpha\cdots N_\beta$ contacts between the neighboring azido groups with $E \sim 3.8$ kcal mol$^{-1}$ and a $C\cdots N_\beta$ contact between the azido and cyano groups with $E \sim 2.2$ kcal mol$^{-1}$.

To investigate the thermal stability of triazide **2**, the thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) of **2** and isomeric TAPDN were carried out.$^§$ The gaseous products formed during the thermal decomposition of **2** and TAPDN were analyzed by mass spectrometry. The results of these studies are summarized in Table 1. It was found that, as compared with TAPDN, triazide **2** has the lower points of melting and thermal decomposition, but produces more heat and volatile products during its decomposition. In both cases, $N_2$ and $(CN)_2$ were the major gaseous products formed during the thermolysis. Earlier, the same gaseous products were detected during the thermolysis of TAT.[5] The formation of cyanogen is also observed during the fragmentation of **2** upon the action of electron impact.$^§$ The main pathway of this fragmentation involves the generation of $[M]^{+\cdot}$ (14%), $[M–N_2]^{+\cdot}$ (5%), $[M–N_2–2CN_3]^{+\cdot}$ (66%), $[M–N_2–2CN_3–2CN]^{+\cdot}$ (100%) and $[M–N_2–2CN_3–2CN–C]^{+\cdot}$ (10%), among which the ion of carbene NCCCN is

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$^‡$ *Crystallographic data.* The crystals of **2** ($C_7N_{12}$, $M = 252.19$) were grown up on cooling the solution of **2** in ethanol, orthorhombic, space group $Pca2_1$, at 100.0(2) K: $a = 14.7596(11)$, $b = 7.0507(5)$ and $c = 9.8837(8)$ Å, $V = 1028.6(1)$ Å$^3$, $Z = 4$, $d_{calc} = 1.629$ g cm$^{-3}$, $\mu$(MoK$\alpha$) = 0.123 cm$^{-1}$, $F(000) = 504$. Intensities of 2810 reflections were measured with a CCD diffractometer Agilent XCalibur with EOS detector (Agilent Technologies UK Ltd., Yarnton, Oxfordshire, England) [$\lambda$(MoK$\alpha$) = 0.71073 Å, $\omega$-scans, $2\theta < 53.98°$] and 1685 independent reflections ($R_{int} = 0.0293$) were used in the further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against $F^2$ in the anisotropic approximation. The refinement converged to $wR_2 = 0.0761$ and GOF = 1.024 for all independent reflections [$R_1 = 0.0458$ was calculated for 1423 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL program.[19]

CCDC 1483911 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

$^§$ The details of physicochemical studies, $^{13}$C and $^{15}$N NMR spectra, mass spectrum, IR spectrum, selected crystallographic data, TGA and DSC plots and DFT and CBS-4M calculations on isodesmic reactions are presented in Online Supplementary Materials.

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**Table 1** TGA and DSC parameters of triazides **2** and TAPDN under the heating rate of 5.0 K min$^{-1}$.

| Azide | Mp/°C$^a$ | Tp/°C$^b$ | $\Delta H^c$/J g$^{-1}$ | Mass change (%) |
|---|---|---|---|---|
| **2** | 112.7 | 138.0 | 1876 | –56.75 |
| TAPDN | 127.8 | 173.0 | 1830 | –35.80 |

$^a$ Peak temperature of melting. $^b$ Peak temperature of decomposition. $^c$ Total heat release.

the most intense. Previous studies have shown that this carbene was also one of the major products of the photolysis of TAT[7] and 2,4,6-triazidopyrimidine.[9] The most interesting feature of fragmentation of **2** is the generation of intense ion $[M–N_2–2CN_3]^{+\cdot}$ as the result of decomposition of the β-azido group of **2** followed by a formal elimination of the $N_3CCN_3$ fragment from the $[M–N_2]^{+\cdot}$ ion. This process occurs only for triazide **2** containing three adjacent azido groups on the aromatic ring.

Unfortunately, triazide **2** appeared to be too explosive to experimentally determine its positive heat of formation using the bomb calorimetry technique. Therefore, we used the isodesmic reaction method in combination with density functional theory (DFT) calculations with the CBS-4M approach$^{18(a)}$ to estimate the positive heat of formation of **2**.$^§$ This method is rather accurate and widely employed in the chemistry of high-energy compounds.$^{18(b),(c)}$ The isodesmic reactions used for **2** and TAPDN are shown in Scheme 2.
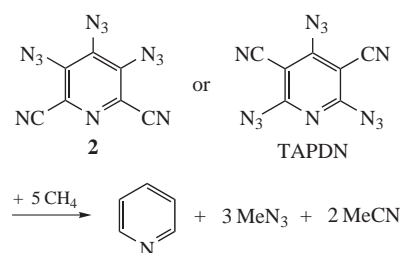


**Scheme 2**

The calculations show that the positive heat of formation of TAPDN for a gas phase at 298 K equals to $\Delta H_f = 1406$ kJ mol$^{-1}$ what is quite close to the experimentally measured value of $\Delta H_f = 1446$ kJ mol$^{-1}$. For triazide **2**, the calculations predict $\Delta H_f = 1470$ kJ mol$^{-1}$ or by 64 kJ mol$^{-1}$ higher than that of TAPDN. These data suggest that triazide **2** should have the record positive heat of formation of $\Delta H_f \approx 6000$ J g$^{-1}$ among all known to date six-membered aromatic triazides. It should also be noted that, according to preliminary tests, triazide **2** has nearly the same sensitivity to mechanical stimuli as TAPDN[14] and is quite safe on careful handling.

In summary, we have reported on the synthesis, structure and properties of 3,4,5-triazidopyridine-2,6-dicarbonitrile **2** as the first representative of aromatic triazides with three adjacent azido groups in the ring, possessing the record positive heat of formation among aromatic triazides. This triazide is readily obtained in one step and in high yield from a commercially available precursor and may be of interest as a promising component of high-energy materials.

*Online Supplementary Materials*
Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.03.002.

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