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Bis(furazano)pyridinone *N*,*N′*-dioxide: a new high-density insensitive explosive

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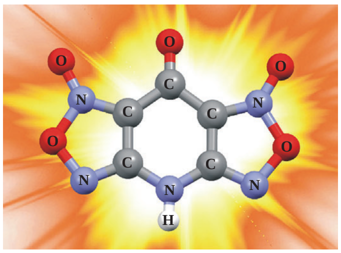
The synthesis and properties of novel high-dense energetic material based on new 4*H*,8*H*-bis(furazano)[3,4-*b*:3′,4′-*e*]pyridine ring system are described. An operationally simple, efficient and scalable protocol towards 4*H*,8*H*-bis(furazano)[3,4-*b*:3′,4′-*e*]pyridin-8-one 1,7-dioxide from commercially available 4-amino-2,6-dichloropyridine in three steps, namely, nitration–azidation–cascade ring closure, has been developed.

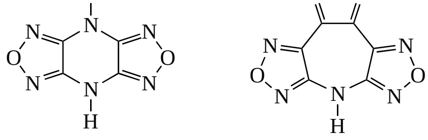


Keywords: fused pyridine, furazan, furoxan, cascade reaction, energetic compound.

The first derivative of the [1,2,5]oxadiazolo[3,4-*b*]pyridine ring system, often called furazano[3,4-*b*]pyridine and furoxano[3,4-*b*]pyridine for the *N*-oxide, has been reported about seventy years ago, when Boyer *et al*. described its synthesis by heating 8-nitrotetrazolo[1,5-*a*]pyridine.[1] In subsequent years, several methods for the preparation of compounds with this ring system, their reactivity and fields of application were described. A comprehensive review on the development of the furazanopyridine chemistry appeared in 1999.[2] While polycyclic compounds in which two and three furazan rings are fused to the same benzene ring have been described,[3] similar polycyclic structures based on the pyridine ring are not known.

The furazan ring is important building block used to construct high-performance energetic materials.[4] Many furazan-fused polycycle-based high-performance energetic compounds have been developed by our group and others. For example, 4*H*,8*H*-bis(furazano)[3,4-*b*:3′,4′-*e*]pyrazine **1**[5] and 7*H*-tris(furazano)-[3,4-*b*:3′,4′-*d*:3″,4″-*f*]azepine 1-oxide **2**[6] (Figure 1) possessed high thermal stability and low sensitivity towards mechanical stimuli which are induced by the NH-bridge between rings. A number of methods for N-functionalization have been developed, which made it possible to tune the properties of parent polycycles **1**[7] and **2**.[8]

Recognizing that new NH-containing high-nitrogen framework should attract interest of chemists involved in the creation of new energetic materials, we turned our attention to pyridin-4-one fused with two furazan rings as an unexplored chemotype of energetic polycycles. Herein we report our results toward this goal.

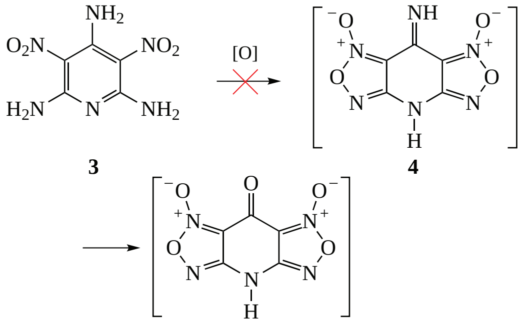


1 **2**

Figure 1 Parent energetic polycycles on the basis of the difurazanyl amine.

Oxidation of *o*-nitroaminopyridines and thermolysis of nitrotetrazolo[1,5-*a*]pyridines are two general and convenient protocols for the synthesis of various furoxano[3,4-*b*]pyridines.[2,3(*a*)] We first attempted the direct oxidation of commercially available 3,5-dinitro-2,4,6-triaminopyridine **3** (Scheme 1) using PhI(OAc)$_2$, NaOCl, or NaOBr, however, these attepmts were unsuccessful despite significant efforts to optimize all oxidation protocols.

We concentrated therefore on the route outlined in Scheme 2 employing a tetrazole chemistry. Commercially available 4-amino-2,6-dichloropyridine **6** was nitrated by a modified procedure[9] with a mixture of 100% nitric acid in sulfuric acid to give dinitro derivative **7** in 84% yield. The next step[9] was improved using acetone/methanol as the reaction medium. Simple treatment of compound **7** with sodium azide at 40 °C afforded 4-amino-5-nitrofurazano[3,4-*e*]tetrazolo[1,5-*a*]pyridine 3-oxide **9** in 90% isolated yield. It is important to note that one azido group of



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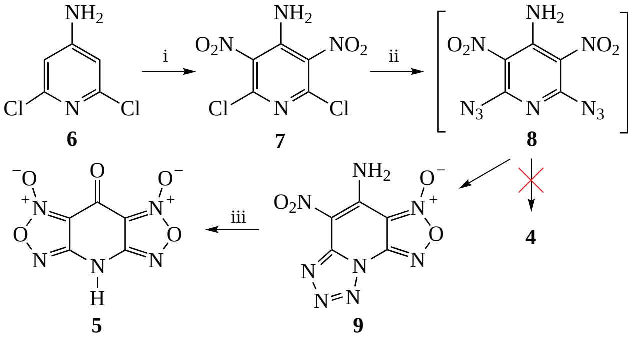
Scheme 1



Scheme 2 *Reagents and conditions*: i, HNO_3/H_2SO_4, 80–85 °C; ii, NaN_3, MeOH/acetone/H_2O, 40 °C; iii, selection of conditions.

intermediate diazide **8** undergoes the transformation with the loss of the N_2 molecule followed by furoxan ring closure. The other azido group undergoes azido–tetrazole tautomerism leading to stable tetrazolo form **9**. Evidently, the nitrotetrazolo[1,5-*a*]pyridine fragment of compound **9** is stable under these conditions and does not undergo transformation into a second furoxan unit and, as a result, compound **4** is not formed.

Possibility of hydrolysis of amino group is consistent with the chemistry observed for fused *p*-aminopyridines when they are transformed into the corresponding pyridin-4-ones.[10] To put this possibility to the test, amino compound **9** was exposed to an excess of various bases (NaOH, Na_2CO_3, $NaHCO_3$, *etc*.) under reflux in aqueous ethanol. In fact, fused tetrazole **9** underwent hydrolysis/ring opening/ring closure cascade reaction giving the first example of a derivative of the novel bis([1,2,5]oxadiazolo)-[3,4-*b*:3′,4′-*e*]pyridine heterocyclic system, namely, compound **5**. However, the yield of product **5**, depending on the base used, was only from 1 to 7%; high polarity of **5** and other by-products made purification very laborious.

Although there are several acidic reagents available for the conversion of 4-aminopyridines to pyridin-4-ones, more successful reactions using $NaNO_2$ in sulfuric acid have been reported in the literature.[11] Treatment of compound **9** with $NaNO_2$ in 25% H_2SO_4 at 0 → 30 °C for 5 h followed by chromatographic purification afforded yellow crystalline product **5** in 18% yield. Notably, efforts toward process optimization revealed that the addition of stoichiometric amounts of $NaNO_2$ and replacing H_2SO_4 with 25% HNO_3 accelerates the transformation and enables the delivery of a reproducible, good-yielding (46%) process. Surprisingly, when a control experiment was run in 65% HNO_3 at brief refluxing in the absence of $NaNO_2$, the cascade reaction also occurred, and the highest yield of product **5** (71%) was attained, which did not require further purification.

The structure of 4*H*,8*H*-bis(furazano)[3,4-*b*:3′,4′-*e*]pyridin-8-one 1,7-dioxide **5** was confirmed by IR, ^1H and ^{13}C NMR, elemental analysis (see Online Supplementary Materials). Unlike **9**, the IR spectrum of **5** showed the indicative loss of the amino bands at *ca*. 3290/3400 cm^{-1}, demonstrating strong $\nu_{C=O}$ in the *ca*. 1710–1730 cm^{-1} region and NH band at 3330 cm^{-1}. Ketone **5** had only three signals in the ^{13}C NMR spectrum, which confirmed the symmetry of its molecule. The structure of **5** was unequivocally determined by single crystal X-ray crystallography (Figure 2), both at room temperature and at 100 K, using a sample recrystallized from $CHCl_3$.[†]

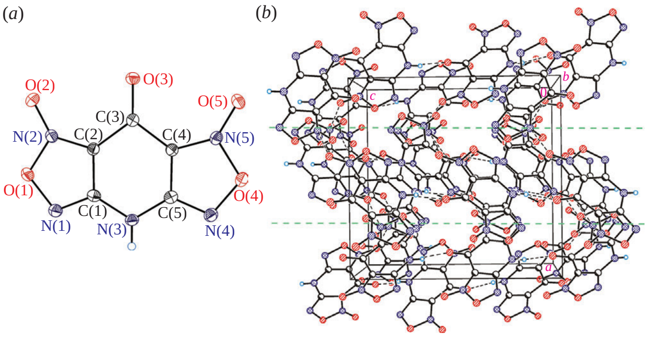


Figure 2 (*a*) Thermal-ellipsoid plot (50%) and atom-labeling scheme for compound **5**. (*b*) Crystal packing view for **5**. H-bonded chains along the *c* axis are connected to each other by π···π interactions to form planes parallel to *bc* crystallographic plane (shown by green dashed lines); interplanar connection is provided by O(N)···π interactions. Small dashed lines indicate hydrogen bonding.

A number of interesting features in structure **5** can be noted on the basis of the X-ray study. First, the orientation of the carbonyl oxygen atom and exocyclic oxygen atoms of the furoxan units are such that they are all close together. Second, although molecule **5** is planar, it does not form graphite-like structure. The interactions between the carbonyl and NH groups form an infinite hydrogen-bonded chain, which presumably causes a significant angle between the planes of adjacent molecules. H-Bonded chains are linked by π···π and O(N)···π interactions into quite dense crystal structure [d = 1.972 g cm^{-3} at 100 K, and 1.925 g cm^{-3} at 297 K, Figure 2(*b*)]. An analysis of crystal packing of compound **5** was carried out in terms of a Δ_{OED}-based densification approach[12] (for details, see Online Supplementary Materials).

For preliminary safety and performance testing, the properties of compound **5** were compared with those of 3-nitro-1,2,4-triazol-5-one (NTO), which is considered the benchmark insensitive thermostable explosive.[13] According to differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) measurements (scanning at 5 K min^{-1}), compound **5** decomposes (onset temperature) without melting at 184 °C. Thus, this compound is less stable thermally than NTO ($T_{d/onset}$ = 236 °C). Moreover, with more positive enthalpy of formation (+0.998 *vs*. –0.828 kJ g^{-1}) and a slightly higher experimental density (1.925 *vs*. 1.911 g cm^{-3}), compound **5** exhibits better detonation performance than NTO (detonation pressure, *P*, 33.6 *vs*. 32.3 Gpa; detonation velocity, *D*, 8543 *vs*. 8390 m s^{-1}) while its impact sensitivity is also slightly higher, 90 *vs*. 80% (K-44-II impact machine, set no. 1,[14] 10 kg per 25 cm). Thus, it is a promising energetic material that could be of interest for future applications.

In conclusion, we have developed an operationally simple, efficient and scalable protocol for the three-step synthesis of 4*H*,8*H*-bis(furazano)[3,4-*b*:3′,4′-*e*]pyridin-8-one 1,7-dioxide (**5**) from commercially available 4-amino-2,6-dichloropyridine, followed by nitration, azidation and cascade ring closure. All reactions occur with inexpensive reagents under mild conditions. Compound **5**, being the first example of a derivative of the new

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[†] *Crystallographic data for compound* **5**. Experiment at 100 K: $C_5HN_5O_5$, M = 211.11, orthorhombic, space group *Pbca*, a = 11.7455(12), b = 9.7598(9) and c = 12.4030(12) Å, V = 1421.8(2) $Å^3$, Z = 8, d_{cryst} = 1.972 g cm^{-3}, wR_2 = 0.0926 calculated on F^2_{hkl} for all 1889 independent reflections with $2\theta < 58.0°$, [GOF = 1.048, R = 0.0335 calculated on F_{hkl} for 1731 reflections with $I > 2\sigma(I)$].

Experiment at 298 K: $C_5HN_5O_5$, M = 211.11, orthorhombic, space group *Pbca*, a = 11.7901(16), b = 9.9005(14) and c = 12.4808(17) Å, V = 1456.9(3) $Å^3$, Z = 8, d_{cryst} = 1.925 g cm^{-3}. wR_2 = 0.1481 calculated on F^2_{hkl} for all 3374 independent reflections with $2\theta < 71.4°$, [GOF = 1.041, R = 0.0493 calculated on F_{hkl} for 2165 reflections with $I > 2\sigma(I)$].

CCDC 2108305 and 2108306 contain 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.

heterocyclic system, displays high density, acceptable thermal stability and sensitive to impact, and is predicted to be superior to NTO performance.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.037.

References

1 J. H. Boyer, D. I. McCane, W. J. McCarville and A. T. Tweedie, *J. Am. Chem. Soc*., 1953, **75**, 5298.

2 A. B. Sheremetev, *Russ. Chem. Rev*., 1999, **68**, 137 (*Usp. Khim*., 1999, **68**, 154).

3 (*a*) L. I. Khmel'nitskii, S. S. Novikov and T. I. Godovikova, *Khimiya furoksanov*: *stroenie i sintez* (*Chemistry of Furoxans: Structure and Synthesis*), 2nd edn., Nauka, Moscow, 1996 (in Russian); (*b*) L. Türker and S. Variş, *Polycyclic Aromat. Compd*., 2009, **29**, 228; (*c*) E. A. Chugunova, A. S. Gazizov, A. R. Burilov, L. M. Yusupova, M. A. Pudovik and O. G. Sinyashin, *Russ. Chem. Bull., Int. Ed*., 2019, **68**, 887 (*Izv. Akad. Nauk, Ser. Khim*., 2019, 887).

4 (*a*) L. L. Fershtat and N. N. Makhova, *ChemPlusChem*, 2020, **85**, 13; (*b*) J. Zhang, J. Zhou, F. Bi and B. Wang, *Chin. Chem. Lett*., 2020, **31**, 2375; (*c*) S. G. Zlotin, A. M. Churakov, M. P. Egorov, L. L. Fershtat, M. S. Klenov, I. V. Kuchurov, N. N. Makhova, G. A. Smirnov, Yu. V. Tomilov and V. A. Tartakovsky, *Mendeleev Commun*., 2021, **31**, 731; (*d*) J. Zhou, J. L. Zhang, B. Z. Wang, L. L. Qiu, R. Q. Xu and A. B. Sheremetev, *FirePhysChem*, 2022, **2** (1), doi: 10.1016/j.fpc.2021.09.005.

5 (*a*) I. B. Starchenkov and V. G. Andrianov, *Chem. Heterocycl. Compd*., 1996, **32**, 618 (*Khim. Geterotsikl. Soedin*., 1996, 717); (*b*) A. B. Sheremetev and I. L. Yudin, *Mendeleev Commun*., 1996, **6**, 247; (*c*) B. B. Averkiev, A. A. Korlyukov, M. Yu. Antipin, A. B. Sheremetev and T. V. Timofeeva, *Cryst. Growth Des*., 2014, **14**, 5418; (*d*) D. B. Lempert, A. I. Kazakov, A. B. Sheremetev, A. G. Gladyshkin, A. V. Nabatova and L. S. Yanovskii, *Russ. Chem. Bull*., *Int. Ed*., 2019, **68**, 1856 (*Izv. Akad. Nauk, Ser. Khim*., 2019, 1856).

6 (*a*) A. A. Astrat'ev, D. V. Dashko and A. I. Stepanov, *Cent. Eur. J. Chem*., 2012, **10**, 1087; (*b*) S. M. Aldoshin, D. B. Lempert, T. K. Goncharov, A. I. Kazakov, S. I. Soglasnova, E. M. Dorofeenko and N. A. Plishkin, *Russ. Chem. Bull., Int. Ed*., 2016, **65**, 2018 (*Izv. Akad. Nauk, Ser. Khim*., 2016, 2018); (*c*) Z. G. Aliev, T. K. Goncharov, D. V. Dashko, E. L. Ignat'eva, A. A. Vasil'eva, N. I. Shishov, D. V. Korchagin, Yu. M. Milekhin and S. M. Aldoshin, *Russ. Chem. Bull., Int. Ed*., 2017, **66**, 694 (*Izv. Akad. Nauk, Ser. Khim*., 2017, 694); (*d*) D. B. Lempert, V. V. Raznoschikov and L. S. Yanovskiy, *Russ. J. Appl. Chem*., 2019, **92**, 1690 (*Zh. Prikl. Khim*., 2019, **92**, 1578).

7 (*a*) A. B. Sheremetev, V. O. Kulagina, I. L. Yudin and N. E. Kuzmina, *Mendeleev Commun*., 2001, **11**, 112; (*b*) I. N. Zyuzin, K. Yu. Suponitsky and A. B. Sheremetev, *J. Heterocycl. Chem*., 2012, **49**, 561; (*c*) A. B. Sheremetev and I. L. Yudin, *Russ. Chem. Rev*., 2003, **72**, 87 (*Usp. Khim*., 2003, **72**, 93); (*d*) N. Liu, Y. Shu, H. Li, L. Zhai, Y. Li and B. Wang, *RSC Adv*., 2015, **5**, 43780; (*e*) W. Li, J. Tian, X. Qi, K. Wang, Y. Jin, B. Wang and Q. Zhang, *ChemistrySelect*, 2018, **3**, 849; (*f*) W. Li, K. Wang, X. Qi, Y. Jin and Q. Zhang, *Cryst. Growth Des*., 2018, **18**, 1896; (*g*) C. J. Snyder, L. A. Wells, D. E. Chavez, G. H. Imler and D. A. Parrish, *Chem. Commun*., 2019, **55**, 2461.

8 (*a*) A. I. Stepanov, A. A. Astrat'ev, D. V. Dashko, N. P. Spiridonova, S. F. Mel'nikova and I. V. Tselinskii, *Russ. Chem. Bull., Int. Ed*., 2012, **61**, 1024 (*Izv. Akad. Nauk, Ser. Khim*., 2012, 1019); (*b*) A. I. Stepanov, D. V. Dashko and A. A. Astrat'ev, *Chem. Heterocycl. Compd*., 2013, **49**, 1068; (*c*) B.-H. Duan, N. Liu, B. Wang, X. Lu, H. Mo, M. Xu and Y. Shu, *Chin. J. Explos. Propellants*, 2019, **42**, 114, doi: 10.14077/j.issn.1007-7812.2019.02.002; (*d*) A. I. Kazakov, D. B. Lempert, A. V. Nabatova, D. V. Dashko, V. V. Raznoschikov, L. S. Yanovskii and S. M. Aldoshin, *Russ. J. Appl. Chem*., 2019, **92**, 1696 (*Zh. Prikl. Khim*., 2019, **92**, 1657); (*e*) L. Zhai, F. Bi, H. Huo, Y. Luo, X. Li, S. Chen and B. Wang, *Front. Chem*., 2019, **7**, doi.org/10.3389/fchem.2019.00559; (*f*) D. B. Lempert, A. I. Kazakov, A. V. Nabatova, D. V. Dashko, A. I. Stepanov, G. V. Shilov and S. M. Aldoshin, *Combust., Explos. Shock Waves*, 2020, **56**, 621 [*Fiz. Goreniya Vzryva*, 2020, **56** (6), 3]. (*g*) N. Liu, C. Xiao, B. Duan, X. Lu, B. Wang, J. Zhang and Q.-L. Yan, *ACS Appl. Energy Mater.*, 2020, 7129.

9 C. Ma, Y. Pan, J. Jiang, Z. Liu and Q. Yao, *New J. Chem*., 2018, **42**, 11259.

10 (*a*) J. H. Wilkinson and I. L. Finar, *J. Chem. Soc*., 1948, 32; (*b*) A. Tatibouet, M. Demeunynck and J. Lhomme, *Synth. Commun*., 1996, **26**, 4375.

11 (*a*) A. Hampton and D. Magrath, *J. Chem. Soc*., 1949, 1008; (*b*) K. H. Oh, J. G. Kim and J. K. Park, *Org. Lett*., 2017, **19**, 3994.

12 (*a*) I. L. Dalinger, K. Yu. Suponitsky, T. K. Shkineva, D. B Lempert and A. B. Sheremetev, *J. Mater. Chem. A*, 2018, **6**, 14780; (*b*) N. V. Palysaeva, A. G. Gladyshkin, I. A. Vatsadze, K. Yu. Suponitsky, D. E. Dmitriev and A. B. Sheremetev, *Org. Chem. Front.*, 2019, **6**, 249; (*c*) K. Yu. Suponitsky, A. F. Smol'yakov, I. V. Ananyev, A.V. Khakhalev, A. A. Gidaspov and A. B. Sheremetev, *ChemistrySelect*, 2020, **5**, 14543.

13 R. R. Sirach and P. N. Dave, *Chem. Heterocycl. Compd*., 2021, **57**, 720.

14 *Fizika Vzryva* (*Physics of Explosion*), ed. L. P. Orlenko, 3rd edn., Fizmatlit, Moscow, 2002, vol. 1 (in Russian).

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