Electronic supplementary materials *Mendeleev Commun.*, 2016, **26**, 16−18

Insertion of 1,3-diphenylprop-2-yn-1-one into imidazo[4,5-*b*]pyridines in the presence of water: one-pot synthesis of pyrido[2,3-*b*][1,4]diazocin-9-ones

Boris A. Trofimov, Lina P. Nikitina, Kseniya V. Belyaeva, Ludmila V. Andriyankova, Anastasiya G. Mal'kina, Irina Yu. Bagryanskaya, Andrei V. Afonin and Igor A. Ushakov

The XRD data (Table S1) for pyridodiazocinone **3a** was collected with a Bruker Kappa Apex II diffractometer, using Mo-Kα (λ = 0.71073 Å) radiation with a graphite monochromator. Absorption corrections were applied using the empirical multiscan method with the SADABS program.[1] The structures were solved by direct methods using the SHELXS-97 program[2] and refined by the least-squares method in the fullmatrix anisotropic approximation using the SHELXL-97 program.[2] The H atom positions were located geometrically and refined using a riding model. The obtained structure was analyzed for exposing shortened contacts between nonbonded atoms with the programs PLATON[3] and MERCURY.[4] CCDC 1032968 (for **3a**) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

The bond lengths and bond angles of pyridodiazocinone **3a** are typical.[5] The conformation of 8-membered ring in molecules of compound is very similar to the boat. The molecules of compound are packed into infinite chains in crystal along *b* axis (Figure S2) by intermolecular H-bonds C-H…O with parameters specified in Table S2.

Table S1 XRD data for compound pyridodiazocinone **3a**.

Compound	Pyridodiazocinone **3a**
Empirical formula	$C_{22}H_{17}N_3O$
Formula weight	339.39
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions *a* Å	18.588(2)
b Å	9.0500(7)
c Å	21.296(2)
β °	100.020(4)
Volume $Å^3$	3527.9(5)
Z	8
Density (calcd.) $Mg.m^{-3}$	1.278
Abs. coefficient mm^{-1}	0.080
F(000)	1424
Crystal size mm^3	0.80 x 0.60 x 0.40
Θ range for data collection °	1.3 - 26.0
Index ranges	$-20 \leq h \leq 20$, $-4 \leq k \leq 4$, $-13 \leq l \leq 13$
Reflections collected	57680
Independent reflections	6941 R(int)= 0.052
Observed data (I > 2.0 σ(I))	4710
Completeness to θ %	99.3
Data / restraints / parameters	6941 / 0 / 471
Goodness-of-fit on F^2	1.07
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0515$, $wR_2 = 0.1416$
Final R indices (all data)	$R_1 = 0.0854$, $wR_2 = 0.1862$
Largest diff. peak / hole $e.Å^{-3}$	0.35 / -0.42

Table S2 Values of H-bond according to the of X-ray diffraction data for pyridodiazocinone **3a**.

intermolecular H-bond				intramolecular H-bond			
interaction	H...O* Å	C...O Å	C-H...O °	interaction	H...O Å	C(N)...O Å	C(N)-H...O °
C3A-H3A...O1A	2.57	3.464(2)	161	C10A-H10A...O1A	2.37	2.773(3)	105
C3B-H3B...O1B	2.58	3.454(2)	157	C10B-H10F...O1B	2.35	2.765(3)	105
C7A-H7A...O1A	2.46	3.261(2)	144	C22A-H22A...O1A	2.57	3.141(3)	120
C7B-H7B...O1B	2.54	3.314(3)	141				

*Note, that normal H...O are 2.68 Å.[6]

The structure of compound **3a** is formed by two crystallographically independent molecules (molecule **A** and **B**), one of which is shown in Figure S1.

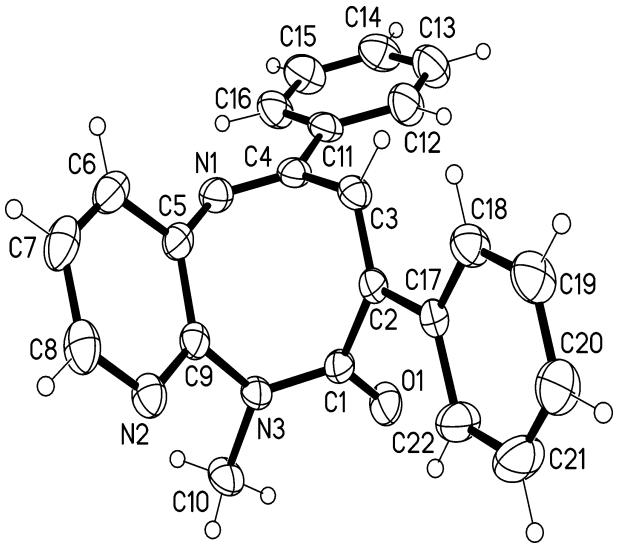

Figure S1 Structure of molecule of pyridodiazocinone **3a** in crystal.

Molecular A

Bond Lengths (Angstrom). - (Bonds are ordered on the first label, left to right and top to bottom) - su in last digit in ().

O(1A) - C(1A)	1.220(2)	N(1A) - C(4A)	1.290(3)	N(1A) - C(5A)	1.414(3)	N(2A) - C(8A)	1.333(2)		
N(2A) - C(9A)	1.332(2)	N(3A) - C(1A)	1.359(2)	N(3A) - C(9A)	1.422(2)	N(3A) - C(10A)	1.470(3)		
C(1A) > C(2A)	1.513(3)	C(2A) - C(3A)	1.336(3)	C(2A) > C(17A)	1.488(3)	C(3A) > C(4A)	1.481(3)		
C(4A) > C(11A)	1.481(3)	C(5A) - C(6A)	1.387(3)	C(5A) - C(9A)	1.398(3)	C(6A) - C(7A)	1.373(3)		
C(7A) - C(8A)	1.370(3)	C(11A) - C(12A)	1.386(3)	C(11A) - C(16A)	1.389(3)	C(12A) - C(13A)	1.389(4)		
C(13A) - C(14A)	1.366(4)	C(14A) - C(15A)	1.373(5)	C(15A) - C(16A)	1.389(4)	C(17A) - C(18A)	1.395(3)		
C(17A) - C(22A)	1.393(3)	C(18A) - C(19A)	1.386(3)	C(19A) - C(20A)	1.369(4)	C(20A) - C(21A)	1.364(4)		
C(21A) - C(22A)	1.397(4)								

Bond/Valence Angles (Degrees) - (Angles are ordered on the middle label, left to right and top to bottom) - su in last digit in ().

C(4A) - N(1A) - C(5A)	121.23(17)	C(8A) - N(2A) - C(9A)	117.48(18)	C(1A) - N(3A) - C(9A)	122.27(15)				
C(1A) - N(3A) - C(10A)	120.05(15)	C(9A) - N(3A) - C(10A)	117.66(15)	O(1A) - C(1A) - N(3A)	122.76(18)				
O(1A) - C(1A) - C(2A)	120.19(17)	N(3A) - C(1A) - C(2A)	116.99(16)	C(1A) - C(2A) - C(3A)	118.83(17)				
C(1A) - C(2A) - C(17A)	116.02(16)	C(3A) - C(2A) - C(17A)	125.02(17)	C(2A) - C(3A) - C(4A)	121.42(17)				
N(1A) - C(4A) - C(3A)	121.87(17)	N(1A) - C(4A) - C(11A)	119.18(17)	C(3A) - C(4A) - C(11A)	118.94(16)				

N(1A) - C(5A) - C(6A) 119.41(18) N(1A) - C(5A) - C(9A) 123.70(17) C(6A) - C(5A) - C(9A) 116.60(18)
C(5A) - C(6A) - C(7A) 119.9(2) C(6A) - C(7A) - C(8A) 118.92(18) N(2A) - C(8A) - C(7A) 123.2(2)
N(2A) - C(9A) - N(3A) 115.75(16) N(2A) - C(9A) - C(5A) 123.89(17) N(3A) - C(9A) - C(5A) 120.23(17)
C(4A) - C(11A) - C(12A) 120.41(19) C(4A) - C(11A) - C(16A) 121.13(19) C(12A) - C(11A) - C(16A) 118.5(2)
C(11A) - C(12A) - C(13A) 121.3(2) C(12A) - C(13A) - C(14A) 119.4(3) C(13A) - C(14A) - C(15A) 120.5(3)
C(14A) - C(15A) - C(16A) 120.5(3) C(11A) - C(16A) - C(15A) 120.0(2) C(2A) - C(17A) - C(18A) 121.14(17)
C(2A) - C(17A) - C(22A) 121.01(18) C(18A) - C(17A) - C(22A) 117.83(19) C(17A) - C(18A) - C(19A) 120.9(2)
C(18A) - C(19A) - C(20A) 120.5(2) C(19A) - C(20A) - C(21A) 119.7(2) C(20A) - C(21A) - C(22A) 120.9(2)
C(17A) - C(22A) - C(21A) 120.2(2)

Torsion/Dihedral Angles (Deg.)-Klyne & Prelog Convention (Dunitz, p241)-(Excl. Minor Disorder & Embedded Bond Angl. > 160. Deg.)
O(1A) C(1A) N(3A) C(9A) 171.95(19) O(1A) C(1A) N(3A) C(10A) -9.9(3) C(2A) C(1A) N(3A) C(9A) -10.9(3)
C(2A) C(1A) N(3A) C(10A) 167.20(18) O(1A) C(1A) C(2A) C(3A) -101.1(2) O(1A) C(1A) C(2A) C(17A) 75.0(2)
N(3A) C(1A) C(2A) C(3A) 81.7(2) N(3A) C(1A) C(2A) C(17A) -102.2(2) C(1A) C(2A) C(3A) C(4A) -9.6(3)
C(17A) C(2A) C(3A) C(4A) 174.72(17) C(1A) C(2A) C(17A)C(18A) 172.44(18) C(1A) C(2A) C(17A)C(22A) -6.3(3)
C(3A) C(2A) C(17A) C(18A) -11.8(3) C(3A) C(2A) C(17A) C(22A) 169.5(2) C(2A) C(3A) C(4A) N(1A) -62.0(3)
C(2A) C(3A) C(4A) C(11A) 118.4(2) C(3A) C(4A) N(1A) C(5A) -1.9(3) C(11A) C(4A) N(1A) C(5A) 177.72(17)
N(1A) C(4A) C(11A) C(12A) 175.7(2) N(1A) C(4A) C(11A) C(16A) -4.5(3) C(3A) C(4A) C(11A) C(12A) -4.8(3)
C(3A) C(4A) C(11A) C(16A) 175.1(2) C(6A) C(5A) N(1A) C(4A) -114.0(2) C(9A) C(5A) N(1A) C(4A) 72.3(2)
N(1A) C(5A) C(6A) C(7A) -174.53(19) C(9A) C(5A) C(6A) C(7A) -0.4(3) N(1A) C(5A) C(9A) N(2A) 171.71(17)
N(1A) C(5A) C(9A) N(3A) -3.9(3) C(6A) C(5A) C(9A) N(2A) -2.1(3) C(6A) C(5A) C(9A) N(3A) -177.73(17)
C(5A) C(6A) C(7A) C(8A) 2.4(3) C(6A) C(7A) C(8A) N(2A) -2.0(4) C(7A) C(8A) N(2A) C(9A) -0.4(3)
N(3A) C(9A) N(2A) C(8A) 178.32(18) C(5A) C(9A) N(2A) C(8A) 2.5(3) N(2A) C(9A) N(3A) C(1A) 125.34(19)
N(2A) C(9A) N(3A) C(10A) -52.8(2) C(5A) C(9A) N(3A) C(1A) -58.7(2) C(5A) C(9A) N(3A) C(10A) 123.1(2)
C(4A) C(11A) C(12A) C(13A) 179.5(2) C(16A) C(11A) C(12A) C(13A) -0.4(4) C(4A) C(11A) C(16A) C(15A) -179.8(2)
C(12A) C(11A) C(16A) C(15A) 0.1(4) C(11A) C(12A) C(13A) C(14A) 0.1(5) C(12A) C(13A) C(14A) C(15A) 0.6(5)
C(13A) C(14A) C(15A) C(16A) -0.9(5) C(14A) C(15A) C(16A) C(11A) 0.6(5) C(2A) C(17A) C(18A) C(19A) 178.7(2)
C(22A) C(17A) C(18A) C(19A) -2.5(3) C(2A) C(17A) C(22A) C(21A) 179.9(2) C(18A) C(17A) C(22A) C(21A) 1.1(3)
C(17A) C(18A) C(19A) C(20A) 2.1(4) C(18A) C(19A) C(20A) C(21A) -0.3(4) C(19A) C(20A) C(21A) C(22A) -1.1(4)
C(20A) C(21A) C(22A) C(17A) 0.7(4)

Molecular B

Bond Lengths (Angstrom). - (Bonds are ordered on the first label, left to right and top to bottom) - su in last digit in ().
O(1B) - C(1B) 1.222(2) N(1B) - C(4B) 1.289(3) N(1B) - C(5B) 1.408(3) N(2B) - C(8B) 1.338(3)
N(2B) - C(9B) 1.331(3) N(3B) - C(1B) 1.359(2) N(3B) - C(9B) 1.423(2) N(3B) - C(10B) 1.466(3)
C(1B) > C(2B) 1.516(3) C(2B) - C(3B) 1.334(3) C(2B) > C(17B) 1.490(3) C(3B) > C(4B) 1.485(3)
C(4B) > C(11B) 1.478(3) C(5B) - C(6B) 1.389(3) C(5B) - C(9B) 1.401(3) C(6B) - C(7B) 1.371(4)
C(7B) - C(8B) 1.370(4) C(11B) - C(12B) 1.388(3) C(11B) - C(16B) 1.396(3) C(12B) - C(13B) 1.390(4)
C(13B) - C(14B) 1.372(4) C(14B) - C(15B) 1.372(4) C(15B) - C(16B) 1.379(4) C(17B) - C(18B) 1.393(3)
C(17B) - C(22B) 1.385(3) C(18B) - C(19B) 1.381(3) C(19B) - C(20B) 1.362(4) C(20B) - C(21B) 1.362(4)
C(21B) - C(22B) 1.387(4)

Bond/Valence Angles (Degrees) - (Angles are ordered on the middle label, left to right and top to bottom) - su in last digit in ().
C(4B) - N(1B) - C(5B) 121.27(17) C(8B) - N(2B) - C(9B) 117.26(19) C(1B) - N(3B) - C(9B) 122.66(15)
C(1B) - N(3B) - C(10B) 120.16(15) C(9B) - N(3B) - C(10B) 117.17(14) O(1B) - C(1B) - N(3B) 122.42(18)
O(1B) - C(1B) - C(2B) 120.32(17) N(3B) - C(1B) - C(2B) 117.24(16) C(1B) - C(2B) - C(3B) 118.46(17)
C(1B) - C(2B) - C(17B) 116.09(16) C(3B) - C(2B) - C(17B) 125.34(17) C(2B) - C(3B) - C(4B) 121.77(17)
N(1B) - C(4B) - C(3B) 121.98(17) N(1B) - C(4B) - C(11B) 119.05(17) C(3B) - C(4B) - C(11B) 118.96(16)
N(1B) - C(5B) - C(6B) 119.52(19) N(1B) - C(5B) - C(9B) 123.39(17) C(6B) - C(5B) - C(9B) 116.78(19)
C(5B) - C(6B) - C(7B) 119.6(2) C(6B) - C(7B) - C(8B) 119.2(2) N(2B) - C(8B) - C(7B) 123.2(2)
N(2B) - C(9B) - N(3B) 115.81(16) N(2B) - C(9B) - C(5B) 123.91(17) N(3B) - C(9B) - C(5B) 120.12(16)
C(4B) - C(11B) - C(12B) 120.85(19) C(4B) - C(11B) - C(16B) 120.90(19) C(12B) - C(11B) - C(16B) 118.2(2)
C(11B) - C(12B) - C(13B) 121.1(2) C(12B) - C(13B) - C(14B) 119.7(3) C(13B) - C(14B) - C(15B) 119.9(2)
C(14B) - C(15B) - C(16B) 121.0(2) C(11B) - C(16B) - C(15B) 120.1(2) C(2B) - C(17B) - C(18B) 121.36(17)
C(2B) - C(17B) - C(22B) 121.40(18) C(18B) - C(17B) - C(22B) 117.20(19) C(17B) - C(18B) - C(19B) 120.9(2)
C(18B) - C(19B) - C(20B) 120.7(2) C(19B) - C(20B) - C(21B) 119.6(2) C(20B) - C(21B) - C(22B) 120.4(3)
C(17B) - C(22B) - C(21B) 121.2(2)
Torsion/Dihedral Angles (Deg.) - Klyne & Prelog Convention (Dunitz, p241) - (Excl. Minor Disorder & Embedded Bond Angl. > 160. Deg.)
O(1B) C(1B) N(3B) C(9B) -173.04(18) O(1B) C(1B) N(3B) C(10B) 8.0(3) C(2B) C(1B) N(3B) C(9B) 9.0(3)
C(2B) C(1B) N(3B) C(10B) -169.99(17) O(1B) C(1B) C(2B) C(3B) 102.5(2) O(1B) C(1B) C(2B) C(17B) -73.7(2)
N(3B) C(1B) C(2B) C(3B) -79.4(2) N(3B) C(1B) C(2B) C(17B) 104.37(19) C(1B) C(2B) C(3B) C(4B) 8.5(3)
C(17B) C(2B) C(3B) C(4B) -175.68(17) C(1B) C(2B) C(17B) C(18B) -175.90(18) C(1B) C(2B) C(17B) C(22B) 1.7(3)
C(3B) C(2B) C(17B) C(18B) 8.2(3) C(3B) C(2B) C(17B) C(22B) -174.3(2) C(2B) C(3B) C(4B) N(1B) 63.8(3)
C(2B) C(3B) C(4B) C(11B) -116.6(2) C(3B) C(4B) N(1B) C(5B) 0.6(3) C(11B) C(4B) N(1B) C(5B) -179.08(18)
N(1B) C(4B) C(11B) C(12B) -178.6(2) N(1B) C(4B) C(11B) C(16B) -0.1(3) C(3B) C(4B) C(11B) C(12B) 1.8(3)
C(3B) C(4B) C(11B) C(16B) -179.8(2) C(6B) C(5B) N(1B) C(4B) 115.6(2) C(9B) C(5B) N(1B) C(4B) -71.1(3)
N(1B) C(5B) C(6B) C(7B) 174.17(19) C(9B) C(5B) C(6B) C(7B) 0.4(3) N(1B) C(5B) C(9B) N(2B) -171.76(17)

N(1B) C(5B) C(9B) N(3B) 3.5(3) C(6B) C(5B) C(9B) N(2B) 1.8(3) C(6B) C(5B) C(9B) N(3B) 177.07(17)
C(5B) C(6B) C(7B) C(8B) -2.0(3) C(6B) C(7B) C(8B) N(2B) 1.7(4) C(7B) C(8B) N(2B) C(9B) 0.3(3)
N(3B) C(9B) N(2B) C(8B) -177.60(18) C(5B) C(9B) N(2B) C(8B) -2.1(3) N(2B) C(9B) N(3B) C(1B) -123.82(19)
N(2B) C(9B) N(3B) C(10B) 55.2(2) C(5B) C(9B) N(3B) C(1B) 60.5(2) C(5B) C(9B) N(3B) C(10B) -120.50(19)
C(4B) C(11B) C(12B) C(13B) 179.2(2) C(16B) C(11B) C(12B) C(13B) 0.7(4) C(4B) C(11B) C(16B) C(15B) -178.0(2)
C(12B) C(11B) C(16B) C(15B) 0.6(4) C(11B) C(12B) C(13B) C(14B) -1.1(5) C(12B) C(13B) C(14B) C(15B) 0.3(5)
C(13B) C(14B) C(15B) C(16B) 0.9(4) C(14B) C(15B) C(16B) C(11B) -1.4(4) C(2B) C(17B) C(18B) C(19B) 179.1(2)
C(22B) C(17B) C(18B) C(19B) 1.4(3) C(2B) C(17B) C(22B) C(21B) -178.3(2) C(18B) C(17B) C(22B) C(21B) -0.7(4)
C(17B) C(18B) C(19B) C(20B) -1.6(4) C(18B) C(19B) C(20B) C(21B) 1.0(4) C(19B) C(20B) C(21B) C(22B) -0.2(4)
C(20B) C(21B) C(22B) C(17B) 0.1(4)

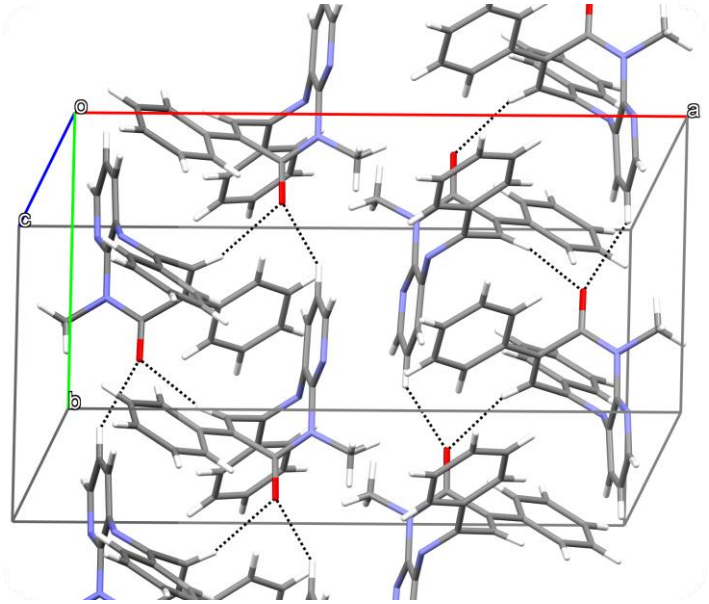

Figure S2 The crystal packing of pyridodiazocinone **3a**.

References

1 *SADABS, v. 2008-1*, Bruker AXS, Madison, WI, USA, 2008.

2 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.

3 (*a*) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool, version 10M*, Utrecht University, The Netherlands, 2003; (*b*) A. L. Spek, *J. Appl. Crystallogr*., 2003, **36**, 7.

4 C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Stree, *J. Appl. Crystallogr*., 2006, **39**, 453.

5 F. H. Allen, O. Kenard, D. G. Watson, L. Bramer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans 2*, 1987, 1.

6. R. S. Rowland and R. Taylor, *J. Phys. Chem*., 1996, **100**, 7384.