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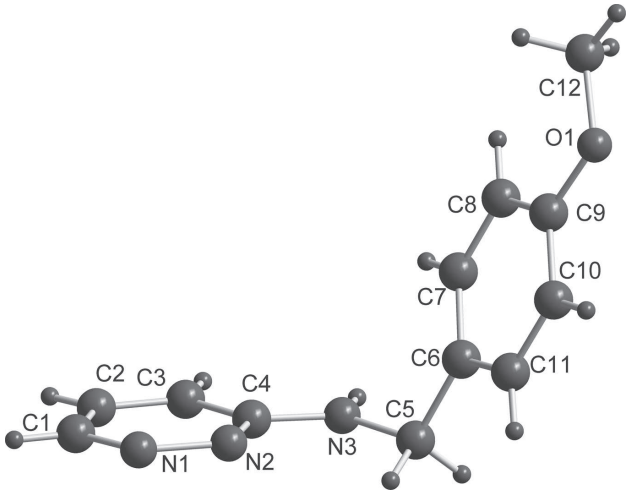
Crystal structure of *N*-(4-methoxybenzyl) pyridazin-3-amine- a rare $Z' = 4$ structure, $C_{12}H_{13}N_3O$



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Abstract

$C_{12}H_{13}N_3O$, triclinic, $P\bar{1}$ (no. 2), $a = 10.2233(9)$ Å, $b = 10.2902(9)$ Å, $c = 24.2253(19)$ Å, $\alpha = 86.607(7)°$, $\beta = 88.529(7)°$, $\gamma = 62.515(9)°$, $V = 2256.9(4)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0425$, $wR_{ref}(F^2) = 0.1239$, $T = 291(2)$ K.

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One of four crystallographically independent molecules of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was obtained from the ruthenium-catalyzed *N*-alkylation of pyridazin-3-amine and (4-methoxyphenyl)methanol as described in literature [3] and

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Table 1: Data collection and handling.

Crystal:	Yellow
Size:	$0.22 \times 0.20 \times 0.08$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	0.68 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16086, 8063, 0.022
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6060
$N(param)_{refined}$:	582
Programs:	SHELX [3], CrysAlis^{PRO} [2]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7370(2)	0.7842(2)	0.15269(8)	0.0728(5)
H1	0.7456	0.7306	0.1220	0.087*
C2	0.6059(2)	0.9111(2)	0.16011(8)	0.0686(5)
H2	0.5282	0.9417	0.1352	0.082*
C3	0.59494(19)	0.98814(19)	0.20446(7)	0.0597(4)
H3	0.5090	1.0729	0.2116	0.072*
C4	0.71843(17)	0.93578(17)	0.23967(6)	0.0504(4)
C5	0.8386(2)	0.9739(2)	0.32022(7)	0.0619(4)
H5A	0.8428	1.0628	0.3287	0.074*
H5B	0.9288	0.9128	0.3009	0.074*
C6	0.83347(18)	0.89358(17)	0.37390(7)	0.0529(4)
C7	0.7051(2)	0.9008(2)	0.39523(7)	0.0650(5)
H7	0.6176	0.9566	0.3759	0.078*
C8	0.7010(2)	0.8276(2)	0.44467(8)	0.0732(5)
H8	0.6122	0.8342	0.4580	0.088*
C9	0.8294(2)	0.7454(2)	0.47374(8)	0.0688(5)
C10	0.9590(2)	0.7380(2)	0.45353(8)	0.0763(6)
H10	1.0461	0.6832	0.4732	0.092*
C11	0.9608(2)	0.8113(2)	0.40423(8)	0.0684(5)
H11	1.0496	0.8052	0.3911	0.082*
C12	0.7093(4)	0.6651(4)	0.54332(11)	0.1409(13)
H12A	0.6735	0.6252	0.5161	0.211*
H12B	0.6351	0.7624	0.5506	0.211*
H12C	0.7319	0.6041	0.5768	0.211*
N1	0.84907(17)	0.73637(16)	0.18670(7)	0.0698(4)
N2	0.84124(15)	0.81329(15)	0.23115(6)	0.0577(3)
N3	0.71485(16)	1.01291(15)	0.28347(6)	0.0634(4)
H3A	0.6340	1.0900	0.2899	0.076*
O1	0.8376(2)	0.67036(19)	0.52346(6)	0.0985(5)
C1B	0.4090(2)	0.4192(2)	0.32310(8)	0.0712(5)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H1B	0.4765	0.4134	0.3494	0.085*
C2B	0.2806(2)	0.5509(2)	0.31505(8)	0.0691(5)
H2B	0.2620	0.6310	0.3357	0.083*
C3B	0.18461(19)	0.55917(19)	0.27681(8)	0.0621(4)
H3B	0.0968	0.6445	0.2703	0.074*
C4B	0.22180(18)	0.43325(18)	0.24663(7)	0.0538(4)
C5B	0.1490(2)	0.3073(2)	0.17973(8)	0.0647(5)
H5BA	0.0519	0.3168	0.1727	0.078*
H5BB	0.1991	0.2228	0.2052	0.078*
C6B	0.23327(18)	0.27770(18)	0.12613(7)	0.0565(4)
C7B	0.3470(2)	0.3127(2)	0.11518(7)	0.0634(5)
H7B	0.3738	0.3567	0.1421	0.076*
C8B	0.4224(2)	0.2845(2)	0.06546(8)	0.0686(5)
H8B	0.4988	0.3089	0.0594	0.082*
C9B	0.3835(2)	0.2203(2)	0.02514(8)	0.0708(5)
C10B	0.2727(3)	0.1818(3)	0.03546(9)	0.0871(7)
H10B	0.2467	0.1370	0.0086	0.105*
C11B	0.2001(2)	0.2095(2)	0.08547(9)	0.0766(6)
H11B	0.1266	0.1812	0.0920	0.092*
C12B	0.5645(3)	0.2222(4)	−0.03825(11)	0.1223(11)
H12D	0.5989	0.1954	−0.0751	0.183*
H12E	0.6430	0.1666	−0.0124	0.183*
H12F	0.5332	0.3250	−0.0352	0.183*
N1B	0.43940(16)	0.30293(17)	0.29549(6)	0.0675(4)
N2B	0.34526(15)	0.30897(15)	0.25608(6)	0.0605(4)
N3B	0.13124(16)	0.43638(16)	0.20645(6)	0.0658(4)
H3BA	0.0591	0.5196	0.1962	0.079*
O1B	0.44547(19)	0.1924(2)	−0.02649(6)	0.1002(5)
C1A	0.9692(2)	0.3947(2)	0.33888(9)	0.0766(5)
H1A	1.0373	0.3831	0.3659	0.092*
C2A	0.8502(3)	0.5327(2)	0.32878(9)	0.0778(6)
H2A	0.8388	0.6121	0.3485	0.093*
C3A	0.7531(2)	0.54814(19)	0.29005(8)	0.0674(5)
H3AA	0.6725	0.6387	0.2817	0.081*
C4A	0.77627(18)	0.42281(18)	0.26213(7)	0.0551(4)
C5A	0.6891(2)	0.3079(2)	0.19491(8)	0.0720(5)
H5AA	0.5910	0.3162	0.1926	0.086*
H5AB	0.7490	0.2190	0.2170	0.086*
C6A	0.75293(18)	0.29266(19)	0.13758(7)	0.0574(4)
C7A	0.7489(2)	0.4101(2)	0.10585(8)	0.0729(5)
H7A	0.7084	0.5018	0.1208	0.087*
C8A	0.8031(2)	0.3958(2)	0.05241(8)	0.0764(6)
H8A	0.7982	0.4771	0.0318	0.092*
C9A	0.8640(2)	0.2609(2)	0.02995(8)	0.0633(4)
C10A	0.8686(2)	0.1416(2)	0.06093(8)	0.0669(5)
H10A	0.9092	0.0499	0.0460	0.080*
C11A	0.81341(19)	0.15856(19)	0.11366(8)	0.0647(5)
H11A	0.8167	0.0775	0.1339	0.078*
C12A	0.9327(3)	0.3494(3)	−0.05330(10)	0.1070(8)
H12G	0.9791	0.3152	−0.0881	0.161*
H12H	0.9896	0.3837	−0.0334	0.161*
H12I	0.8352	0.4283	−0.0596	0.161*
N1A	0.98913(17)	0.28034(17)	0.31190(7)	0.0712(4)
N2A	0.89252(15)	0.29289(15)	0.27255(6)	0.0603(4)
N3A	0.67961(17)	0.43192(18)	0.22318(7)	0.0720(4)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H3AB	0.6079	0.5169	0.2147	0.086*
O1A	0.92396(17)	0.23344(16)	−0.02212(6)	0.0847(4)
C1C	0.7108(2)	0.2755(2)	0.83158(9)	0.0769(6)
H1C	0.6964	0.3409	0.8588	0.092*
C2C	0.8462(2)	0.1502(2)	0.82919(9)	0.0763(5)
H2C	0.9211	0.1317	0.8542	0.092*
C3C	0.86532(19)	0.0564(2)	0.78953(8)	0.0639(5)
H3C	0.9533	−0.0294	0.7866	0.077*
C4C	0.74780(17)	0.09255(17)	0.75271(7)	0.0531(4)
C5C	0.6475(2)	0.0264(2)	0.67326(7)	0.0655(5)
H5CA	0.5522	0.0846	0.6899	0.079*
H5CB	0.6534	−0.0676	0.6655	0.079*
C6C	0.65765(18)	0.10285(18)	0.61971(7)	0.0541(4)
C7C	0.57760(19)	0.25285(19)	0.61066(7)	0.0612(4)
H7C	0.5147	0.3079	0.6382	0.073*
C8C	0.5884(2)	0.32292(18)	0.56203(7)	0.0624(4)
H8C	0.5332	0.4242	0.5570	0.075*
C9C	0.68056(19)	0.24388(18)	0.52064(7)	0.0573(4)
C10C	0.7607(2)	0.0945(2)	0.52809(8)	0.0714(5)
H10C	0.8225	0.0398	0.5003	0.086*
C11C	0.7486(2)	0.0261(2)	0.57739(8)	0.0697(5)
H11C	0.8037	−0.0752	0.5823	0.084*
C12C	0.7717(3)	0.2490(3)	0.42918(9)	0.0993(8)
H12J	0.8730	0.1972	0.4407	0.149*
H12K	0.7616	0.3184	0.3992	0.149*
H12L	0.7404	0.1804	0.4172	0.149*
N1C	0.60280(18)	0.30503(17)	0.79705(7)	0.0723(4)
N2C	0.61978(15)	0.21435(16)	0.75654(6)	0.0621(4)
N3C	0.76221(16)	0.00257(16)	0.71247(6)	0.0656(4)
H3CA	0.8454	−0.0747	0.7098	0.079*
O1C	0.68404(16)	0.32350(14)	0.47373(5)	0.0784(4)

recrystallized from dichloromethane/petroleum ether solution at room temperature to give the desired crystals suitable for single-crystal X-ray diffraction.

Experimental details

Hydrogen atoms were added using the riding models implemented in the SHELX system.

Comment

The C—N bond forming reaction has become widely used in organic synthesis as well as in materials and pharmaceuticals [4, 5]. Among of these routes, the metal-catalyzed hydrogen autotransfer process is highly desirable [6–9], because the use of alcohols as electrophiles in the C—N bond forming reaction improves the atom efficiency of the process, producing only water as by product. However, the *N*-alkylation of heteroaryl amines have been relatively less reported [3]. Considering that the pyridazine derivatives are an important class of heterocyclic molecules [10–12],

we prepared the *N*-alkylation product of pyridazin-3-amine and (4-methoxyphenyl)methanol.

The molecular structure of one of the four crystallographically independent molecules forming the asymmetric unit of the title crystal structure of the title compound is shown in the figure. The pyridazine ring and aryl moiety are not coplanar and their best planes enclose an angle of 72°, which is similar to that of related derivatives [13]. In the crystal there exist intermolecular NH···N hydrogen bonds (N···H = 2.277 and 2.185 Å) and some weak non classical CH···N hydrogen bonds (N···H = 2.516 or 2.547 Å), which are attributed to construct the one-dimensional structure. Owing to the CH/π hydrogen bonds (the distance is 3.374 Å) [14], the crystal structure of the title compound is extended into a 2D architecture. This network is very complex as each of the four crystallographically independent molecules shows an at least slightly different surrounding [15].

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References

1. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
2. Agilent Technologies: CrysAlis^{PRO} software system, version 1.171.38.41r, Agilent Technologies UK Ltd, Oxford, UK (2011).
3. Li, H. M.; Xu, C.; Wang, Z. Q.; Fu, W. J.: A half sandwich ruthenium(II) complex with *N*-4,6-dimethyl-2-pyrimidinylimidazole: synthesis, crystal structure and application in *N*-alkylation of amines with alcohols. Bull. Korean Chem. Soc. **36** (2015) 2557–2560.
4. Maiti, D.; Fors, B. P.; Henderson, J. L.; Nakamura, Y.; Buchwald, S. L.: Palladium-catalyzed coupling of functionlized primary and secondary amines with aryl and heteroaryl halides: two ligands suffice in most cases. Chem. Sci. **2** (2011) 57–68.
5. Ricci, A.: Modern amination reaction. Wiley-VCH, Weinheim (2000).
6. Guillena, G.; Ramon, D. J.; Yus, M.: Hydrogen autotransfer in the *N*-alkylation of amines and related compounds using alcohols and amines as electrophiles. Chem. Rev. **110** (2010) 1611–1641.
7. Xu, C.; Hao, X. Q.; Xiao, Z. Q.; Wang, Z. Q.; Yuan, X. E.; Fu, W. J.; Ji, B. M.; Song, M. P.: One-pot synthesis of ferrocenyl ketones containing biaryls and 6-aryl-2-ferrocenylquinolines *via* Ir/Pd-cocatalyzed A-alkylation/Suzuki reaction. J. Org. Chem. **78** (2013) 8730–8738.
8. Cano, R.; Ramon, D. J.; Yus, M.: Impregnated ruthenium on magnetite as a recyclable catalyst for the *N*-alkylation of amines, sulfonamides, sulfinamides, and nitroarenes using alcohols as electrophiles by a hydrogen autotransfer process. J. Org. Chem. **76** (2011) 5547–5557.
9. Xu, C.; Xiao, Z. Q.; Li, H. M.; Han, X.; Wang, Z. Q.; Fu, W. J.; Ji, B. M.; Hao, X. Q.; Song, M. P.: Ligand-free Pd/C-catalyzed one-pot, three-component synthesis of arylsubstituted benzimidazoles by hydrogen-transfer reaction and Suzuki reaction in water. Eur. J. Org. Chem. **2015** (2015) 7427–7432.
10. Chelini, A.; Brogi, S.; Paolino, M.; Capua, A. D.; Cappelli, A.; Giorgi, G.; Farzad, M.; Mannelli, L. D. C.; Micheli, L.; Ghelardini, C.; Anzini, M.: Synthesis and biological evaluation of novel neuroprotective pyridazine derivatives as excitatory amino acid transporter 2 (EAAT2) activators. J. Med. Chem. **60** (2017) 5216–5221.
11. Xu, C.; Li, H. M.; Wang, Z. Q.; Fu, W. J.; Zhang, Y. Q.; Ji, B. M.: *N*-Heterocyclic carbene adducts of cyclopalladated ferrocenylpyridazine: synthesis, structural characterization and application in A-arylation of ketones with aryl chlorides. Aust. J. Chem. **65** (2012) 366–370.
12. Abed, H. B.; Mammoliti, O.; Bande, O.; Lommmen, G. V.; Herdewijn. P.: Strategy for the synthesis of pyridazine heterocycles and their derivatives. J. Org. Chem. **78** (2013) 7845–7858.
13. Li, H. M.; Zu, E. P.; Xu, C.: Crystal structure of 2-(4-methoxyphenyl)-2,3-dihydro-1*H*-perimidine, $C_{18}H_{16}N_2O$. Z. Kristallogr. NCS **231** (2016) 133–134.
14. Nishio, M.: CH/π hydrogen bonds in crystals. CrystEngComm **6** (2004) 130–158.
15. Steed, K. M.; Steed, J. W.: Packing Problems: high *Z′* crystal structures and their relationship to cocrystals, inclusion compounds, and polymorphism. Chem. Rev. **115** (2015) 2895–2933.