Iliya B. Yerima, Sizwe J. Zamisa* and Muhammad D. Bala

Crystal structure of 4-*tert*-butyl-1-(2,6-dimethylphenyl)-1*H*-1,2,3-triazole, C₁₄H₁₉N₃

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.44 × 0.26 × 0.25 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.07 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	72736, 5979, 0.025
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5773
$N(\text{param})_{\text{refined}}$:	311
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3]

<https://doi.org/10.1515/ncrs-2018-0574>

Received December 10, 2018; accepted February 21, 2019; available online March 26, 2019

Abstract

C₁₄H₁₉N₃, orthorhombic, *Pca*2₁ (no. 29), $a = 22.2821(8)$ Å, $b = 10.8464(4)$ Å, $c = 10.8509(4)$ Å, $V = 2622.5(2)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0318$, $wR_{\text{ref}}(F^2) = 0.0865$, $T = 100(2)$ K.

CCDC no.: 1898619

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

To a stirred solution of 2,6-dimethylamine (0.5 mmol, 109.5 mg) dissolved in a mixture of 10 mL acetic acid (10 mL) and water (10 mL) was added NaNO₃ (0.75 mmol, 51.7 mg) at 0 °C for 1 hour. The ice was removed while cooling at room

temperature, NaN₃ (0.75 mmol, 48.7 mg) was added and was stirred for two hours at room temperature. Excess Na₂CO₃ was added to neutralize the acetic acid, then 3,3-dimethylbut-1-yne (0.5 mmol, 0.041 mg, 0.06 mL), CuBr (0.45 mg, 0.03 mmol), sodium *L*-ascorbate 10% (0.05 mmol, 9.91 mg) were mixed and stirred overnight; the mixture was separated (partitioned) into aqueous and organic phases using 5% ammonium solution (30 mL x 3) and dichloromethane (30 mL x 3). The organic phase was washed with 100 mL of water and then 100 mL of brine solution, and finally dried with MgSO₄. A white crystal of the compound was obtained after evaporation of the solvent. Yield: 75% (0.77 mmol, 177.4 mg). M.p. 223–225 °C; ¹H NMR (DMSO, 400 MHz): δ (ppm) = 1.34 (9H, –3CH₃–, s), 1.91 (6H, –CH₃, s), 7.27 (1H, –CH, d, $J = 7.56$ Hz), 7.36 (2H, –CH, t, $J = 7.36$ Hz), 8.11 (1H, –CH, triazole); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm) 17.3, 30.5, 30.9, 120.3 (C-triazole), 128.3, 129.8, 135.6, 136.3, 157.6 (C–N benzene bound to N1 of triazole). HR-MS (ESI+) calcd. for C₁₄H₁₉N₃ (M + Na)⁺ 252.1479 m/z, found 252.1479 m/z.

Experimental details

The C–H_{aromatic} and C–H_{methyl} bond distances were restrained to 0.95 Å and 0.98 Å with $U_{\text{iso}}(\text{H}_{\text{aromatic}}) = 1.2U_{\text{eq}}$ and $U_{\text{iso}}(\text{H}_{\text{methyl}}) = 1.5U_{\text{eq}}$ of parent atom, respectively.

Comment

Based on their ease of synthesis and versatile donor abilities, there has been intense interest in the applications of

*Corresponding author: Sizwe J. Zamisa, School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa, e-mail: zamisas@ukzn.ac.za, sizwejamisa@gmail.com. <https://orcid.org/0000-0003-1968-381X>

Iliya B. Yerima and Muhammad D. Bala: School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.70307(7)	0.38396(14)	0.43648(14)	0.0153(3)
C2	0.75697(7)	0.42424(14)	0.38431(15)	0.0181(3)
C3	0.81006(7)	0.37433(16)	0.43103(16)	0.0217(3)
H3	0.847534	0.400505	0.398486	0.026*
C4	0.80877(8)	0.28688(15)	0.52451(16)	0.0209(3)
H4	0.845282	0.253377	0.554884	0.025*
C5	0.75470(7)	0.24828(14)	0.57362(16)	0.0191(3)
H5	0.754479	0.188168	0.637296	0.023*
C6	0.70054(7)	0.29626(15)	0.53110(15)	0.0169(3)
C7	0.64183(8)	0.25353(17)	0.58471(18)	0.0268(4)
H7A	0.649477	0.191681	0.648647	0.040*
H7B	0.617114	0.217135	0.519466	0.040*
H7C	0.620667	0.323962	0.620934	0.040*
C8	0.75829(8)	0.51641(16)	0.28038(17)	0.0236(3)
H8A	0.799164	0.522335	0.247580	0.035*
H8B	0.745587	0.597269	0.311116	0.035*
H8C	0.730970	0.489565	0.214887	0.035*
C9	0.60965(7)	0.38343(14)	0.30650(15)	0.0163(3)
H9	0.610986	0.302391	0.273389	0.020*
C10	0.56838(7)	0.47402(14)	0.28144(14)	0.0143(3)
C11	0.51467(7)	0.47172(14)	0.19617(15)	0.0157(3)
C12	0.51446(7)	0.58739(15)	0.11468(16)	0.0208(3)
H12A	0.479566	0.585237	0.059752	0.031*
H12B	0.512382	0.661013	0.166865	0.031*
H12C	0.551300	0.589776	0.065405	0.031*
C14	0.45680(7)	0.46738(18)	0.27213(17)	0.0256(4)
H14A	0.422132	0.465898	0.216583	0.038*
H14B	0.456675	0.392995	0.323397	0.038*
H14C	0.454563	0.540467	0.325029	0.038*
C15	0.51814(8)	0.35765(15)	0.11334(17)	0.0220(3)
H15A	0.483362	0.356081	0.058071	0.033*
H15B	0.555082	0.360666	0.064420	0.033*
H15C	0.518192	0.283194	0.164502	0.033*
C16	0.71746(7)	0.87876(15)	0.20703(15)	0.0160(3)
C17	0.76986(7)	0.92056(15)	0.26432(16)	0.0201(3)
C18	0.82418(8)	0.87134(16)	0.22288(18)	0.0245(4)
H18	0.860739	0.898255	0.259025	0.029*
C19	0.82554(8)	0.78391(16)	0.12989(17)	0.0236(4)
H19	0.862911	0.751458	0.103002	0.028*
C20	0.77282(7)	0.74349(15)	0.07588(16)	0.0204(3)
H20	0.774318	0.683305	0.012346	0.025*
C21	0.71747(7)	0.79031(14)	0.11387(15)	0.0176(3)
C22	0.66043(8)	0.74362(18)	0.05665(18)	0.0274(4)
H22A	0.632178	0.812152	0.046687	0.041*
H22B	0.642598	0.680660	0.110074	0.041*
H22C	0.669308	0.707612	−0.024154	0.041*
C23	0.76827(8)	1.01344(17)	0.36751(18)	0.0265(4)
H23A	0.758927	1.095102	0.333969	0.040*
H23B	0.807464	1.015846	0.408408	0.040*
H23C	0.737372	0.989778	0.427288	0.040*
C24	0.61704(7)	0.88303(14)	0.31517(15)	0.0170(3)
H24	0.615105	0.801986	0.348126	0.020*
C25	0.57548(7)	0.97587(14)	0.32809(14)	0.0149(3)
C27	0.51724(7)	0.97660(14)	0.39987(15)	0.0159(3)
C28	0.48538(7)	1.10062(16)	0.38487(17)	0.0225(3)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H28A	0.447791	1.099795	0.431762	0.034*
H28B	0.511319	1.166726	0.415733	0.034*
H28C	0.476612	1.114790	0.297509	0.034*
C29	0.53173(8)	0.95632(16)	0.53691(15)	0.0210(3)
H29A	0.494408	0.956556	0.584708	0.031*
H29B	0.552024	0.876839	0.547238	0.031*
H29C	0.557979	1.022655	0.566136	0.031*
C30	0.47648(7)	0.87174(16)	0.35522(16)	0.0221(3)
H30A	0.438885	0.872816	0.402090	0.033*
H30B	0.467739	0.882880	0.267407	0.033*
H30C	0.496764	0.792545	0.367634	0.033*
N1	0.64796(6)	0.43451(12)	0.38848(12)	0.0158(3)
N2	0.63172(6)	0.55171(13)	0.41429(13)	0.0190(3)
N3	0.58322(6)	0.57529(12)	0.34949(13)	0.0181(3)
N4	0.66117(6)	0.93211(12)	0.24546(13)	0.0166(3)
N5	0.64846(6)	1.04973(13)	0.21523(15)	0.0232(3)
N6	0.59617(6)	1.07586(12)	0.26556(15)	0.0210(3)

1,2,3-triazole compounds in homogeneous catalysis and coordination chemistry [4]. As precursors to triazolium-based *N*-heterocyclic carbene (NHC) ligands, they offer high covalent ability in the formation of metal-NHC bonds, high variability of steric and electronic properties, ease of adaptation and cost-effective synthesis. Hence, their transition metal complexes have been found as active catalysts for various transformations in homogenous catalysis. In our bid to design M-NHC catalyst systems for paraffin activation, the title compound was synthesized *via* the conventional copper catalyzed azide-alkyne bipolar cycloaddition reactions (CuAAC). Adopting established procedures developed by Crowley et al. [5] and Brotherton et al. [6]; a multi-component reaction of 3,3-dimethylbut-1-yne with the *in situ* generated organic azide afforded the triazole in an excellent yield of 75%. Similar compounds have been reported [7, 8].

The asymmetric unit of the title compound contains two molecules that are symmetrically non-equivalent. The pseudosymmetry share is ~80%. Each molecule consists of a *tert*-butyl group, 1,2,3-triazolyl and 2,6-dimethylphenyl moieties, which confirm the successful synthesis of the title compound. The dihedral angle between the triazolyl and 2,6-dimethylphenyl moieties in both molecules were found to range between 107.49(5)° and 75.97(4)°. All bond distances and angles appear to be normal and are comparable to those of closely related compounds [9, 10]. Non-classical, intermolecular C—H...N hydrogen bonding is observed between the hydrogen and nitrogen atoms of triazolyl moiety of neighbouring molecules (C24...N3 = 3.440(2) Å, C24—H24...N3 = 155° “x, y, z”; C9...N6 = 3.378(2) Å, C9—H9...N6 = 158° “x, y + 1, z”). Linking neighbouring

molecules in this manner results in the formation of a one dimensional supramolecular structure that propagates along the crystallographic *b* axis.

Acknowledgements: We thank the University of KwaZulu-Natal and the National Research Foundation (NRF) for financial support. IBY also thanks Gombe State University for a study fellowship.

References

1. Bruker. APEX2. Bruker AXS Inc., Madison, WI, USA (2011).
2. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
3. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.
4. Han, Y.; Huynh, H. V.; Tan, G. K.: Palladium(II) pyrazolin-4-ylidenes: remote N-heterocyclic carbene complexes and their catalytic application in aqueous Suzuki-Miyaura coupling. *Organometallics* **26** (2007) 6581–6585.
5. Crowley, J. D.; Bandeen, P. H.; Hanton, L. R.: A one pot multi-component CuAAC “click” approach to bidentate and tridentate pyridyl-1,2,3-triazole ligands: synthesis, X-ray structures and copper(II) and silver(I) complexes. *Polyhedron* **29** (2010) 70–83.
6. Brotherton, W. S.; Guha, P. M.; Phan, H.; Clark, R. J.; Shatruk, M.; Zhu, L.: Tridentate complexes of 2,6-bis(4-substituted-1,2,3-triazol-1-ylmethyl) pyridine and its organic azide precursors: an application of the copper(II) acetate-accelerated azide–alkyne cycloaddition. *Dalton Trans.* **40** (2011) 3655–3665.
7. Costa, M. S.; Boechat, N.; Ferreira, V. F.; Wardell, S. M.; Skakle, J. M.: 4-Difluoromethyl-1-(4-methylphenyl)-1*H*-1,2,3-triazole. *Acta Crystallogr.* **E62** (2006) o1925–o1927.
8. Wang, J.; Eychenne, R.; Wolff, M.; Mallet-Ladeira, S.; Lepareur, N.; Benoist, E.: Design, synthesis, and reactivity of multidentate ligands with rhenium(I) and rhenium(V) cores. *Eur. J. Inorg. Chem.* **33** (2017) 3908–3918.
9. Hohloch, S.; Suntrup, L.; Sarkar, B.: Arene–ruthenium(II) and -iridium(III) complexes with “Click”-based pyridyl-triazoles, bis-triazoles, and chelating abnormal carbenes: applications in catalytic transfer hydrogenation of nitrobenzene. *Organometallics* **32** (2013) 7376–7385.
10. Zhang, L.-L.; Yu, K.; Liu, L.-L.; Guo, D.-S.: 2-[4-(2-Hydroxypropan-2-yl)-1*H*-1,2,3-triazol-1-yl]phenol. *Acta Crystallogr.* **E68** (2012) o1262.