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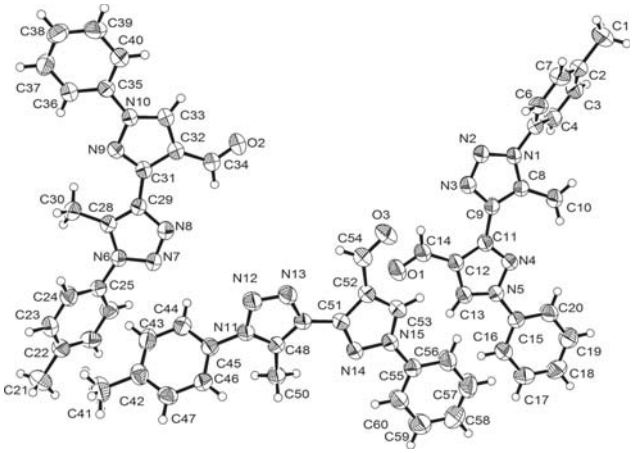
Crystal structure of 3-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde, a rare $Z' = 3$ structure, $C_{20}H_{17}N_5O$



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Abstract

$C_{20}H_{17}N_5O$, triclinic, $P\bar{1}$ (no. 2), $a = 11.5358(7)$ Å, $b = 13.8746(9)$ Å, $c = 16.3942(10)$ Å, $\alpha = 85.958(5)°$, $\beta = 87.407(5)°$, $\gamma = 87.619(5)°$, $V = 2612.8(3)$Å^3, $Z = 6$, $R_{gt}(F) = 0.0607$, $wR_{ref}(F^2) = 0.1510$, $T = 293(2)$ K.

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The asymmetric unit of the title crystal structure, with three crystallographically independent molecules, is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless needle
Size:	0.46 × 0.21 × 0.15 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.9 cm^{-1}
Diffractometer, scan mode:	SuperNova, ω-scans
$2\theta_{max}$, completeness:	60°, 82.3%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	23147, 12359, 0.026
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7462
$N(param)_{refined}$:	708
Programs:	CrysAlis^{PRO} [1], SHELX [2], PLATON [3], ChemDraw [4]

Source of material

3-(5-Methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde was synthesized from treatment of 5-methyl-4-((2-phenylhydrazono)methyl)-1-*p*-tolyl-1*H*-1,2,3-triazole with phosphorus oxychloride and dimethylformamide (Vilsmeier-Haack reaction) at 0–5 °C. The reaction was left overnight at room temperature, poured onto ice-cold water and neutralized with ammonium hydroxide solution (5%). The solid obtained was filtered, dried and recrystallized from dimethylformamide to give colorless crystals of the title compound (Mp 229–230 °C) [5].

Experimental details

Non-hydrogen atoms were refined with anisotropic diaplacement parameters. All hydrogen atoms were placed in calculated positions and refined using a riding model. Methyl C—H bonds were fixed at 0.96 Å, with isotropic displacement parameters of the corresponding hydrogen atoms set to 1.5 times U_{eq}(C), and were allowed to spin about the C—C bond.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5837(3)	1.2072(2)	−0.35853(17)	0.0893(9)
H1A	0.6588	1.1886	−0.3813	0.134*
H1B	0.5863	1.2704	−0.3385	0.134*
H1C	0.5275	1.2082	−0.4001	0.134*
C2	0.5498(2)	1.13542(16)	−0.28889(14)	0.0591(6)
C3	0.4667(2)	1.15996(15)	−0.22981(14)	0.0595(6)
H3	0.4313	1.2215	−0.2334	0.071*
C4	0.43494(19)	1.09528(14)	−0.16536(13)	0.0547(5)
H4	0.3797	1.1134	−0.1256	0.066*
C5	0.48633(17)	1.00347(13)	−0.16085(12)	0.0471(5)
C6	0.56954(18)	0.97730(15)	−0.21870(13)	0.0528(5)
H6	0.6043	0.9156	−0.2154	0.063*
C7	0.6008(2)	1.04366(16)	−0.28158(14)	0.0610(6)
H7	0.6580	1.0261	−0.3202	0.073*
C8	0.34403(17)	0.90783(14)	−0.07013(12)	0.0463(4)
C9	0.36366(16)	0.83480(14)	−0.01070(11)	0.0453(4)
C10	0.23450(18)	0.95040(16)	−0.10442(14)	0.0614(6)
H10A	0.2034	0.9999	−0.0707	0.092*
H10B	0.1792	0.9008	−0.1058	0.092*
H10C	0.2503	0.9780	−0.1589	0.092*
C11	0.28006(17)	0.77584(13)	0.03711(12)	0.0464(5)
C12	0.29786(17)	0.69943(13)	0.09794(12)	0.0478(5)
C13	0.18816(18)	0.67041(14)	0.12169(12)	0.0500(5)
H13	0.1699	0.6212	0.1611	0.060*
C14	0.40469(19)	0.65853(15)	0.13092(14)	0.0606(6)
H14	0.4741	0.6764	0.1040	0.073*
C15	−0.01161(17)	0.72332(14)	0.07813(12)	0.0490(5)
C16	−0.0704(2)	0.65878(17)	0.13051(14)	0.0667(6)
H16	−0.0305	0.6182	0.1682	0.080*
C17	−0.1892(2)	0.65501(19)	0.12641(16)	0.0740(7)
H17	−0.2292	0.6110	0.1614	0.089*
C18	−0.2495(2)	0.71475(18)	0.07182(15)	0.0672(6)
H18	−0.3294	0.7107	0.0690	0.081*
C19	−0.1906(2)	0.78037(18)	0.02151(16)	0.0710(7)
H19	−0.2311	0.8224	−0.0147	0.085*
C20	−0.07219(19)	0.78484(16)	0.02390(15)	0.0637(6)
H20	−0.0327	0.8293	−0.0110	0.076*
C21	0.8783(3)	−0.01809(19)	0.85670(16)	0.0825(8)
H21A	0.8896	−0.0823	0.8387	0.124*
H21B	0.7974	−0.0055	0.8697	0.124*
H21C	0.9220	−0.0123	0.9045	0.124*
C22	0.9192(2)	0.05409(15)	0.78943(13)	0.0556(5)
C23	1.0215(2)	0.03783(16)	0.74434(14)	0.0619(6)
H23	1.0651	−0.0192	0.7552	0.074*
C24	1.06060(18)	0.10431(15)	0.68356(13)	0.0580(6)
H24	1.1296	0.0922	0.6538	0.070*
C25	0.99589(17)	0.18890(13)	0.66755(12)	0.0459(5)
C26	0.89352(18)	0.20651(14)	0.71080(13)	0.0523(5)
H26	0.8500	0.2635	0.7000	0.063*
C27	0.85592(19)	0.13852(15)	0.77060(13)	0.0571(5)
H27	0.7857	0.1501	0.7991	0.069*
C28	1.13904(17)	0.29433(13)	0.58506(12)	0.0459(4)
C29	1.12698(16)	0.34506(13)	0.51064(12)	0.0444(4)
C30	1.23670(19)	0.28372(16)	0.64173(13)	0.0607(6)
H30A	1.2062	0.2798	0.6973	0.091*
H30B	1.2847	0.3387	0.6328	0.091*
H30C	1.2821	0.2259	0.6316	0.091*
C31	1.21337(17)	0.39641(13)	0.45809(12)	0.0444(4)
C32	1.19619(17)	0.46291(13)	0.38921(12)	0.0478(5)
C33	1.30661(17)	0.48380(13)	0.35982(12)	0.0491(5)
H33	1.3257	0.5253	0.3146	0.059*
C34	1.08854(19)	0.50342(15)	0.35610(14)	0.0598(6)
H34	1.0193	0.4865	0.3837	0.072*
C35	1.50596(17)	0.42941(12)	0.40207(12)	0.0451(4)
C36	1.56754(18)	0.38670(14)	0.46653(13)	0.0534(5)
H36	1.5283	0.3636	0.5143	0.064*
C37	1.6872(2)	0.37856(16)	0.45981(15)	0.0621(6)
H37	1.7285	0.3496	0.5030	0.075*
C38	1.7455(2)	0.41297(16)	0.38959(16)	0.0653(6)
H38	1.8260	0.4066	0.3849	0.078*
C39	1.6842(2)	0.45682(16)	0.32626(15)	0.0658(6)
H39	1.7239	0.4809	0.2791	0.079*
C40	1.56400(19)	0.46557(15)	0.33182(13)	0.0553(5)
H40	1.5231	0.4954	0.2888	0.066*
C41	0.8478(2)	−0.11266(18)	0.59993(15)	0.0736(7)
H41A[a]	0.8055	−0.1709	0.6011	0.110*
H41B[a]	0.8357	−0.0840	0.6514	0.110*
H41C[a]	0.9290	−0.1276	0.5905	0.110*
H41D[a]	0.9080	−0.0841	0.6275	0.110*
H41E[a]	0.8778	−0.1710	0.5772	0.110*
H41F[a]	0.7844	−0.1274	0.6382	0.110*
C42	0.80536(18)	−0.04255(15)	0.53197(12)	0.0531(5)
C43	0.8520(2)	0.04740(16)	0.51683(14)	0.0636(6)
H43	0.9099	0.0653	0.5497	0.076*
C44	0.81505(18)	0.11137(15)	0.45443(14)	0.0574(5)
H44	0.8476	0.1716	0.4455	0.069*
C45	0.72963(16)	0.08518(13)	0.40557(12)	0.0450(4)
C46	0.68009(17)	−0.00362(14)	0.41920(13)	0.0513(5)
H46	0.6217	−0.0209	0.3864	0.062*
C47	0.71846(18)	−0.06680(14)	0.48248(13)	0.0526(5)
H47	0.6852	−0.1267	0.4919	0.063*
C48	0.58588(16)	0.18712(13)	0.32257(12)	0.0429(4)
C49	0.60166(16)	0.23997(13)	0.24931(12)	0.0448(4)
C50	0.48398(17)	0.17299(14)	0.38008(12)	0.0514(5)
H50A	0.4495	0.1130	0.3712	0.077*
H50B	0.4280	0.2254	0.3709	0.077*
H50C	0.5085	0.1714	0.4354	0.077*
C51	0.51597(17)	0.29574(13)	0.20050(12)	0.0453(4)
C52	0.53391(18)	0.36505(14)	0.13362(12)	0.0487(5)
C53	0.42401(19)	0.39389(14)	0.11154(13)	0.0525(5)
H53	0.4052	0.4390	0.0690	0.063*
C54	0.6414(2)	0.40189(16)	0.09763(14)	0.0646(6)
H54	0.7103	0.3749	0.1180	0.078*
C55	0.22398(18)	0.35042(14)	0.16356(13)	0.0515(5)
C56	0.1655(2)	0.40945(16)	0.10694(14)	0.0631(6)
H56	0.2061	0.4479	0.0676	0.076*
C57	0.0459(2)	0.4108(2)	0.10937(17)	0.0781(7)
H57	0.0059	0.4502	0.0710	0.094*
C58	−0.0146(2)	0.3555(2)	0.16704(19)	0.0864(8)
H58	−0.0953	0.3571	0.1679	0.104*
C59	0.0438(2)	0.2976(2)	0.2237(2)	0.0946(10)

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Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H59	0.0028	0.2598	0.2633	0.114*
C60	0.1629(2)	0.29523(18)	0.22220(17)	0.0786(8)
H60	0.2025	0.2561	0.2610	0.094*
N1	0.45217(13)	0.93438(11)	−0.09626(9)	0.0467(4)
N2	0.53532(14)	0.88023(12)	−0.05527(10)	0.0543(4)
N3	0.48085(14)	0.82014(12)	−0.00338(10)	0.0541(4)
N4	0.16724(14)	0.79213(12)	0.02524(10)	0.0511(4)
N5	0.11219(14)	0.72591(11)	0.07767(10)	0.0487(4)
N6	1.03332(14)	0.25626(11)	0.60200(10)	0.0463(4)
N7	0.95884(14)	0.28316(12)	0.54184(11)	0.0545(4)
N8	1.01618(15)	0.33728(12)	0.48647(11)	0.0535(4)
N9	1.32598(14)	0.37813(11)	0.46925(10)	0.0466(4)
N10	1.38207(14)	0.43328(11)	0.40828(9)	0.0451(4)
N11	0.69354(13)	0.14981(11)	0.33874(10)	0.0464(4)
N12	0.77293(15)	0.17919(13)	0.27893(11)	0.0582(5)
N13	0.71603(15)	0.23375(12)	0.22477(11)	0.0572(5)
N14	0.40405(14)	0.28389(11)	0.21795(10)	0.0497(4)
N15	0.34801(14)	0.34560(11)	0.16206(10)	0.0492(4)
O1	0.41041(14)	0.60292(12)	0.19079(11)	0.0797(5)
O2	1.08280(14)	0.55765(11)	0.29511(10)	0.0737(5)
O3	0.64867(16)	0.46490(13)	0.04334(11)	0.0873(6)

[a]Occupancy: 0.5.

Aromatic C—H distances were set to 0.93 Å and U_{iso} parameters of aromatic hydrogen atoms were set to 1.2 times the U_{eq} of the atoms to which they are bonded. The methyl group C41 shows a disorder of its hydrogen atoms (*cf*. the figure).

Comment

Compounds containing a pyrazole ring system [6–10] exhibit a wide range of biological applications. Hence, it has been shown that many derivatives show antimicrobial, fungicidal, anticancer and antioxidant activities [11–14].

The asymmetric unit comprises three crystallographically independent molecules of $C_{20}H_{17}N_5O$. Molecular conformation in the three molecules is very similar with twist angles between the triazole, pyrazole and phenyl rings ranging from 2.40(14) to 18.71(11)° (*cf*. the figure). The twist between the triazole and methylbenzene groups is greater in all three molecules, being in the range 47.53(8)–58.30(8)°. In the crystal structure, the molecules stack with planes roughly parallel to (011). All bond lengths and angles are in the expected ranges.

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References

1. Agilent. CrysAlis^{PRO}. Agilent Technologies, Yarnton, England (2014).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
4. Cambridge Soft. CHEMDRAW Ultra. Cambridge Soft Corporation, Cambridge, MA, USA (2001).
5. Abdel-Wahab, B. F.; Mohamed, H. A.; Ali, M. M.: Synthesis and in vitro cytotoxicity of new 3-(5-methyl-1-aryl-1*H*-1,2,3-triazol-4-yl)-1-phenyl-1*H*-pyrazoles. J. Mod. Med. Chem. **3** (2015) 9–15.
6. Harigae, R.; Moriyama, K.; Togo, H.: Preparation of 3,5-disubstituted pyrazoles and isoxazoles from terminal alkynes, aldehydes, hydrazines and hydroxylamine. J. Org. Chem. **79** (2014) 2049–2058.
7. Specklin, S.; Decuypere, E.; Plougastel, L.; Aliani, S.; Taran, F.: One-pot synthesis of 1,4-disubstituted pyrazoles from arylglycines *via* copper-catalyzed Sydnone-alkyne cycloaddition reaction. J. Org. Chem. **79** (2014) 7772–7777.
8. Zhang, X.; Kang, J.; Niu, P.; Wu, J.; Yu, W.; Chang, J.: I2-Mediated oxidative C-N bond formation for metal-free one-pot synthesis of di-, tri-, and tetrasubstituted pyrazoles from α,β-unsaturated aldehydes/ketones and hydrazines. J. Org. Chem. **79** (2014) 10170–10178.
9. Genung, N. E.; Wei, L.; Aspnes, G. E.: Regioselective synthesis of 2*H*-indazoles using a mild, one-pot condensation-Cadogan reductive cyclization. Org. Lett. **16** (2014) 3114–3117.
10. Wen, J.-J.; Tang, H.-T.; Xiong, K.; Ding, Z.-C.; Zhan, Z.-P.: Synthesis of polysubstituted pyrazoles by a platinum-catalyzed sigmatropic rearrangement/cyclization cascade. Org. Lett. **16** (2014) 5940–5943.
11. Cabeza, M.; Posada, A.; Sánchez-Márquez, A.; Heuze, Y.; Moreno, I.; Soriano, J.; Garrido, M.; Cortés, F.; Bratoeff, E.: Biological activity of pyrazole and imidazole-dehydroepiandrosterone derivatives on the activity of 17β-hydroxysteroid dehydrogenase. J. Enzyme Inhib. Med. Chem. **31** (2016) 53–62.
12. Mohareb, R. M.; El-Sayed, N. N. E.; Abdelaziz, M. A.: Uses of cyanoacetylhydrazine in heterocyclic synthesis: novel synthesis of pyrazole derivatives with anti-tumor activities. Molecules **17** (2012) 8449–8463.
13. Farghaly, A.-R.; Esmail, S.; Abdel-Hafez, A.; Vanelle, P.; El-Kashef, H.: New pyrazole derivatives of potential biological activity. ARKIVOC **VII** (2012) 228–241.
14. Abdel-Wahab, B. F.; Khidre, R. E.; Farahat, A. A.: Pyrazole-3(4)-carbaldehyde: synthesis, reactions and biological activity. ARKIVOC **I** (2011) 196–245.

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