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Crystal structure of ethyl 3-(4-methoxyphenyl)-5-methylcarbamoyl-1*H*-pyrazole-4-carboxylate, $C_{15}H_{17}N_3O_4$

<https://doi.org/10.1515/ncrs-2019-0203>

Received March 19, 2019; accepted April 29, 2019; available online September 9, 2019

Abstract

$C_{15}H_{17}N_3O_4$, triclinic, $P\bar{1}$ (no. 2), $a = 10.5986(5)$ Å, $b = 11.5298(5)$ Å, $c = 13.5386(6)$ Å, $\alpha = 102.694(1)^\circ$, $\beta = 102.999(1)^\circ$, $\gamma = 108.918(1)^\circ$, $V = 1446.03(11)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0525$, $wR_{ref}(F^2) = 0.1526$, $T = 100(1)$ K.

CCDC no.: 1479039

Table 1: Data collection and handling.

Crystal:	Orange block
Size:	$0.24 \times 0.21 \times 0.13$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.10 mm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX-II Duo, φ and ω
$\theta_{\max}$, completeness:	33.4° , 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	73858, 11136, 0.050
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 7872
$N(\text{param})_{\text{refined}}$:	419
Programs:	Bruker [1], SHELX [2], Spek [3], Mercury [4]

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Hydrazine hydrate (3.3 mmol) was added to a mixture of ethyl 4-hydroxy-2-(4-methoxyphenyl)-1-methyl-5-oxo-2,5-dihydro-1*H*-pyrrole-3-carboxylate (3 mmol) and 15 mL of acetic acid. The mixture was refluxed for 3 h and cooled. The reaction mixture was evaporated under reduced pressure and

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1A	0.65213(11)	0.41861(11)	0.48761(8)	0.0208(2)
N2A	0.75650(10)	0.41828(10)	0.56589(8)	0.0208(2)
N3A	0.27976(11)	0.23705(11)	0.36196(8)	0.0216(2)
O1A	0.43652(10)	0.39827(10)	0.33063(8)	0.0338(2)
O2A	0.31426(9)	0.10495(9)	0.50149(7)	0.02256(18)
O3A	0.48760(9)	0.10627(9)	0.63086(7)	0.02215(18)
O4A	1.05834(9)	0.24363(8)	0.93112(7)	0.02120(18)
C1A	0.52645(12)	0.32543(11)	0.46876(9)	0.0176(2)
C2A	0.54855(12)	0.25726(11)	0.54094(9)	0.0172(2)
C3A	0.69571(12)	0.32016(11)	0.59972(9)	0.0177(2)
C4A	0.78790(12)	0.29839(11)	0.68710(9)	0.0175(2)
C5A	0.78258(12)	0.17554(11)	0.68716(9)	0.0181(2)
H5AA	0.7144	0.1015	0.6305	0.022*
C6A	0.87491(12)	0.16028(11)	0.76840(9)	0.0179(2)
H6AA	0.8700	0.0762	0.7671	0.022*
C7A	0.97529(11)	0.26827(11)	0.85228(9)	0.0172(2)
C8A	0.98506(12)	0.39121(11)	0.85215(9)	0.0200(2)
H8AA	1.0551	0.4653	0.9078	0.024*
C9A	0.89131(12)	0.40509(12)	0.76965(9)	0.0201(2)
H9AA	0.8982	0.4894	0.7698	0.024*
C10A	0.40860(12)	0.32193(12)	0.38133(9)	0.0202(2)
C11A	0.15894(13)	0.23705(14)	0.28471(11)	0.0267(3)
H11A	0.0746	0.1620	0.2750	0.040*
H11B	0.1764	0.2326	0.2162	0.040*
H11C	0.1448	0.3166	0.3112	0.040*
C12A	0.43929(12)	0.15065(11)	0.55421(9)	0.0173(2)
C13A	0.38507(12)	−0.00275(12)	0.64493(9)	0.0204(2)
H13A	0.3485	−0.0796	0.5806	0.024*
H13B	0.3050	0.0181	0.6567	0.024*
C14A	0.45907(15)	−0.02924(14)	0.74070(11)	0.0292(3)
H14A	0.3922	−0.1010	0.7539	0.044*
H14B	0.4969	0.0482	0.8034	0.044*
H14C	0.5363	−0.0522	0.7272	0.044*
C15A	1.17205(13)	0.35331(12)	1.01190(10)	0.0231(2)
H15A	1.2258	0.3237	1.0623	0.035*
H15B	1.1340	0.4091	1.0502	0.035*
H15C	1.2340	0.4020	0.9783	0.035*
N1B	0.54141(10)	0.59549(10)	0.25371(8)	0.01830(19)
N2B	0.44011(10)	0.58408(10)	0.16723(8)	0.01920(19)
N3B	0.90511(10)	0.80346(11)	0.38993(8)	0.0207(2)
O1B	0.76239(9)	0.62764(9)	0.41632(7)	0.02308(19)
O2B	0.86270(9)	0.92868(9)	0.24178(7)	0.02146(18)
O3B	0.70762(9)	0.86463(8)	0.07794(7)	0.02111(18)
O4B	0.12929(9)	0.68998(9)	−0.23482(7)	0.02364(19)
C1B	0.66734(12)	0.68711(11)	0.27008(9)	0.0166(2)
C2B	0.64854(11)	0.74108(11)	0.18698(9)	0.0165(2)
C3B	0.50377(12)	0.67138(11)	0.12482(9)	0.0171(2)
C4B	0.41443(12)	0.68267(11)	0.02924(9)	0.0176(2)
C5B	0.43412(12)	0.65344(12)	−0.07021(9)	0.0206(2)
H5BA	0.5122	0.6325	−0.0764	0.025*
C6B	0.34120(13)	0.65437(12)	−0.16076(9)	0.0214(2)
H6BA	0.3553	0.6334	−0.2282	0.026*
C7B	0.22768(12)	0.68630(11)	−0.15148(9)	0.0189(2)
C8B	0.20752(12)	0.71718(11)	−0.05218(9)	0.0188(2)
H8BA	0.1307	0.7402	−0.0457	0.023*
C9B	0.29956(12)	0.71424(11)	0.03684(9)	0.0184(2)
H9BA	0.2844	0.7339	0.1040	0.022*

Table 2 (continued)

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C10B	0.78378(12)	0.70430(11)	0.36456(9)	0.0176(2)
C11B	1.02207(13)	0.83072(14)	0.48354(10)	0.0279(3)
H11D	1.0994	0.9113	0.4928	0.042*
H11E	1.0543	0.7596	0.4741	0.042*
H11F	0.9914	0.8396	0.5469	0.042*
C12B	0.75130(12)	0.85248(11)	0.17349(9)	0.0172(2)
C13B	0.80215(14)	0.97189(13)	0.05564(10)	0.0249(3)
H13C	0.8943	0.9652	0.0622	0.030*
H13D	0.8176	1.0555	0.1060	0.030*
C14B	0.73009(18)	0.96135(15)	−0.05726(11)	0.0345(3)
H14D	0.7908	1.0294	−0.0780	0.052*
H14E	0.6407	0.9712	−0.0617	0.052*
H14F	0.7118	0.8766	−0.1056	0.052*
C15B	0.12541(14)	0.63066(14)	−0.34055(10)	0.0274(3)
H15D	0.0405	0.6245	−0.3925	0.041*
H15E	0.1240	0.5438	−0.3474	0.041*
H15F	0.2090	0.6830	−0.3543	0.041*
H1NB	0.5194(16)	0.5392(16)	0.2904(12)	0.024(4)*
H1NA	0.6678(18)	0.4786(17)	0.4517(14)	0.035(5)*
H3NB	0.9094(19)	0.8547(18)	0.3466(14)	0.038(5)*
H3NA	0.270(2)	0.1825(19)	0.4080(15)	0.046(5)*

the crude was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 80/20) to afford the product [5].

Experimental details

Data collection was performed by using the APEX2 software [1] and the cell refinement and data reduction were performed under the SAINT software [1]. The crystal structure was solved by direct method [2] and refined by full-matrix least squares technique on F^2 using SHELXTL [2]. Absorption correction was applied to the final crystal data by using the SADABS software [1]. All geometrical calculations were carried out using the program PLATON [2]. The molecular graphics were drawn using SHELXTL [2] and Mercury [4] program. In this compound, the N-bound H atoms were located in difference Fourier maps and allowed to be refined freely [refined distance: N–H = 0.904(16)–0.976(19) Å]. The remaining hydrogen atoms were positioned geometrically [C–H = 0.95–0.99 Å] and were refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}(\text{methyl C})$. A rotating-group model was used for the methyl groups.

Comment

Pyrazoles play a vital role in pharmaceuticals, since they possess an interesting pharmacological profile, such as anti-inflammatory [6], antimicrobial [7], antiviral [8], anti-tumor [9], anticonvulsant [10], antidepressant activities [11] and antihistaminic [12] etc. It commonly synthesized either by condensation of hydrazines with 1,3-dicarbonyl or by intermolecular cycloaddition reaction of alkynes to 3-dipoles

[13]. During the course of our study, we have unexpectedly found that substituted pyrazole could be synthesized by condensation of pyrrolidine with hydrazine in acidic condition. To the best of our knowledge; this is the first report that synthesizes substituted pyrazole from pyrrolidine ring transformation.

The asymmetric unit of the title compound consists of two crystallographically independent molecules, *A* and *B* (left part of the figure). The bond lengths and angles are within the normal ranges and comparable to the related structures [14–17]. In each molecule (*A* and *B*), intramolecular $N3A-H3NA \cdots O2A$ and $N3B-H3NB \cdots O2B$ hydrogen bond are found, respectively, forming *S*(7) ring motif [18]. This interaction further stabilizes the molecular structure and locks its atoms in a nearly planar arrangement. In the independent molecule *A*, the 1-methoxy-4-methylbenzene ($C4A-C9A/O4A/C15A$) moiety is slightly twisted at $C3A-C4A$ bond with $C2A-C3A-C4A-C5A$ torsion angle of $44.46(19)^\circ$. Meanwhile, in molecule *B* the 1-methoxy-4-methylbenzene ($C4B-C9B/O4B/C15B$) and ethyl acetate ($O2B/O3B/C12B-C14B$) moieties are observed to be slightly twisted at $C3B-C4B$ and $C2B-C12B$ bonds, respectively. The twisted angle of $C2B-C3B-C4B-C5B$ is found to be $67.48(18)^\circ$ while the twisted angle for $C1B-C2B-C12B-O2B$ is $-12.4(2)^\circ$ (right part of the figure). In both molecules, the pyrazole rings ($N1A/N2A/C1A-C3A$ and $N1B/N2B/C1B-C3B$) form dihedral angles of $41.72(7)^\circ$ and $62.81(7)^\circ$ with the phenyl rings ($C4A-C9A$ and $C4B-C9B$), respectively.

Acknowledgements: The authors would like to acknowledge Universiti Teknologi MARA and Malaysian Government (MOHE) for the financial support (600-IRMI/FRGS 5/3 (0071/2016)).

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