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ISSN 2414-3146

5-Methyl-*N*′-[(*Z*)-4-methylbenzylidene]-1*H*-pyrazole-3-carbohydrazide

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Received 8 May 2016
Accepted 14 May 2016

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

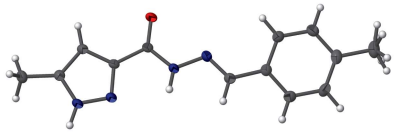
Keywords: crystal structure; pyrazole dereva-tives; carbohydrazide; C—H ···O hydrogen bonds.

CCDC reference: 1479830

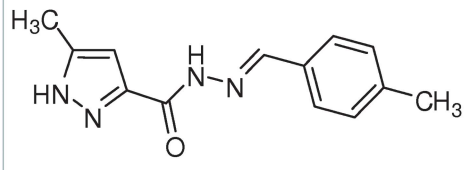
Structural data: full structural data are available from iucrdata.iucr.org

The title 1-*H*-pyrazole-3-carbohydrazide molecule, $C_{13}H_{14}N_4O$, shows a slight twist from end to end. The packing features N—H···N and bifurcated N—H···(N,O) hydrogen bonds, which generate (010) sheets.

3D view



Chemical scheme



Structure description

As a continuation of our research work devoted to the development of pyrazole carbohydrazides (Karrouchi *et al.*, 2015), the title compound was prepared and characterized by single-crystal X-ray diffraction.

The title molecule Fig. 1 is slightly bowed, as well as slightly twisted, from end to end. This can be seen from the dihedral angle of 8.32 (7)° between the five- and six-membered rings. The packing is directed by N—H···N and bifurcated N—H···(N,O) hydrogen bonds (Table 1 and Figs. 2 and 3), which generate (010) sheets.

Synthesis and crystallization

To a solution of 5-methyl-1*H*-pyrazole-3-carbohydrazide (1 mmol, 250 mg) in 10 ml of ethanol was added an equimolar amount of 4-bromobenzaldehyde in the presence of acetic acid. The mixture was maintained under reflux for 2 h, until thin-layer chromatography (TLC) indicated the end of the reaction. The mixture was then poured into cold water and the precipitate which formed was filtered off washed with ethanol. Single crystals of the title compound were obtained on slow evaporation of a DMF solution [yield 59%; m.p. 565–567 K (methanol/DMF)].

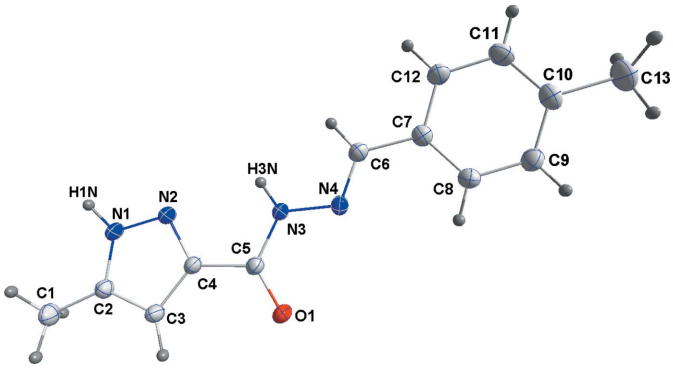


Figure 1
The title molecule shown with 50% probability displacement ellipsoids.

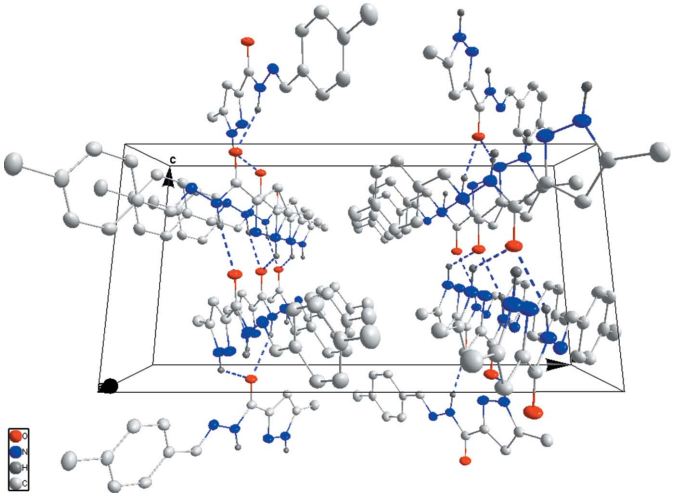


Figure 2
Packing viewed along the *a* axis, with intermolecular N—H···N and N—H···O hydrogen bonds shown as dotted lines.

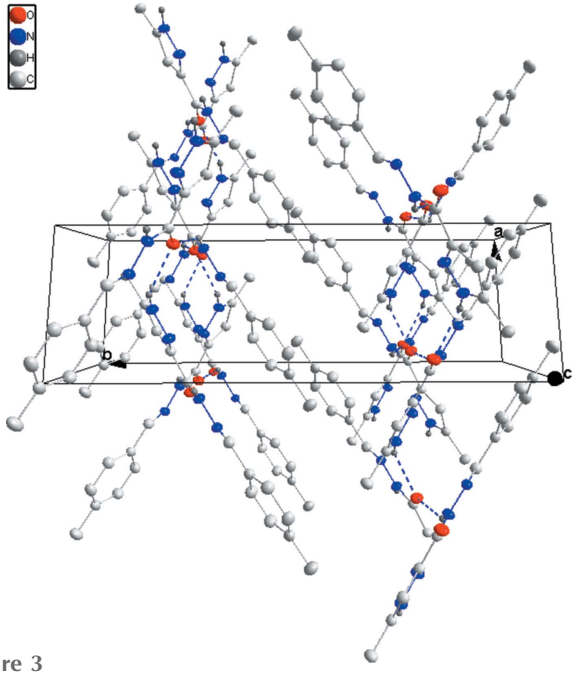


Figure 3
Packing viewed along the *c* axis, with intermolecular N—H···N and N—H···O hydrogen bonds shown as dotted lines.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O1^{i}	0.905 (18)	2.191 (18)	2.8655 (13)	130.8 (14)
N1—H1N···N4^{i}	0.905 (18)	2.395 (18)	3.2419 (14)	155.9 (15)
N3—H3N···O1^{ii}	0.885 (18)	2.232 (18)	2.9971 (13)	144.4 (15)

Symmetry codes: (i) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The methyl group on the phenyl ring is rotationally disordered and refined with a *SHELX* AFIX 123 instruction.

Acknowledgements

The support of NSF–MRI Grant #1228232 for the purchase of the diffractometer and Tulane University for support of the Tulane Crystallography Laboratory are gratefully acknowledged.

References

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Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_{14}N_4O$
M_r	242.28
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, *b*, *c* (Å)	6.3283 (1), 19.6204 (4), 10.1245 (2)
β (°)	105.746 (1)
V (Å^3)	1209.92 (4)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.72
Crystal size (mm)	0.18 × 0.11 × 0.05
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.88, 0.96
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13389, 2396, 2144
R_{int}	0.036
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.036, 0.091, 1.05
No. of reflections	2396
No. of parameters	174
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, −0.22

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
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full crystallographic data

IUCrData (2016). **1**, x160793 [doi:10.1107/S2414314616007938]

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Crystal data

$C_{13}H_{14}N_4O$
M_r = 242.28
Monoclinic, $P2_1/c$
a = 6.3283 (1) Å
b = 19.6204 (4) Å
c = 10.1245 (2) Å
β = 105.746 (1)°
V = 1209.92 (4) Å^3
Z = 4
$F(000)$ = 512
D_x = 1.330 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9985 reflections
θ = 4.5–72.4°
μ = 0.72 mm^{-1}
T = 150 K
Slab, colourless
0.18 × 0.11 × 0.05 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro–focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
T_{min} = 0.88, T_{max} = 0.96
13389 measured reflections
2396 independent reflections
2144 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 72.4°, θ_{min} = 4.5°
h = −7→7
k = −22→24
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.091
S = 1.05
2396 reflections
174 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 0.4538P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0028 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.98 Å) and included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. The methyl group on the phenyl ring is rotationally disordered and refined with a SHELX AFIX 123 instruction.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.13164 (14)	0.25617 (5)	0.45005 (8)	0.0234 (2)	
N1	−0.45027 (16)	0.19423 (5)	0.10816 (10)	0.0219 (2)	
H1N	−0.548 (3)	0.1943 (9)	0.0242 (18)	0.041 (5)*	
N2	−0.26056 (16)	0.22876 (5)	0.12750 (10)	0.0230 (2)	
N3	0.13616 (16)	0.28777 (5)	0.23431 (10)	0.0199 (2)	
H3N	0.075 (3)	0.2822 (9)	0.1453 (19)	0.040 (5)*	
N4	0.33063 (16)	0.32301 (5)	0.28110 (10)	0.0197 (2)	
C1	−0.6798 (2)	0.12747 (7)	0.22526 (13)	0.0257 (3)	
H1A	−0.7097	0.1311	0.3150	0.038*	
H1B	−0.6543	0.0796	0.2064	0.038*	
H1C	−0.8061	0.1448	0.1541	0.038*	
C2	−0.48123 (19)	0.16845 (6)	0.22564 (12)	0.0194 (3)	
C3	−0.29917 (19)	0.18685 (6)	0.32884 (12)	0.0202 (3)	
H3A	−0.2692	0.1768	0.4239	0.024*	
C4	−0.16778 (18)	0.22376 (6)	0.26275 (11)	0.0181 (2)	
C5	0.04539 (18)	0.25684 (6)	0.32520 (11)	0.0183 (2)	
C6	0.3987 (2)	0.35207 (6)	0.18704 (12)	0.0215 (3)	
H6	0.3148	0.3475	0.0942	0.026*	
C7	0.60155 (19)	0.39211 (6)	0.21779 (12)	0.0208 (3)	
C8	0.7525 (2)	0.39328 (6)	0.34711 (13)	0.0254 (3)	
H8	0.7255	0.3672	0.4199	0.031*	
C9	0.9410 (2)	0.43211 (7)	0.36968 (13)	0.0274 (3)	
H9	1.0421	0.4322	0.4583	0.033*	
C10	0.9870 (2)	0.47127 (6)	0.26588 (13)	0.0251 (3)	
C11	0.8371 (2)	0.46969 (7)	0.13747 (13)	0.0274 (3)	
H11	0.8646	0.4958	0.0648	0.033*	
C12	0.6474 (2)	0.43060 (6)	0.11315 (12)	0.0249 (3)	
H12	0.5476	0.4301	0.0241	0.030*	
C13	1.1923 (2)	0.51398 (8)	0.29335 (16)	0.0362 (3)	
H13A	1.2769	0.5084	0.3893	0.054*	0.514 (19)
H13B	1.2813	0.4993	0.2330	0.054*	0.514 (19)
H13C	1.1521	0.5620	0.2756	0.054*	0.514 (19)
H13E	1.1966	0.5380	0.2093	0.054*	0.486 (19)

H13D	1.1923	0.5472	0.3656	0.054*	0.486 (19)
H13F	1.3214	0.4845	0.3230	0.054*	0.486 (19)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0202 (4)	0.0333 (5)	0.0147 (4)	−0.0029 (3)	0.0013 (3)	0.0003 (3)
N1	0.0180 (5)	0.0285 (5)	0.0162 (5)	−0.0025 (4)	−0.0004 (4)	0.0007 (4)
N2	0.0190 (5)	0.0311 (6)	0.0169 (5)	−0.0040 (4)	0.0016 (4)	0.0023 (4)
N3	0.0182 (5)	0.0250 (5)	0.0150 (5)	−0.0042 (4)	0.0020 (4)	−0.0008 (4)
N4	0.0171 (5)	0.0214 (5)	0.0201 (5)	−0.0015 (4)	0.0039 (4)	−0.0016 (4)
C1	0.0216 (6)	0.0269 (6)	0.0273 (6)	−0.0040 (5)	0.0046 (5)	−0.0006 (5)
C2	0.0190 (6)	0.0190 (5)	0.0199 (6)	0.0012 (4)	0.0049 (4)	−0.0002 (4)
C3	0.0211 (6)	0.0226 (6)	0.0164 (5)	−0.0008 (4)	0.0040 (4)	0.0004 (4)
C4	0.0174 (5)	0.0202 (5)	0.0155 (5)	0.0013 (4)	0.0023 (4)	−0.0001 (4)
C5	0.0172 (5)	0.0202 (5)	0.0167 (5)	0.0019 (4)	0.0035 (4)	−0.0003 (4)
C6	0.0223 (6)	0.0231 (6)	0.0184 (5)	−0.0008 (5)	0.0044 (4)	−0.0013 (4)
C7	0.0210 (6)	0.0194 (6)	0.0228 (6)	0.0007 (4)	0.0075 (5)	−0.0013 (4)
C8	0.0267 (6)	0.0260 (6)	0.0230 (6)	−0.0025 (5)	0.0056 (5)	0.0038 (5)
C9	0.0246 (6)	0.0277 (6)	0.0265 (6)	−0.0015 (5)	0.0011 (5)	0.0015 (5)
C10	0.0232 (6)	0.0204 (6)	0.0341 (7)	−0.0004 (5)	0.0119 (5)	−0.0029 (5)
C11	0.0325 (7)	0.0265 (6)	0.0273 (6)	−0.0033 (5)	0.0150 (5)	0.0014 (5)
C12	0.0273 (6)	0.0278 (6)	0.0199 (6)	−0.0011 (5)	0.0069 (5)	−0.0004 (5)
C13	0.0303 (7)	0.0333 (7)	0.0474 (9)	−0.0089 (6)	0.0144 (6)	−0.0041 (6)

Geometric parameters (Å, º)

O1—C5	1.2335 (14)	C6—H6	0.9500
N1—N2	1.3457 (14)	C7—C12	1.3941 (17)
N1—C2	1.3547 (15)	C7—C8	1.3960 (17)
N1—H1N	0.905 (18)	C8—C9	1.3813 (18)
N2—C4	1.3390 (14)	C8—H8	0.9500
N3—C5	1.3535 (15)	C9—C10	1.3949 (18)
N3—N4	1.3786 (13)	C9—H9	0.9500
N3—H3N	0.885 (18)	C10—C11	1.3863 (18)
N4—C6	1.2808 (15)	C10—C13	1.5068 (17)
C1—C2	1.4911 (16)	C11—C12	1.3893 (18)
C1—H1A	0.9800	C11—H11	0.9500
C1—H1B	0.9800	C12—H12	0.9500
C1—H1C	0.9800	C13—H13A	0.9800
C2—C3	1.3770 (16)	C13—H13B	0.9800
C3—C4	1.4020 (16)	C13—H13C	0.9800
C3—H3A	0.9500	C13—H13E	0.9800
C4—C5	1.4757 (15)	C13—H13D	0.9800
C6—C7	1.4643 (16)	C13—H13F	0.9800
N2—N1—C2	113.34 (9)	C7—C8—H8	119.8
N2—N1—H1N	119.3 (11)	C8—C9—C10	121.78 (12)

C2—N1—H1N	127.0 (11)	C8—C9—H9	119.1
C4—N2—N1	103.78 (9)	C10—C9—H9	119.1
C5—N3—N4	119.69 (9)	C11—C10—C9	117.68 (12)
C5—N3—H3N	119.3 (11)	C11—C10—C13	121.46 (12)
N4—N3—H3N	120.9 (11)	C9—C10—C13	120.86 (12)
C6—N4—N3	114.64 (10)	C10—C11—C12	121.14 (12)
C2—C1—H1A	109.5	C10—C11—H11	119.4
C2—C1—H1B	109.5	C12—C11—H11	119.4
H1A—C1—H1B	109.5	C11—C12—C7	120.82 (11)
C2—C1—H1C	109.5	C11—C12—H12	119.6
H1A—C1—H1C	109.5	C7—C12—H12	119.6
H1B—C1—H1C	109.5	C10—C13—H13A	109.5
N1—C2—C3	106.12 (10)	C10—C13—H13B	109.5
N1—C2—C1	121.44 (10)	H13A—C13—H13B	109.5
C3—C2—C1	132.41 (11)	C10—C13—H13C	109.5
C2—C3—C4	104.82 (10)	H13A—C13—H13C	109.5
C2—C3—H3A	127.6	H13B—C13—H13C	109.5
C4—C3—H3A	127.6	C10—C13—H13E	109.5
N2—C4—C3	111.94 (10)	H13A—C13—H13E	141.1
N2—C4—C5	120.14 (10)	H13B—C13—H13E	56.3
C3—C4—C5	127.90 (10)	H13C—C13—H13E	56.3
O1—C5—N3	123.37 (11)	C10—C13—H13D	109.5
O1—C5—C4	122.23 (10)	H13A—C13—H13D	56.3
N3—C5—C4	114.40 (10)	H13B—C13—H13D	141.1
N4—C6—C7	122.21 (11)	H13C—C13—H13D	56.3
N4—C6—H6	118.9	H13E—C13—H13D	109.5
C7—C6—H6	118.9	C10—C13—H13F	109.5
C12—C7—C8	118.25 (11)	H13A—C13—H13F	56.3
C12—C7—C6	118.69 (11)	H13B—C13—H13F	56.3
C8—C7—C6	123.06 (11)	H13C—C13—H13F	141.1
C9—C8—C7	120.32 (12)	H13E—C13—H13F	109.5
C9—C8—H8	119.8	H13D—C13—H13F	109.5

C2—N1—N2—C4	0.65 (13)	C3—C4—C5—N3	178.69 (11)
C5—N3—N4—C6	−177.96 (10)	N3—N4—C6—C7	179.59 (10)
N2—N1—C2—C3	−0.43 (14)	N4—C6—C7—C12	−170.31 (11)
N2—N1—C2—C1	−178.88 (10)	N4—C6—C7—C8	10.09 (19)
N1—C2—C3—C4	0.03 (13)	C12—C7—C8—C9	0.41 (19)
C1—C2—C3—C4	178.23 (12)	C6—C7—C8—C9	−179.99 (11)
N1—N2—C4—C3	−0.62 (13)	C7—C8—C9—C10	0.2 (2)
N1—N2—C4—C5	−178.99 (10)	C8—C9—C10—C11	−0.47 (19)
C2—C3—C4—N2	0.38 (14)	C8—C9—C10—C13	179.18 (12)
C2—C3—C4—C5	178.60 (11)	C9—C10—C11—C12	0.15 (19)
N4—N3—C5—O1	−2.66 (17)	C13—C10—C11—C12	−179.50 (12)
N4—N3—C5—C4	177.13 (9)	C10—C11—C12—C7	0.45 (19)
N2—C4—C5—O1	176.57 (11)	C8—C7—C12—C11	−0.73 (18)
C3—C4—C5—O1	−1.52 (19)	C6—C7—C12—C11	179.65 (11)
N2—C4—C5—N3	−3.22 (16)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1^{i}	0.905 (18)	2.191 (18)	2.8655 (13)	130.8 (14)
N1—H1*N*···N4^{i}	0.905 (18)	2.395 (18)	3.2419 (14)	155.9 (15)
N3—H3*N*···O1^{ii}	0.885 (18)	2.232 (18)	2.9971 (13)	144.4 (15)

Symmetry codes: (i) $x-1, -y+1/2, z-1/2$; (ii) $x, -y+1/2, z-1/2$.