

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

3-(4-Bromophenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehydeR. Prasath,^a P. Bhavana,^{a‡} Seik Weng Ng^{b,c} and Edward R. T. Tiekink^{b*}

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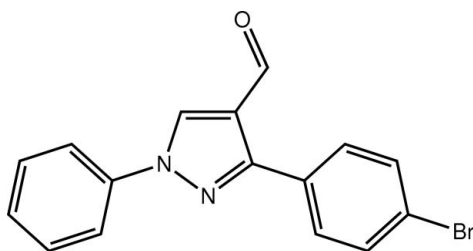
Received 11 September 2011; accepted 11 September 2011

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.025; wR factor = 0.069; data-to-parameter ratio = 14.3.

In the title compound, $\text{C}_{16}\text{H}_{11}\text{BrN}_2\text{O}$, the phenyl and chlorobenzene rings are twisted out of the mean plane of the pyrazole ring, forming dihedral angles of 13.70 (10) and 36.48 (10)°, respectively. The carbaldehyde group is also twisted out of the pyrazole plane [the C–C–C–O torsion angle is 7.9 (3)°]. A helical supramolecular chain along the b axis and mediated by C–H···O interactions is the most prominent feature of the crystal packing.

Related literature

For background details and biological applications of pyrazoles, see: Kaushik *et al.* (2010); Ali *et al.* (2007); Krishnamurthy *et al.* (2004). For a related structure, see: Asiri *et al.* (2011).



Experimental

Crystal data

$\text{C}_{16}\text{H}_{11}\text{BrN}_2\text{O}$
 $M_r = 327.18$

Monoclinic, $P2_1/n$
 $a = 17.7233$ (4) Å

$b = 3.8630$ (1) Å
 $c = 20.4224$ (5) Å
 $\beta = 110.137$ (3)°
 $V = 1312.75$ (6) Å³
 $Z = 4$

Cu $K\alpha$ radiation
 $\mu = 4.23$ mm⁻¹
 $T = 100$ K
 $0.25 \times 0.20 \times 0.15$ mm

Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010)
 $T_{\min} = 0.418$, $T_{\max} = 0.569$

4619 measured reflections
2593 independent reflections
2542 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.069$
 $S = 1.02$
2593 reflections

181 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.66$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C12–H12···O1 ⁱ	0.95	2.49	3.435 (2)	171
C16–H16···O1 ⁱⁱ	0.95	2.46	3.288 (3)	145

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

Data collection: *CrysAlis PRO* (Agilent, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

PB acknowledges the Department of Science and Technology (DST), India, for a research grant (SR/FTP/CS-57/2007). The authors also thank the University of Malaya for support of the crystallographic facility.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6403).

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supporting information

Acta Cryst. (2011). E67, o2650 [https://doi.org/10.1107/S1600536811036841]

3-(4-Bromophenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde**R. Prasath, P. Bhavana, Seik Weng Ng and Edward R. T. Tiekink****S1. Comment**

A broad spectrum of biological activities [anti-bacterial, anti-depressant, anti-convulsive, anti-hypertensive, anti-oxidant anti-viral and anti-tumour] have been noted for pyrazoles and their derivatives (Kaushik *et al.*, 2010; Ali *et al.*, 2007; Krishnamurthy *et al.*, 2004). In continuation of structural studies in this area (Asiri *et al.*, 2011), the title compound, (I), was investigated.

The dihedral angles formed between the central pyrazole ring [r.m.s. deviation = 0.003 Å] and the N- and C-bound benzene rings of 13.70 (10) and 36.48 (10)°, respectively, indicate significant twists in the molecule of (I), Fig. 1. Similarly, the carbaldehyde group is twisted out of the plane of the five-membered ring as seen in the value of the C13—C14—C16—O1 torsion angle of 7.9 (3)°. The relative disposition of the benzene rings preclude close intermolecular association with the imine-N2 atom which, indeed, forms a close intramolecular C2—H···N2 contact, Table 1.

The crystal packing features C—H···O interactions involving a bifurcated carbonyl-O1 atom, Table 1. These result in the formation of a helical supramolecular chain along the *b* axis, Fig. 2.

S2. Experimental

Phosphoryl chloride (5.6 ml) was added drop wise to cold *N,N*-dimethylformamide (22.5 ml) under continuous stirring at 273–278 K for about 30 min. 4-Bromoacetophenone phenylhydrazone (5 g, 17 mmol) was added to the above reaction mixture. The resulting mixture was further stirred at 333 K for 6 h. and cooled to room temperature. The crude product was poured into crushed ice which resulted in a white precipitate. The resultant solid was filtered, dried and purified by column chromatography using chloroform. Recrystallization was by slow evaporation of chloroform solution of (I) which yielded colourless prisms. *M.pt.* 413–415 K. Yield: 56%.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions [C—H 0.95 Å, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] and were included in the refinement in the riding model approximation.

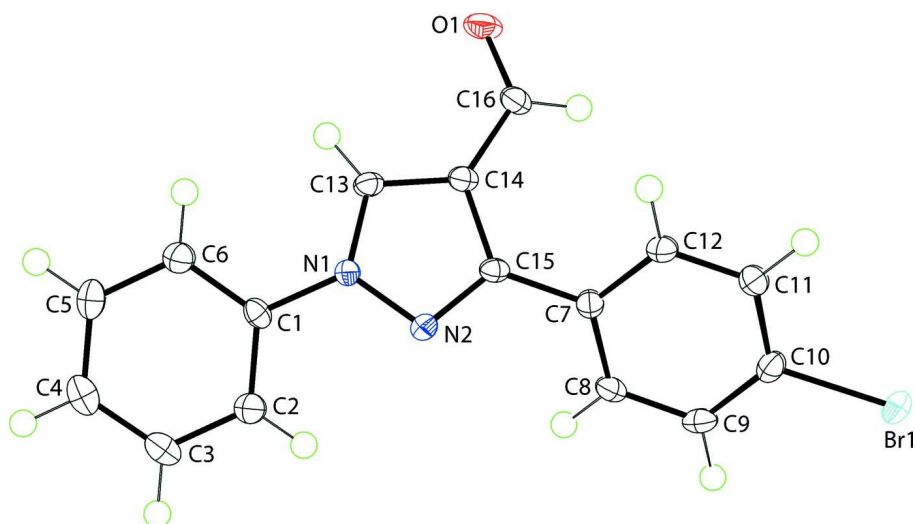


Figure 1

The molecular structures of (I) showing displacement ellipsoids at the 70% probability level.

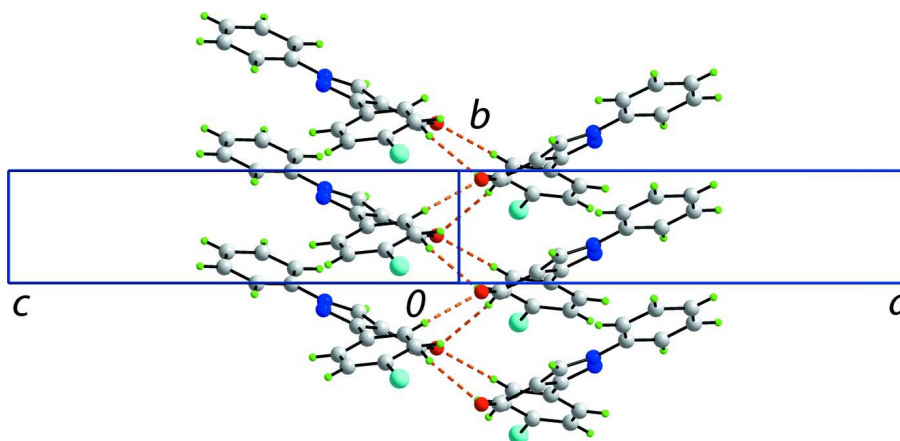


Figure 2

Helical supramolecular chain in (I) mediated by C—H...O (orange dashed lines) interactions.

3-(4-Bromophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde

Crystal data

$C_{16}H_{11}BrN_2O$

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Hall symbol: $-P 2_1n$

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$b = 3.8630$ (1) Å

$c = 20.4224$ (5) Å

$\beta = 110.137$ (3)°

$V = 1312.75$ (6) Å³

$Z = 4$

$F(000) = 656$

$D_x = 1.655$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 3680 reflections

$\theta = 2.7$ – 74.1 °

$\mu = 4.23$ mm⁻¹

$T = 100$ K

Prism, colourless

$0.25 \times 0.20 \times 0.15$ mm

Data collection

Agilent SuperNova Dual
diffractometer with an Atlas detector
Radiation source: SuperNova (Cu) X-ray
Source
Mirror monochromator
Detector resolution: 10.4041 pixels mm⁻¹
 ω scans
Absorption correction: multi-scan
(*CrysAlis PRO*; Agilent, 2010)

$T_{\min} = 0.418$, $T_{\max} = 0.569$
4619 measured reflections
2593 independent reflections
2542 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$
 $\theta_{\max} = 74.3^\circ$, $\theta_{\min} = 2.9^\circ$
 $h = -21 \rightarrow 21$
 $k = -4 \rightarrow 4$
 $l = -19 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.069$
 $S = 1.02$
2593 reflections
181 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 1.2934P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.004$
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.66 \text{ e } \text{Å}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s 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 $F^2 > 2\sigma(F^2)$ 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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.979494 (11)	0.14952 (5)	1.111751 (9)	0.01554 (9)
O1	0.66107 (9)	0.4209 (4)	0.71084 (7)	0.0183 (3)
N1	0.54596 (9)	0.8378 (4)	0.84419 (8)	0.0106 (3)
N2	0.60504 (9)	0.7642 (4)	0.90629 (8)	0.0114 (3)
C1	0.47250 (10)	0.9916 (5)	0.84392 (9)	0.0112 (3)
C2	0.45581 (11)	0.9963 (5)	0.90561 (10)	0.0146 (4)
H2	0.4929	0.9008	0.9471	0.018*
C3	0.38437 (12)	1.1422 (5)	0.90583 (11)	0.0170 (4)
H3	0.3729	1.1496	0.9480	0.020*
C4	0.32952 (12)	1.2773 (5)	0.84520 (11)	0.0169 (4)
H4	0.2805	1.3744	0.8456	0.020*
C5	0.34673 (11)	1.2698 (5)	0.78370 (10)	0.0165 (4)
H5	0.3092	1.3617	0.7421	0.020*
C6	0.41865 (12)	1.1284 (5)	0.78272 (10)	0.0148 (4)
H6	0.4307	1.1255	0.7408	0.018*
C7	0.73867 (11)	0.5078 (5)	0.94282 (9)	0.0112 (4)

C8	0.73831 (12)	0.3647 (5)	1.00557 (10)	0.0128 (4)
H8	0.6888	0.3396	1.0135	0.015*
C9	0.80911 (12)	0.2589 (5)	1.05641 (9)	0.0141 (4)
H9	0.8085	0.1639	1.0991	0.017*
C10	0.88090 (11)	0.2942 (5)	1.04391 (10)	0.0135 (4)
C11	0.88296 (11)	0.4357 (5)	0.98216 (10)	0.0146 (4)
H11	0.9326	0.4580	0.9744	0.018*
C12	0.81210 (11)	0.5442 (5)	0.93190 (9)	0.0133 (4)
H12	0.8133	0.6440	0.8898	0.016*
C13	0.56590 (11)	0.7418 (5)	0.78887 (9)	0.0117 (3)
H13	0.5340	0.7694	0.7411	0.014*
C14	0.64162 (11)	0.5954 (5)	0.81478 (10)	0.0115 (4)
C15	0.66323 (11)	0.6177 (5)	0.88888 (9)	0.0105 (4)
C16	0.68436 (11)	0.4243 (5)	0.77447 (10)	0.0135 (4)
H16	0.7332	0.3085	0.7991	0.016*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01392 (13)	0.01863 (13)	0.01135 (12)	0.00306 (7)	0.00088 (9)	0.00292 (7)
O1	0.0176 (7)	0.0277 (7)	0.0116 (6)	-0.0046 (6)	0.0076 (5)	-0.0054 (6)
N1	0.0085 (7)	0.0138 (8)	0.0094 (7)	0.0002 (6)	0.0029 (6)	-0.0001 (5)
N2	0.0103 (7)	0.0144 (7)	0.0089 (7)	0.0004 (6)	0.0024 (6)	0.0000 (6)
C1	0.0089 (8)	0.0110 (9)	0.0143 (8)	-0.0015 (7)	0.0048 (7)	-0.0025 (7)
C2	0.0142 (9)	0.0164 (9)	0.0134 (8)	0.0000 (7)	0.0051 (7)	-0.0003 (7)
C3	0.0168 (10)	0.0180 (10)	0.0195 (10)	-0.0001 (7)	0.0103 (8)	-0.0031 (7)
C4	0.0130 (9)	0.0141 (9)	0.0246 (10)	-0.0002 (8)	0.0076 (8)	-0.0026 (8)
C5	0.0113 (9)	0.0161 (9)	0.0192 (9)	0.0009 (8)	0.0014 (7)	0.0006 (8)
C6	0.0139 (9)	0.0172 (10)	0.0136 (9)	-0.0002 (7)	0.0051 (8)	0.0002 (7)
C7	0.0107 (8)	0.0111 (9)	0.0113 (8)	0.0002 (7)	0.0032 (7)	-0.0014 (7)
C8	0.0131 (9)	0.0150 (9)	0.0127 (9)	-0.0004 (7)	0.0075 (7)	-0.0008 (7)
C9	0.0190 (9)	0.0149 (9)	0.0097 (8)	0.0004 (8)	0.0067 (7)	0.0011 (7)
C10	0.0129 (9)	0.0141 (9)	0.0110 (8)	0.0007 (7)	0.0010 (7)	-0.0009 (7)
C11	0.0106 (9)	0.0200 (9)	0.0138 (9)	-0.0019 (7)	0.0049 (7)	0.0012 (8)
C12	0.0135 (9)	0.0167 (9)	0.0108 (8)	-0.0006 (7)	0.0053 (7)	0.0018 (7)
C13	0.0123 (8)	0.0145 (9)	0.0082 (8)	-0.0018 (7)	0.0034 (7)	-0.0014 (7)
C14	0.0119 (8)	0.0132 (8)	0.0103 (8)	-0.0016 (7)	0.0051 (7)	-0.0010 (7)
C15	0.0114 (9)	0.0117 (8)	0.0094 (9)	-0.0026 (6)	0.0048 (7)	-0.0009 (6)
C16	0.0118 (8)	0.0168 (9)	0.0134 (9)	-0.0020 (7)	0.0064 (7)	-0.0031 (7)

Geometric parameters (Å, °)

Br1—C10	1.9023 (19)	C7—C8	1.398 (3)
O1—C16	1.220 (2)	C7—C12	1.401 (2)
N1—C13	1.347 (2)	C7—C15	1.472 (3)
N1—N2	1.368 (2)	C8—C9	1.387 (3)
N1—C1	1.429 (2)	C8—H8	0.9500
N2—C15	1.328 (2)	C9—C10	1.388 (3)

C1—C6	1.390 (3)	C9—H9	0.9500
C1—C2	1.390 (3)	C10—C11	1.386 (3)
C2—C3	1.387 (3)	C11—C12	1.385 (3)
C2—H2	0.9500	C11—H11	0.9500
C3—C4	1.386 (3)	C12—H12	0.9500
C3—H3	0.9500	C13—C14	1.383 (3)
C4—C5	1.391 (3)	C13—H13	0.9500
C4—H4	0.9500	C14—C15	1.430 (2)
C5—C6	1.393 (3)	C14—C16	1.455 (3)
C5—H5	0.9500	C16—H16	0.9500
C6—H6	0.9500		
C13—N1—N2	112.47 (15)	C9—C8—H8	119.5
C13—N1—C1	127.81 (16)	C7—C8—H8	119.5
N2—N1—C1	119.70 (15)	C8—C9—C10	118.95 (17)
C15—N2—N1	104.93 (14)	C8—C9—H9	120.5
C6—C1—C2	121.05 (17)	C10—C9—H9	120.5
C6—C1—N1	120.28 (16)	C11—C10—C9	121.26 (17)
C2—C1—N1	118.67 (17)	C11—C10—Br1	118.24 (14)
C3—C2—C1	119.17 (18)	C9—C10—Br1	120.50 (14)
C3—C2—H2	120.4	C12—C11—C10	119.49 (17)
C1—C2—H2	120.4	C12—C11—H11	120.3
C2—C3—C4	120.68 (18)	C10—C11—H11	120.3
C2—C3—H3	119.7	C11—C12—C7	120.44 (17)
C4—C3—H3	119.7	C11—C12—H12	119.8
C3—C4—C5	119.61 (18)	C7—C12—H12	119.8
C3—C4—H4	120.2	N1—C13—C14	106.98 (16)
C5—C4—H4	120.2	N1—C13—H13	126.5
C4—C5—C6	120.48 (19)	C14—C13—H13	126.5
C4—C5—H5	119.8	C13—C14—C15	104.56 (16)
C6—C5—H5	119.8	C13—C14—C16	126.51 (17)
C1—C6—C5	118.99 (18)	C15—C14—C16	128.61 (17)
C1—C6—H6	120.5	N2—C15—C14	111.05 (16)
C5—C6—H6	120.5	N2—C15—C7	120.77 (16)
C8—C7—C12	118.90 (17)	C14—C15—C7	128.17 (16)
C8—C7—C15	120.71 (16)	O1—C16—C14	123.78 (18)
C12—C7—C15	120.40 (16)	O1—C16—H16	118.1
C9—C8—C7	120.97 (17)	C14—C16—H16	118.1
C13—N1—N2—C15	-0.1 (2)	Br1—C10—C11—C12	-179.81 (15)
C1—N1—N2—C15	178.39 (16)	C10—C11—C12—C7	-0.8 (3)
C13—N1—C1—C6	-14.2 (3)	C8—C7—C12—C11	0.9 (3)
N2—N1—C1—C6	167.59 (17)	C15—C7—C12—C11	-178.95 (18)
C13—N1—C1—C2	164.85 (18)	N2—N1—C13—C14	0.3 (2)
N2—N1—C1—C2	-13.4 (3)	C1—N1—C13—C14	-178.04 (17)
C6—C1—C2—C3	-0.4 (3)	N1—C13—C14—C15	-0.3 (2)
N1—C1—C2—C3	-179.44 (17)	N1—C13—C14—C16	173.58 (18)
C1—C2—C3—C4	1.0 (3)	N1—N2—C15—C14	-0.1 (2)

C2—C3—C4—C5	-0.7 (3)	N1—N2—C15—C7	178.76 (16)
C3—C4—C5—C6	-0.1 (3)	C13—C14—C15—N2	0.3 (2)
C2—C1—C6—C5	-0.4 (3)	C16—C14—C15—N2	-173.44 (19)
N1—C1—C6—C5	178.59 (18)	C13—C14—C15—C7	-178.49 (18)
C4—C5—C6—C1	0.7 (3)	C16—C14—C15—C7	7.8 (3)
C12—C7—C8—C9	-0.2 (3)	C8—C7—C15—N2	37.3 (3)
C15—C7—C8—C9	179.64 (17)	C12—C7—C15—N2	-142.86 (19)
C7—C8—C9—C10	-0.6 (3)	C8—C7—C15—C14	-143.99 (19)
C8—C9—C10—C11	0.7 (3)	C12—C7—C15—C14	35.8 (3)
C8—C9—C10—Br1	-179.51 (15)	C13—C14—C16—O1	7.9 (3)
C9—C10—C11—C12	0.0 (3)	C15—C14—C16—O1	-179.63 (19)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C12—H12...O1 ⁱ	0.95	2.49	3.435 (2)	171
C16—H16...O1 ⁱⁱ	0.95	2.46	3.288 (3)	145

Symmetry codes: (i) $-x+3/2, y+1/2, -z+3/2$; (ii) $-x+3/2, y-1/2, -z+3/2$.