organic compounds

Dimethyl 1-(3-cyanobenzyl)-1*H*-pyrazole-3,5-dicarboxylate

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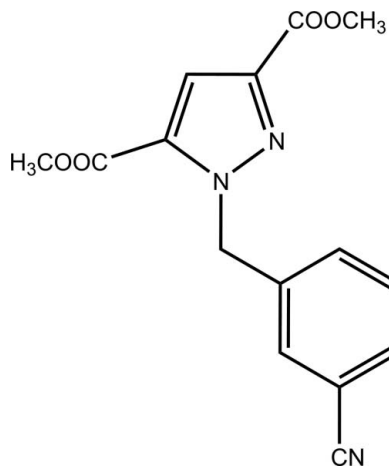Correspondence e-mail: zhaohong@seu.edu.cn

In the molecule of the title compound, $C_{15}H_{13}N_3O_4$, the dihedral angle between the pyrazole and benzene ring planes is 67.7 (1)°. The crystal structure is stabilized by an intramolecular C—H···O hydrogen bond and two weak intermolecular C—H···O interactions.

Related literature

For the biological activity of pyrazoles, see: Lee *et al.* (1989); Chambers *et al.* (1985). For the importance of nitrile derivatives in the synthesis of some heterocyclic molecules, see: Radl *et al.* (2000). For related structures, see: Fu & Zhao (2007); Xiao & Zhao (2008*a*,*b*,*c*).

Experimental

Crystal data

$C_{15}H_{13}N_3O_4$	$\gamma = 82.13$ (4)°
$M_r = 299.28$	$V = 739.7$ (5) Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.783$ (3) Å	Mo $K\alpha$ radiation
$b = 9.538$ (4) Å	$\mu = 0.10$ mm^{-1}
$c = 9.999$ (4) Å	$T = 292$ K
$\alpha = 68.42$ (3)°	$0.40 \times 0.30 \times 0.20$ mm
$\beta = 71.79$ (4)°	

Data collection

Rigaku SCXmini diffractometer	7555 measured reflections
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005) $T_{min} = 0.968$, $T_{max} = 0.979$	3338 independent reflections
	2093 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$	201 parameters
$wR(F^2) = 0.147$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{max} = 0.16$ e Å^{-3}
3338 reflections	$\Delta\rho_{min} = -0.16$ e Å^{-3}

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

$D-$H$\cdots A$	$D-$H	H$\cdots A$	$D\cdots A$	$D-$H$\cdots A$
C15—H15B···O1^i	0.96	2.43	3.363 (3)	163
C9—H9···O1^{ii}	0.93	2.53	3.348 (3)	147
C6—H6A···O4	0.97	2.41	2.979 (3)	117

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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supplementary materials

Dimethyl 1-(3-cyanobenzyl)-1*H*-pyrazole-3,5-dicarboxylate

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Comment

It is well known that many pyrazole-related molecules have received much attention due to their biological activities (Lee *et al.*, 1989; Chambers *et al.*, 1985). In addition, nitrile derivatives are important materials in the synthesis of some heterocyclic molecules (Radl *et al.*, 2000). Recently, we have reported a few benzonitrile compounds (Fu *et al.*, 2007; Xiao *et al.*,2008*a*, 2008*b*,2008*c*). As an extension of our work on the structural characterization of nitrile compounds, the structure of the title compound is reported here. In the molecule of the title compound (Fig. 1) bond lengths and angles have normal values. The dihedral angle between the planes of the pyrazole and phenyl rings is 67.74 (14) °. The molecular conformation is stabilized by an intramolecular C—H···O hydrogen bond and weak intermolecular C—H···O interactions (Table 1)..

Experimental

Dimethyl 1*H*-Pyrazole-3,5-dicarboxylate (0.185 mg,1 mmol) and 3-(bromomethyl)benzonitrile (0.196 mg,1 mmol) were dissolved in acetone in the presence of K_2CO_3 (0.138 mg,1 mmol) and heated under reflux for 1 d. After the mixture was cooled to room temperature, the solution was filtered and the solvent removed in vacuum to afford a white precipitate of the title compound. Colourless crystals suitable for X-ray diffraction were obtained from a solution of 100 mg in 15 ml diethylether by slow evaporation after 7 d.

Refinement

All H atoms were detected in a difference Fourier map but were placed in calculated positions and refined using a riding motion approximation, with C_{aryl}—H, $C_{methylene}$—H, C_{methyl}—H = 0.93, 097 and 0.96 Å. $U_{iso}(H_{aryl})=1.2U_{eq}(C_{aryl})$; $U_{iso}(H_{methylene})=1.2U_{eq}(C_{methylene})$; $U_{iso}(H_{methyl})=1.5U_{eq}(C_{methyl})$.
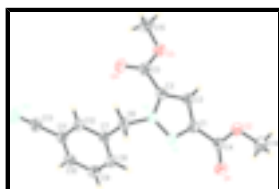
Figures

Fig. 1. The molecular structure of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Dimethyl 1-(3-cyanobenzyl)-1*H*-pyrazole-3,5-dicarboxylate

Crystal data

$C_{15}H_{13}N_3O_4$	$Z = 2$
$M_r = 299.28$	$F_{000} = 312$

supplementary materials

Triclinic, $P\bar{1}$	$D_x = 1.344$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 8.783$ (3) Å	Cell parameters from 1442 reflections
$b = 9.538$ (4) Å	$\theta = 2.4–27.3°$
$c = 9.999$ (4) Å	$\mu = 0.10$ mm^{-1}
$\alpha = 68.42$ (3)°	$T = 292$ K
$\beta = 71.79$ (4)°	Block, colorless
$\gamma = 82.13$ (4)°	$0.40 \times 0.30 \times 0.20$ mm
$V = 739.7$ (5) Å^3	

Data collection

Rigaku SCXmini diffractometer	3338 independent reflections
Radiation source: fine-focus sealed tube	2093 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.031$
Detector resolution: 13.6612 pixels mm^{-1}	$\theta_{max} = 27.4°$
$T = 292$ K	$\theta_{min} = 2.3°$
ω scans	$h = -11 \rightarrow 11$
Absorption correction: multi-scan (CrystalClear; Rigaku, 2005)	$k = -12 \rightarrow 12$
$T_{min} = 0.968$, $T_{max} = 0.979$	$l = -12 \rightarrow 12$
7555 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.056$	H-atom parameters constrained
$wR(F^2) = 0.147$	$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 0.0696P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
3338 reflections	$\Delta\rho_{max} = 0.16$ e Å^{-3}
201 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

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

	x	*y*	*z*	$U_{iso}*/U_{eq}$
C1	0.2466 (2)	0.1608 (2)	0.4437 (2)	0.0473 (5)
C2	0.2324 (2)	0.0151 (2)	0.4487 (2)	0.0485 (5)
H2	0.2544	−0.0753	0.5185	0.058*
C3	0.1787 (2)	0.0343 (2)	0.3276 (2)	0.0453 (5)
C4	0.2972 (2)	0.2120 (3)	0.5461 (2)	0.0530 (5)
C5	0.1399 (2)	−0.0794 (2)	0.2763 (2)	0.0516 (5)
C6	0.1126 (2)	0.2702 (2)	0.1210 (2)	0.0513 (5)
H6A	0.1388	0.2105	0.0561	0.062*
H6B	0.1713	0.3630	0.0669	0.062*
C7	−0.0655 (2)	0.3076 (2)	0.1568 (2)	0.0441 (5)
C8	−0.1362 (3)	0.3905 (2)	0.2511 (2)	0.0548 (5)
H8	−0.0735	0.4208	0.2948	0.066*
C9	−0.2976 (3)	0.4282 (3)	0.2806 (3)	0.0618 (6)
H9	−0.3429	0.4818	0.3453	0.074*
C10	−0.3928 (3)	0.3868 (2)	0.2143 (2)	0.0564 (6)
H10	−0.5012	0.4135	0.2327	0.068*
C11	−0.3234 (2)	0.3050 (2)	0.1206 (2)	0.0501 (5)
C12	−0.1607 (2)	0.2639 (2)	0.0923 (2)	0.0476 (5)
H12	−0.1163	0.2074	0.0303	0.057*
C13	−0.4218 (3)	0.2621 (3)	0.0498 (3)	0.0625 (6)
C14	0.3840 (4)	0.1361 (3)	0.7627 (3)	0.0947 (10)
H14A	0.4685	0.2077	0.7128	0.142*
H14B	0.4199	0.0470	0.8309	0.142*
H14C	0.2922	0.1797	0.8174	0.142*
C15	0.1386 (3)	−0.3432 (3)	0.3310 (3)	0.0756 (7)
H15A	0.0277	−0.3388	0.3343	0.113*
H15B	0.1612	−0.4358	0.4042	0.113*
H15C	0.2046	−0.3388	0.2329	0.113*
N1	0.2055 (2)	0.26560 (19)	0.32636 (19)	0.0517 (4)
N2	0.16398 (19)	0.18644 (18)	0.25641 (17)	0.0460 (4)
N3	−0.4990 (3)	0.2293 (3)	−0.0067 (3)	0.0878 (7)
O1	0.2979 (2)	0.34090 (19)	0.5354 (2)	0.0816 (6)
O2	0.3407 (2)	0.09684 (17)	0.65206 (18)	0.0724 (5)
O3	0.1723 (2)	−0.21721 (16)	0.36374 (17)	0.0659 (5)
O4	0.0863 (2)	−0.05489 (18)	0.1728 (2)	0.0769 (5)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0473 (12)	0.0513 (12)	0.0480 (12)	−0.0011 (9)	−0.0202 (9)	−0.0170 (9)
C2	0.0510 (12)	0.0492 (12)	0.0461 (12)	−0.0012 (9)	−0.0194 (9)	−0.0126 (9)
C3	0.0429 (11)	0.0480 (11)	0.0461 (11)	−0.0024 (8)	−0.0145 (9)	−0.0153 (9)

C4	0.0528 (13)	0.0599 (14)	0.0562 (13)	0.0044 (10)	−0.0243 (10)	−0.0258 (11)
C5	0.0471 (12)	0.0576 (13)	0.0532 (13)	−0.0022 (9)	−0.0164 (10)	−0.0206 (10)
C6	0.0494 (12)	0.0601 (13)	0.0435 (12)	−0.0053 (9)	−0.0207 (9)	−0.0094 (9)
C7	0.0505 (12)	0.0415 (11)	0.0400 (11)	−0.0054 (8)	−0.0182 (9)	−0.0078 (8)
C8	0.0627 (14)	0.0541 (13)	0.0594 (13)	−0.0035 (10)	−0.0279 (11)	−0.0232 (10)
C9	0.0677 (15)	0.0597 (14)	0.0658 (15)	0.0024 (11)	−0.0194 (12)	−0.0314 (12)
C10	0.0512 (13)	0.0570 (13)	0.0634 (14)	0.0023 (10)	−0.0194 (11)	−0.0219 (11)
C11	0.0499 (12)	0.0522 (12)	0.0526 (12)	−0.0029 (9)	−0.0233 (10)	−0.0151 (9)
C12	0.0529 (12)	0.0511 (12)	0.0459 (11)	−0.0005 (9)	−0.0206 (9)	−0.0195 (9)
C13	0.0509 (13)	0.0758 (16)	0.0698 (16)	0.0021 (11)	−0.0254 (12)	−0.0295 (12)
C14	0.140 (3)	0.098 (2)	0.0809 (19)	0.0188 (18)	−0.075 (2)	−0.0427 (16)
C15	0.097 (2)	0.0552 (15)	0.0804 (18)	−0.0088 (13)	−0.0245 (15)	−0.0280 (13)
N1	0.0544 (10)	0.0532 (10)	0.0552 (11)	−0.0020 (8)	−0.0259 (8)	−0.0185 (8)
N2	0.0464 (9)	0.0503 (10)	0.0446 (9)	−0.0034 (7)	−0.0205 (7)	−0.0131 (7)
N3	0.0656 (14)	0.124 (2)	0.1012 (18)	0.0028 (13)	−0.0437 (13)	−0.0557 (16)
O1	0.1237 (16)	0.0589 (11)	0.0919 (13)	0.0097 (10)	−0.0644 (12)	−0.0358 (9)
O2	0.1047 (14)	0.0650 (10)	0.0687 (11)	0.0110 (9)	−0.0542 (10)	−0.0268 (8)
O3	0.0894 (12)	0.0511 (9)	0.0636 (10)	−0.0076 (8)	−0.0321 (9)	−0.0164 (7)
O4	0.1025 (14)	0.0705 (11)	0.0837 (12)	0.0033 (9)	−0.0579 (11)	−0.0317 (9)

Geometric parameters (Å, °)

C1—N1	1.345 (2)	C8—H8	0.9300
C1—C2	1.393 (3)	C9—C10	1.387 (3)
C1—C4	1.482 (3)	C9—H9	0.9300
C2—C3	1.375 (2)	C10—C11	1.381 (3)
C2—H2	0.9300	C10—H10	0.9300
C3—N2	1.369 (2)	C11—C12	1.397 (3)
C3—C5	1.475 (3)	C11—C13	1.452 (3)
C4—O1	1.195 (2)	C12—H12	0.9300
C4—O2	1.325 (2)	C13—N3	1.143 (3)
C5—O4	1.201 (2)	C14—O2	1.455 (3)
C5—O3	1.334 (3)	C14—H14A	0.9600
C6—N2	1.471 (2)	C14—H14B	0.9600
C6—C7	1.514 (3)	C14—H14C	0.9600
C6—H6A	0.9700	C15—O3	1.444 (3)
C6—H6B	0.9700	C15—H15A	0.9600
C7—C12	1.385 (2)	C15—H15B	0.9600
C7—C8	1.395 (3)	C15—H15C	0.9600
C8—C9	1.380 (3)	N1—N2	1.347 (2)
N1—C1—C2	111.68 (17)	C10—C9—H9	119.8
N1—C1—C4	118.44 (18)	C11—C10—C9	118.7 (2)
C2—C1—C4	129.88 (18)	C11—C10—H10	120.6
C3—C2—C1	104.90 (17)	C9—C10—H10	120.6
C3—C2—H2	127.6	C10—C11—C12	121.23 (18)
C1—C2—H2	127.6	C10—C11—C13	119.1 (2)
N2—C3—C2	107.05 (17)	C12—C11—C13	119.63 (19)
N2—C3—C5	123.21 (17)	C7—C12—C11	119.83 (19)
C2—C3—C5	129.74 (18)	C7—C12—H12	120.1

O1—C4—O2	124.09 (19)	C11—C12—H12	120.1
O1—C4—C1	124.3 (2)	N3—C13—C11	179.5 (3)
O2—C4—C1	111.57 (19)	O2—C14—H14A	109.5
O4—C5—O3	124.0 (2)	O2—C14—H14B	109.5
O4—C5—C3	126.4 (2)	H14A—C14—H14B	109.5
O3—C5—C3	109.59 (18)	O2—C14—H14C	109.5
N2—C6—C7	112.47 (16)	H14A—C14—H14C	109.5
N2—C6—H6A	109.1	H14B—C14—H14C	109.5
C7—C6—H6A	109.1	O3—C15—H15A	109.5
N2—C6—H6B	109.1	O3—C15—H15B	109.5
C7—C6—H6B	109.1	H15A—C15—H15B	109.5
H6A—C6—H6B	107.8	O3—C15—H15C	109.5
C12—C7—C8	118.64 (19)	H15A—C15—H15C	109.5
C12—C7—C6	120.28 (18)	H15B—C15—H15C	109.5
C8—C7—C6	121.05 (17)	C1—N1—N2	104.90 (16)
C9—C8—C7	121.12 (19)	N1—N2—C3	111.47 (15)
C9—C8—H8	119.4	N1—N2—C6	118.28 (16)
C7—C8—H8	119.4	C3—N2—C6	130.24 (16)
C8—C9—C10	120.4 (2)	C4—O2—C14	115.33 (19)
C8—C9—H9	119.8	C5—O3—C15	117.10 (18)
N1—C1—C2—C3	−0.4 (2)	C9—C10—C11—C13	−179.5 (2)
C4—C1—C2—C3	179.1 (2)	C8—C7—C12—C11	0.9 (3)
C1—C2—C3—N2	0.3 (2)	C6—C7—C12—C11	−177.04 (18)
C1—C2—C3—C5	−179.23 (19)	C10—C11—C12—C7	−1.1 (3)
N1—C1—C4—O1	3.2 (3)	C13—C11—C12—C7	178.51 (18)
C2—C1—C4—O1	−176.3 (2)	C2—C1—N1—N2	0.3 (2)
N1—C1—C4—O2	−177.21 (18)	C4—C1—N1—N2	−179.24 (16)
C2—C1—C4—O2	3.3 (3)	C1—N1—N2—C3	−0.1 (2)
N2—C3—C5—O4	−3.1 (3)	C1—N1—N2—C6	−179.84 (16)
C2—C3—C5—O4	176.4 (2)	C2—C3—N2—N1	−0.1 (2)
N2—C3—C5—O3	177.39 (18)	C5—C3—N2—N1	179.45 (17)
C2—C3—C5—O3	−3.1 (3)	C2—C3—N2—C6	179.55 (18)
N2—C6—C7—C12	−124.57 (19)	C5—C3—N2—C6	−0.9 (3)
N2—C6—C7—C8	57.5 (2)	C7—C6—N2—N1	−87.7 (2)
C12—C7—C8—C9	0.2 (3)	C7—C6—N2—C3	92.6 (2)
C6—C7—C8—C9	178.21 (19)	O1—C4—O2—C14	2.8 (4)
C7—C8—C9—C10	−1.3 (3)	C1—C4—O2—C14	−176.8 (2)
C8—C9—C10—C11	1.1 (3)	O4—C5—O3—C15	−0.6 (3)
C9—C10—C11—C12	0.1 (3)	C3—C5—O3—C15	178.93 (18)

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C15—H15B···O1[i]	0.96	2.43	3.363 (3)	163
C9—H9···O1[ii]	0.93	2.53	3.348 (3)	147
C6—H6A···O4	0.97	2.41	2.979 (3)	117

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*, −*y*+1, −*z*+1.

Fig. 1