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The orthorhombic polymorph of pyrazine-2-carboxylic acid revisited

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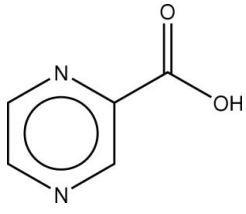
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.003 Å; R factor = 0.030; wR factor = 0.083; data-to-parameter ratio = 10.2.

The crystal structure of the orthorhombic polymorph of the title compound, $C_5H_4N_2O_2$, was previously reported in the space group $Pna2_1$ [Takusagawa, Higuchi, Shimada, Tamura & Sasada (1974). *Bull. Chem. Soc. Jpn*, **47**, 1409–1413]. Redetermination of this structure shows that the space group is centrosymmetric, *Pnma*, with the molecule located at a special position of *m* symmetry. The molecules are joined *via* O—H···N hydrogen bonds into a chain and further *via* C—H···O interactions into a sheet parallel to (010). No face-to-face stacking interactions are observed in this polymorph.

Related literature

For previously reported polymorphs of the title compound, see: Takusagawa *et al.* (1974); Shi *et al.* (2006). For applications of pyrazine-2-carboxylic acid, see: Wieser *et al.* (1997); Shul'pin & Suss-Fink (1995).



Experimental

Crystal data

$C_5H_4N_2O_2$
M_r = 124.10
Orthorhombic, *Pnma*
a = 11.3261 (18) Å
b = 6.3180 (12) Å
c = 7.3389 (11) Å
V = 525.16 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 150 (1) K
0.20 × 0.08 × 0.05 mm

Data collection

Kuma KM-4-CCD diffractometer
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1999)
T_{min} = 0.990, T_{max} = 0.999
3291 measured reflections
561 independent reflections
399 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.083
S = 0.96
561 reflections
55 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···N2^{i}	0.87	1.79	2.664 (2)	179
C2—H2···O1	0.93	2.41	2.736 (2)	101
C2—H2···O2^{ii}	0.93	2.40	3.089 (2)	131
C3—H3···O2^{iii}	0.93	2.42	3.156 (2)	136

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

Data collection: *CrysAlis CCD* (UNILIC & Kuma, 2000); cell refinement: *CrysAlis RED* (UNILIC & Kuma, 2000); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990) and *ORTEP-3* (Version 1.062; Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2089).

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supplementary materials

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The orthorhombic polymorph of pyrazine-2-carboxylic acid revisited

J. G. Malecki, R. Kruszynski and J. Kusz

Comment

The pyrazine-2-carboxylic acid is a one of the most common substances used for synthesis of pyrazine derivatives, which are important due to their bacteriostatic activity (Shi *et al.*, 2006), antituberculous activity (Wieser *et al.*, 1997) and selective oxidizing properties toward alkanes, benzene and alcohols (Shul'pin & Suss-Fink, 1995).

The title compound was reported in two polymorphic forms: orthorhombic, space group $Pna2_1$, (Ia) (Takusagawa *et al.*, 1974), and monoclinic, space group $P2_1$, (Ib) (Shi *et al.*, 2006). The structure of the polymorph (Ia) was determined by photographic methods and, based on solution derived from a sharpened Patterson map, the $Pna2_1$ space group was chosen as the correct one. However closer inspection of the atomic coordinates shows that the entire molecule is located on a mirror plane perpendicular to the *z* axis.

We have redetermined the crystal structure of the polymorph (Ia) in the *Pnma* space group at 150 K. Our results show that for the earlier reported crystal structure the choice of non-centrosymmetric space group was incorrect.

In (Ia) all atoms lie on a symmetry plane. The molecules are connected *via* O1—H1O···N2 hydrogen bonds (Table 1) into a zigzag chain extending along the [100] direction and further through C—H···O interactions (Table 1) into a sheet parallel to the (010) plane. This sheet is nearly identical to that observed in the polymorph (Ib). The main structural difference between the two polymorphs is in stacking of the adjacent sheets: in (Ib) they are related by a translation along the *a* axis (3.7249 (14) Å) whereas in (Ia) they are related by a 2_1 screw axis parallel to **b**. In the first case the sheet packing leads to face-to-face stacking interactions of the aromatic rings whereas in (Ia) no stacking interactions are observed as the closest distance between the ring centroids is 5.1427 (10) Å.

Experimental

Commercially available 2-pyrazinic acid (CAS: 98–97-5) was recrystallized from saturated water solution.

Refinement

The C bonded hydrogen atoms were placed in calculated positions after four cycles of anisotropic refinement and were refined as riding on adjacent carbon atom with $U_{iso}(H) = 1.2U_{eq}(C)$. The O bonded H atom was found in a difference Fourier synthesis after four cycles of anisotropic refinement and was refined as riding on adjacent O atom with $U_{iso}(H) = 1.5U_{eq}(O)$.

Figures

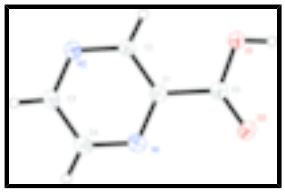

Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

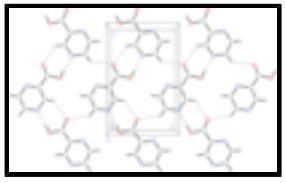

Fig. 2. Sheets parallel to (010) formed *via* O—H···O and C—H···O interactions (dashed lines).

pyrazine-2-carboxylic acid

Crystal data

$C_5H_4N_2O_2$	F_{000} = 256
M_r = 124.10	D_x = 1.570 Mg m^{-3}
Orthorhombic, *Pnma*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2n	Cell parameters from 984 reflections
a = 11.3261 (18) Å	θ = 3–20º
b = 6.3180 (12) Å	μ = 0.13 mm^{-1}
c = 7.3389 (11) Å	*T* = 150 (1) K
V = 525.16 (15) Å^3	Prism, colourless
Z = 4	0.20 × 0.08 × 0.05 mm

Data collection

Kuma KM-4-CCD diffractometer	561 independent reflections
Radiation source: fine-focus sealed tube	399 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.028
Detector resolution: 1048576 pixels mm^{-1}	θ_{max} = 26.0º
T = 150(1) K	θ_{min} = 3.3º
ω scans	*h* = −13→12
Absorption correction: numerical (X-RED; Stoe & Cie, 1999)	*k* = −7→6
T_{min} = 0.990, T_{max} = 0.999	*l* = −9→9
3291 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: mixed

$R[F^2 > 2\sigma(F^2)] = 0.030$	H-atom parameters constrained
$wR(F^2) = 0.083$	$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.96$	$(\Delta/\sigma)_{max} = 0.003$
561 reflections	$\Delta\rho_{max} = 0.12$ e Å^{-3}
55 parameters	$\Delta\rho_{min} = -0.30$ 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 $F^2 > 2$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}
O2	−0.13159 (11)	0.2500	0.57951 (18)	0.0269 (4)
O1	−0.00947 (12)	0.2500	0.82097 (18)	0.0286 (4)
H1O	−0.0764	0.2500	0.8797	0.043*
N1	0.05965 (14)	0.2500	0.3485 (2)	0.0239 (4)
N2	0.28508 (14)	0.2500	0.5024 (2)	0.0249 (4)
C1	0.07595 (16)	0.2500	0.5291 (3)	0.0209 (5)
C2	0.18758 (17)	0.2500	0.6053 (3)	0.0227 (5)
H2	0.1951	0.2500	0.7315	0.027*
C3	0.26968 (18)	0.2500	0.3227 (3)	0.0247 (5)
H3	0.3353	0.2500	0.2465	0.030*
C4	0.15758 (17)	0.2500	0.2468 (3)	0.0254 (5)
H4	0.1502	0.2500	0.1206	0.031*
C5	−0.03326 (18)	0.2500	0.6448 (3)	0.0223 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0166 (8)	0.0410 (9)	0.0232 (8)	0.000	−0.0006 (6)	0.000
O1	0.0170 (7)	0.0515 (9)	0.0174 (8)	0.000	0.0006 (6)	0.000
N1	0.0215 (10)	0.0315 (9)	0.0185 (9)	0.000	−0.0003 (6)	0.000
N2	0.0190 (9)	0.0377 (10)	0.0181 (9)	0.000	0.0019 (7)	0.000
C1	0.0192 (10)	0.0254 (10)	0.0181 (10)	0.000	0.0000 (8)	0.000
C2	0.0192 (10)	0.0333 (11)	0.0156 (10)	0.000	−0.0003 (8)	0.000

C3	0.0206 (10)	0.0340 (11)	0.0194 (11)	0.000	0.0033 (8)	0.000
C4	0.0254 (12)	0.0341 (11)	0.0168 (10)	0.000	0.0008 (8)	0.000
C5	0.0200 (10)	0.0272 (11)	0.0196 (10)	0.000	−0.0006 (8)	0.000

Geometric parameters (Å, °)

O2—C5	1.212 (2)	C1—C2	1.382 (3)
O1—C5	1.321 (2)	C1—C5	1.500 (3)
O1—H1O	0.8718	C2—H2	0.9300
N1—C4	1.337 (3)	C3—C4	1.386 (3)
N1—C1	1.338 (2)	C3—H3	0.9300
N2—C3	1.330 (3)	C4—H4	0.9300
N2—C2	1.338 (2)		
C5—O1—H1O	107.9	N2—C3—C4	121.22 (19)
C4—N1—C1	116.02 (16)	N2—C3—H3	119.4
C3—N2—C2	116.84 (17)	C4—C3—H3	119.4
N1—C1—C2	121.79 (17)	N1—C4—C3	122.36 (19)
N1—C1—C5	116.53 (17)	N1—C4—H4	118.8
C2—C1—C5	121.68 (18)	C3—C4—H4	118.8
N2—C2—C1	121.77 (18)	O2—C5—O1	125.05 (19)
N2—C2—H2	119.1	O2—C5—C1	122.27 (17)
C1—C2—H2	119.1	O1—C5—C1	112.69 (17)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···N2^{i}	0.87	1.79	2.664 (2)	179
C2—H2···O1	0.93	2.41	2.736 (2)	101
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Symmetry codes: (i) *x*−1/2, *y*, −*z*+3/2; (ii) *x*+1/2, *y*, −*z*+3/2; (iii) *x*+1/2, *y*, −*z*+1/2.

Fig. 1

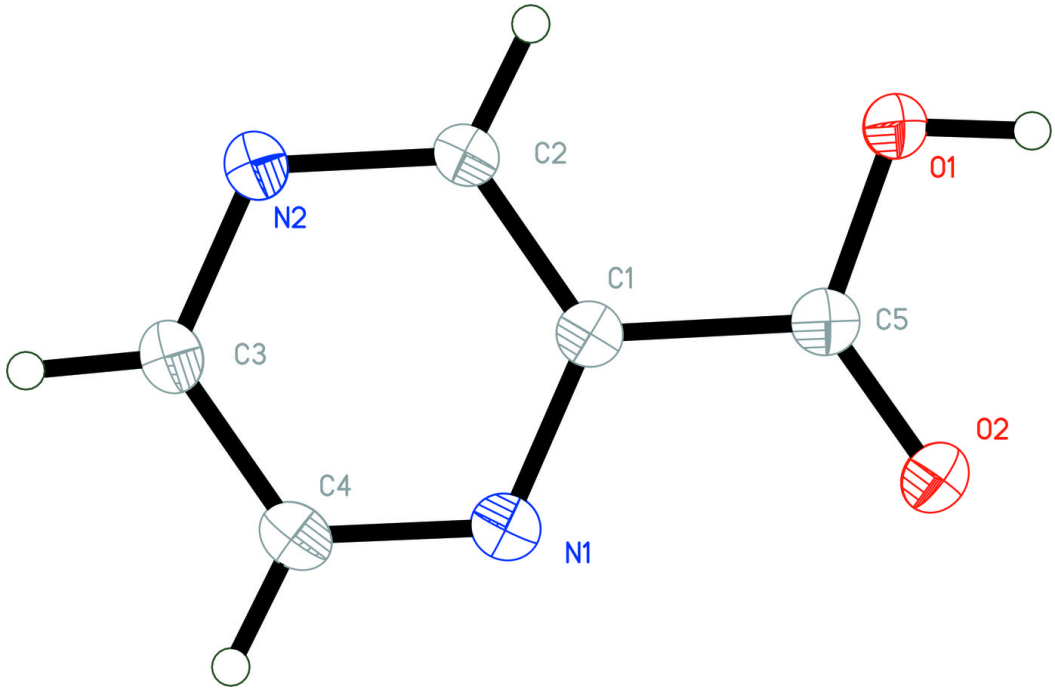

Fig. 2