research communications

Crystal structures and Hirshfeld surface analysis of 5-amino-1-(4-methoxyphenyl)pyrazole-4-carboxylic acid and 5-amino-3-(4-methoxyphenyl)-isoxazole

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The title compounds, $C_{11}H_{11}N_3O_3$, (I), and $C_{10}H_{10}N_2O_2$, (II), are commercially available and were crystallized from ethyl acetate solution. The dihedral angle between the pyrazole and phenyl rings in (I) is 52.34 (7)° and the equivalent angle between the isoxazole and phenyl rings in (II) is 7.30 (13)°. In the crystal of (I), the molecules form carboxylic acid inversion dimers with an $R(8)$ ring motif *via* pairwise O—H···O hydrogen bonds. In the crystal of (II), the molecules are linked *via* N—H···N hydrogen bonds forming chains propagating along [010] with a $C(5)$ motif. A weak N—H···π interaction also features in the packing of (II). Hirshfeld surface analysis was used to explore the intermolecular contacts in the crystals of both title compounds: the most important contacts for (I) are H···H (41.5%) and O···H/H···O (22.4%). For (II), the most significant contact percentages are H···H (36.1%) followed by C···H/H···C (31.3%).
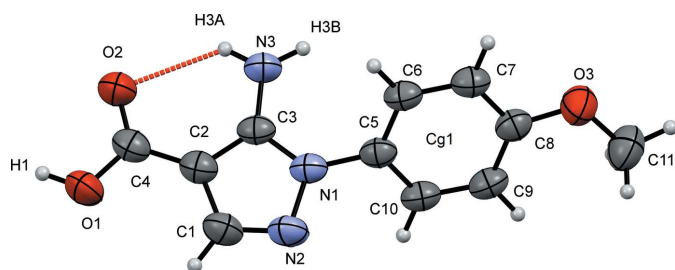
1. Chemical context

This report is one of a series on the structures and hydrogen-bonding motifs in small-molecule aromatic amino carboxylic acids (I) and small-molecule aromatic amino compounds (II). This study follows other reports including, for example, 3-aminopyrazine-2-carboxylic acid (Dobson & Gerkin, 1996), 5-aminoisophthalic acid hemihydrate (Dobson & Gerkin, 1998), and 1,4-dibenzylpiperazine-2,5-dione (Nunez, *et al.*, 2004). We now describe the structures of 5-amino-1-(4-methoxyphenyl)-pyrazole-4-carboxylic acid, (I) and 5-amino-3-(4-methoxyphenyl)isoxazole, (II).
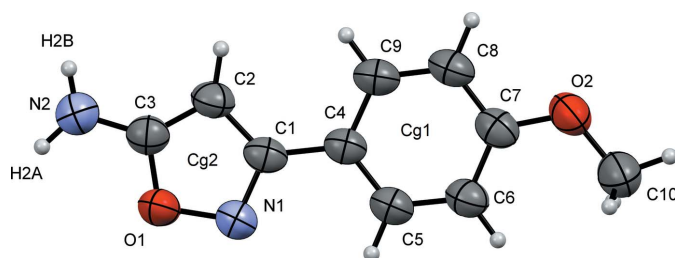

(I)　　　　(II)

2. Structural commentary

The molecular structure of compound (I) is shown in Fig. 1. The pyrazole ring (r.m.s. deviation = 0.010 Å) is rotated by 52.34 (7)° relative to the phenyl ring (r.m.s. deviation = 0.010 Å), which is the primary contribution to the general non-planarity of the molecule. An intramolecular N3—H3A···O2
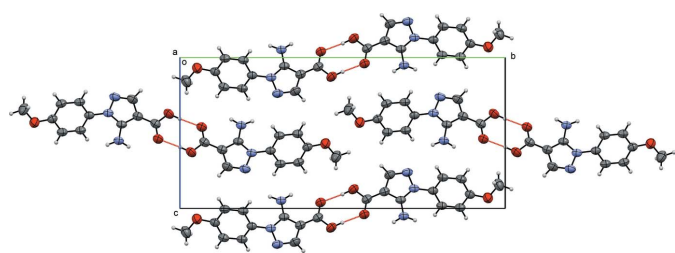
Figure 1
The molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level. The intramolecular hydrogen bond is represented by a red dashed line.

Figure 2
The molecular structure of (II) with displacement ellipsoids drawn at the 50% probability level.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$A\cdots$O2	0.87 (2)	2.32 (2)	2.941 (3)	128.5 (18)
O1—H1$\cdots$O2^i	0.90 (2)	1.75 (2)	2.649 (2)	176 (3)

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

$Cg2$ is the centroid of the C4–C9 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$A\cdots$N1^i	0.89 (3)	2.12 (3)	3.003 (5)	174 (6)
N2—H2$B\cdots Cg2^{ii}$	0.85 (2)	2.97 (4)	3.709 (4)	147 (4)

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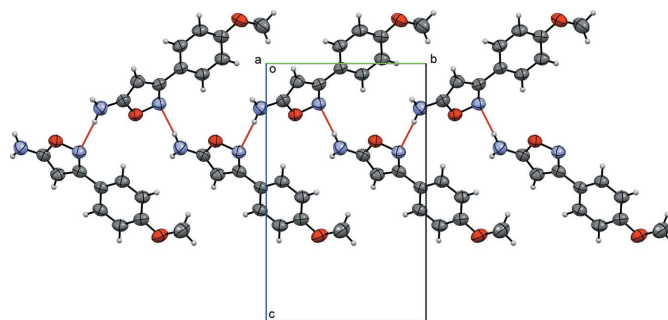
3. Supramolecular features

In the extended structure of (I), the molecules form centrosymmetric hydrogen-bonded dimers *via* the O1—H1$\cdots$O2^i [symmetry code: (i) $-x + 1, -y, -z + 1$] link to generate an $R(8)$ loop with O$\cdots$O = 2.649 (2) Å, see Table 1 and Fig. 3. These dimers are linked *via* π–π interactions, notably weak stacking interactions between the 4-methoxyphenyl rings [$Cg1\cdots Cg1$ $(x + 1, y, z) = 3.9608$ (4) Å, where $Cg1$ is the centroid of the C5–C10 ring] along the *a*-axis direction.

In the packing of (II), the molecules form hydrogen-bonded chains running along the *b*-axis direction *via* the N2—H2$A\cdots$N1^i hydrogen bond [symmetry code: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$] hydrogen bond forms a $C(5)$ chain motif with an N$\cdots$N distance of 3.003 (5) Å, see Table 2 and Fig. 4. No π–π interactions are observed.

4. Hirshfeld surface analysis

The intermolecular interactions were further investigated by quantitative analysis of the Hirshfeld surface, and visualized with *Crystal Explorer 17.5* (Turner *et al.*, 2017; Spackman *et al.*, 2009) and the two-dimensional fingerprint plots (McKinnon *et al.*, 2007). The shorter and longer contacts are indicated as red and blue spots, respectively, on the Hirshfeld surfaces, and contacts with distances approximately equal to the sum of the van der Waals radii are colored white. The function d_{norm} is a

hydrogen bond is observed (Table 1 and Fig. 1). This bond forms an $S(6)$ ring motif (Fig. 1 and Table 1) with an N3$\cdots$O2 distance of 2.941 (3) Å. This is a common feature in analogous compounds (such as those listed in the *Database survey*). The C3—N3 distance of 1.353 (2) Å is typical for an amino group bound to an aromatic ring. The carboxylic carbon–oxygen distances are 1.255 (2) and 1.316 (2) for C4—O2 and C4—O1, respectively, indicating that the former bond may be affected by the intramolecular N—H$\cdots$O hydrogen bond.

The molecular structure of compound (II) is shown in Fig. 2. The angle between the phenyl and isoxazole rings is 7.30 (13)°, resulting in the overall molecule being close to planar with the r.m.s. deviation of all non-hydrogen atoms being 0.054 Å. The N1—O1 distance is 1.434 (4) Å and is consistent with other isoxazoles (see *Database survey* section). The C3—N2 distance is 1.350 (5) Å and is typical of an amino group bound to an aromatic ring.

Figure 3
A view along the *a*-axis direction of the crystal packing of (I) with hydrogen bonds shown as red dashed lines.

Figure 4
A view along the *a*-axis direction of the crystal packing of (II) with hydrogen bonds shown as red dashed lines.

Figure 5
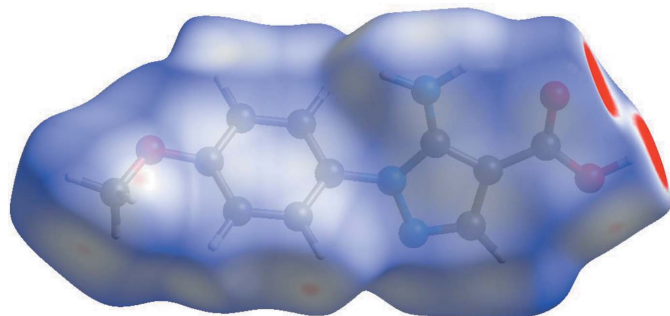Hirshfeld surface for (I) mapped over d_{norm}.

Figure 6
Hirshfeld surface for (II) mapped over d_{norm}.

ratio enclosing the distances of any surface point to the nearest interior (d_i) and exterior (d_e) atom and the van der Waals (vdW) radii of the atoms. The d_{norm} plots were mapped with a color scale between −0.18 au (blue) and +1.4 au (red).

Fig. 5. shows the d_{norm} surface of compound (I). The most intense red spots on the d_{norm} surface correspond to the O1—H1···O2 interactions. The red and blue triangles on the shape-index surface indicate that there are weak π-stacking interactions in the crystal structure. Analysis of the two-dimensional fingerprint plots indicate that the H···H (41.5%) interactions are the major factor in the crystal packing with O···H/H···O (22.4%) interactions making the next highest contribution. The percentage contributions of other significant contacts are: C···H/H···C (13.1%) and N···H/ H···N (8.7%).

Fig. 6 shows the d_{norm} surface of compound (II). The large red spots represent N2—H2A···N1 interactions. Some additional interactions indicated by very light-red spots correspond to contacts around phenyl ring and isoxazole rings: N2—H2B···Cg1[ii] [2.97 (4) Å], C6—H6···Cg1[iii] (2.86 Å) and C9—H9···Cg2[ii] (2.86 Å) [symmetry codes: (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; Cg1 and Cg2 are the centroids of the O1/N1/C1–C3 and C4–C9 rings, respectively]. Analysis of the two-dimensional fingerprint plots indicates that the H···H (36.1%) interactions are the major factor in the crystal packing with C···H/H···C (31.3%) contacts making the next highest contribution. The percentage contributions of other weak interactions are: O···H/H···O (17.3%) and N···H/ H···N (12.1%). Figures showing the shape-index surface for each compound and the overall fingerprint plots are included in the supporting information.

5. Database survey

A search of the Cambridge Structural Database (CSD, version 5.42, update of November 2020; Groom *et al.*, 2016) gave 13 hits for the 3-phenylisoxazol-5-amine moiety. The four most closely related compounds are: 5-diacetylamino-3,4-diphenylisoxazole (CSD refcode ACPIXZ; Simon *et al.*, 1974), 1,5-dimethyl-4-phenyl-3-(3-phenyl-1,2-oxazol-5-yl)imidazolidin-2-one (HOGYAE; Li *et al.*, 2007), *N*-4-dimethyl-*N*-[3-{4-(trifluoromethyl)phenyl]-1,2-oxazol-5-yl}benzene-1-sulfonamide (XOSHUL; Chen & Cui, 2019), 3-phenyl-5-(1*H*-pyrazol-1-yl)-1,2-oxazole (ZEVGIT; Mikhailov *et al.*, 2018).
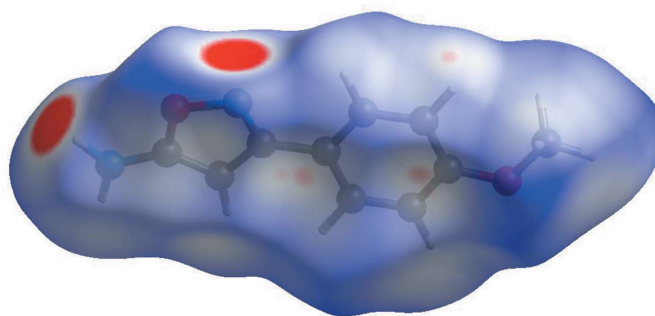
A similar search gave 14 hits for the 5-amino-1-phenyl-1*H*-pyrazole-4-carboxylic acid moiety. The seven most closely related compounds are: ethyl 1-(4-chloro-2-nitrophenyl)-5-nitro-4,5-dihydro-1*H*-pyrazole-4-carboxylate (GOLHEV; Zia-ur-Rehman *et al.*, 2009), 5-amino-1-phenyl-3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylic acid (HUDDEQ; Caruso *et al.*, 2009), 5-amino-1-phenyl-1*H*-pyrazole-4-carboxylic acid (KODXIL; Zia-ur-Rehman *et al.*, 2008), ethyl 5-amino-1-(2,4-dinitrophenyl)-1*H*-pyrazole-4-carboxylate (QAHJER; Ghorab *et al.*, 2016), ethyl 5-amino-1-phenyl-1*H*-pyrazole-4-carboxylate (RUVHUO, Soares *et al.*, 2020), ethyl 5-amino-1-(4-sulfamoylphenyl)-1*H*-pyrazole-4-carboxylate (XUTZIX; Ibrahim *et al.*, 2015) and 2-ethoxyethyl 5-amino-1-(2,4-dimethylphenyl)-3-(methylthio)-1*H*-pyrazole-4-carboxylate (YOYHOK, Liu *et al.*, 2009).

6. Synthesis and crystallization

Compounds (I) and (II) are commercially available and were purchased from Aldrich. Both were dissolved in ethyl acetate until saturated and these solutions were allowed to evaporate slowly at room temperature, which resulted in X-ray quality crystals.

7. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 3. All carbon-bound H atoms were positioned geometrically and refined as riding, with C—H = 0.95 or 0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). In order to ensure a chemically meaningful O—H distance in (I), this was restrained to a target value of 0.84 (2) Å and $U_{iso}(H) = 1.5U_{eq}(O)$. In (I), the amino H atoms were located in a difference-Fourier map. In (II), the N—H distances were restrained to a target value of 0.84 (2) Å and $U_{iso}(H) = 1.5U_{eq}(N)$. The absolute structure of (II) was indeterminate based on the present refinement.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{11}H_{11}N_3O_3$	$C_{10}H_{10}N_2O_2$
M_r	233.23	190.20
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, $P2_12_12_1$
Temperature (K)	170	170
a, b, c (Å)	3.9608 (4), 24.104 (3), 11.1762 (10)	7.6496 (11), 8.7565 (15), 14.128 (2)
α, β, γ (°)	90, 90.189 (9), 90	90, 90, 90
V (Å^3)	1067.0 (2)	946.4 (3)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.11	0.10
Crystal size (mm)	$0.5 \times 0.2 \times 0.2$	$0.4 \times 0.2 \times 0.2$
Data collection		
Diffractometer	Rigaku XtaLAB mini	Rigaku XtaLAB mini
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)
T_{min}, T_{max}	0.975, 1.000	0.757, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8175, 2937, 1667	6912, 2635, 1344
R_{int}	0.032	0.050
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.694	0.694
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.155, 1.03	0.052, 0.168, 1.02
No. of reflections	2937	2635
No. of parameters	168	137
No. of restraints	1	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.16, −0.19	0.17, −0.16
Absolute structure	–	Flack x determined using 385 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	–	−0.7 (10)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2018/1* (Sheldrick, 2015*b*), and *OLEX2* (Dolomanov *et al.*, 2009).

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Crystal structures and Hirshfeld surface analysis of 5-amino-1-(4-methoxyphenyl)pyrazole-4-carboxylic acid and 5-amino-3-(4-methoxyphenyl)isoxazole

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Computing details

For both structures, data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/1* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

5-Amino-1-(4-methoxyphenyl)pyrazole-4-carboxylic acid (I)

Crystal data

$C_{11}H_{11}N_3O_3$	$F(000) = 488$
$M_r = 233.23$	$D_x = 1.452$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 3.9608$ (4) Å	Cell parameters from 1271 reflections
$b = 24.104$ (3) Å	$\theta = 2.0$–23.7°
$c = 11.1762$ (10) Å	$\mu = 0.11$ mm^{-1}
$\beta = 90.189$ (9)°	$T = 170$ K
$V = 1067.0$ (2) Å^3	Block, clear colourless
$Z = 4$	$0.5 \times 0.2 \times 0.2$ mm

Data collection

Rigaku XtaLAB mini diffractometer	$T_{min} = 0.975$, $T_{max} = 1.000$
Radiation source: Sealed Tube, Rigaku (Mo) X-ray Source	8175 measured reflections
	2937 independent reflections
Graphite Monochromator monochromator	1667 reflections with $I > 2\sigma(I)$
Detector resolution: 13.6612 pixels mm^{-1}	$R_{int} = 0.032$
profile data from ω–scans	$\theta_{max} = 29.6°$, $\theta_{min} = 2.0°$
Absorption correction: multi-scan (CrysalisPro; Rigaku OD, 2018)	$h = -5 \rightarrow 5$
	$k = -33 \rightarrow 33$
	$l = -15 \rightarrow 14$

Refinement

Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.155$	
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 0.1763P]$
2937 reflections	where $P = (F_o^2 + 2F_c^2)/3$
168 parameters	$(\Delta/\sigma)_{max} < 0.001$
1 restraint	$\Delta\rho_{max} = 0.16$ e Å^{-3}

$\Delta\rho_{min} = -0.19$ e Å^{-3}

Extinction correction: SHELXL2018/1
(Sheldrick, 2015b),
$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.017 (3)

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.

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

	x	y	z	U_{iso}*/U_{eq}
O1	0.3397 (4)	0.03421 (7)	0.62727 (13)	0.0697 (5)
H1	0.370 (8)	0.0005 (8)	0.594 (2)	0.113 (11)*
C1	0.2875 (5)	0.14586 (10)	0.72321 (18)	0.0595 (5)
H1A	0.208584	0.120332	0.781520	0.071*
N1	0.4218 (4)	0.22042 (7)	0.63223 (12)	0.0495 (4)
C2	0.4182 (5)	0.12959 (8)	0.61090 (17)	0.0519 (5)
O2	0.5820 (4)	0.06706 (6)	0.46040 (12)	0.0648 (4)
N2	0.2864 (5)	0.19977 (8)	0.73857 (14)	0.0608 (5)
O3	0.5775 (4)	0.44729 (6)	0.57003 (13)	0.0699 (5)
C3	0.5066 (4)	0.17936 (8)	0.55617 (15)	0.0463 (4)
N3	0.6542 (5)	0.18839 (9)	0.44896 (14)	0.0573 (5)
H3A	0.704 (5)	0.1581 (9)	0.4099 (19)	0.060 (6)*
H3B	0.692 (6)	0.2227 (10)	0.422 (2)	0.070 (7)*
C4	0.4535 (5)	0.07533 (9)	0.56133 (17)	0.0545 (5)
C5	0.4620 (4)	0.27870 (8)	0.61733 (15)	0.0462 (4)
C6	0.3325 (5)	0.30549 (8)	0.51751 (15)	0.0495 (5)
H6	0.215830	0.285018	0.457648	0.059*
C7	0.3738 (5)	0.36188 (9)	0.50557 (16)	0.0522 (5)
H7	0.285859	0.380302	0.437091	0.063*
C8	0.5434 (5)	0.39210 (8)	0.59310 (16)	0.0504 (5)
C9	0.6654 (5)	0.36518 (8)	0.69428 (16)	0.0524 (5)
H9	0.774143	0.385704	0.755892	0.063*
C10	0.6278 (5)	0.30858 (8)	0.70480 (15)	0.0505 (5)
H10	0.716871	0.289972	0.772872	0.061*
C11	0.7499 (6)	0.48080 (10)	0.6567 (2)	0.0770 (7)
H11A	0.979212	0.466515	0.668620	0.115*
H11B	0.627391	0.479613	0.732705	0.115*
H11C	0.761020	0.519180	0.628081	0.115*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0905 (12)	0.0604 (10)	0.0584 (9)	−0.0021 (9)	0.0143 (8)	0.0150 (7)
C1	0.0614 (12)	0.0677 (14)	0.0495 (11)	−0.0015 (10)	0.0083 (9)	0.0107 (9)
N1	0.0505 (9)	0.0608 (10)	0.0373 (8)	−0.0023 (7)	0.0036 (7)	0.0019 (6)

C2	0.0491 (11)	0.0609 (12)	0.0457 (10)	−0.0016 (9)	−0.0010 (8)	0.0053 (8)
O2	0.0815 (11)	0.0609 (9)	0.0521 (8)	−0.0018 (7)	0.0098 (7)	0.0048 (6)
N2	0.0691 (11)	0.0708 (12)	0.0427 (8)	−0.0016 (9)	0.0140 (8)	0.0069 (7)
O3	0.0846 (11)	0.0573 (9)	0.0678 (9)	−0.0025 (8)	−0.0131 (8)	−0.0037 (7)
C3	0.0403 (9)	0.0623 (12)	0.0362 (8)	−0.0017 (8)	−0.0026 (7)	0.0013 (8)
N3	0.0731 (12)	0.0585 (11)	0.0402 (9)	−0.0022 (9)	0.0104 (8)	0.0009 (8)
C4	0.0528 (11)	0.0610 (13)	0.0495 (11)	0.0002 (9)	−0.0029 (9)	0.0104 (9)
C5	0.0404 (9)	0.0593 (11)	0.0390 (9)	−0.0021 (8)	0.0038 (7)	−0.0005 (7)
C6	0.0468 (10)	0.0638 (12)	0.0379 (9)	−0.0034 (9)	−0.0023 (8)	−0.0026 (8)
C7	0.0511 (11)	0.0647 (13)	0.0409 (9)	0.0033 (9)	−0.0025 (8)	0.0011 (8)
C8	0.0480 (10)	0.0576 (12)	0.0455 (10)	0.0026 (8)	0.0030 (8)	−0.0053 (8)
C9	0.0495 (11)	0.0664 (13)	0.0413 (9)	0.0001 (9)	−0.0026 (8)	−0.0091 (8)
C10	0.0483 (10)	0.0669 (13)	0.0364 (9)	0.0025 (9)	−0.0014 (8)	−0.0024 (8)
C11	0.0820 (16)	0.0637 (14)	0.0852 (16)	−0.0024 (12)	−0.0122 (13)	−0.0173 (12)

Geometric parameters (Å, º)

O1—H1	0.901 (17)	N3—H3B	0.90 (2)
O1—C4	1.316 (2)	C5—C6	1.386 (2)
C1—H1A	0.9500	C5—C10	1.379 (2)
C1—C2	1.415 (3)	C6—H6	0.9500
C1—N2	1.311 (3)	C6—C7	1.376 (3)
N1—N2	1.397 (2)	C7—H7	0.9500
N1—C3	1.348 (2)	C7—C8	1.391 (3)
N1—C5	1.424 (2)	C8—C9	1.389 (3)
C2—C3	1.392 (3)	C9—H9	0.9500
C2—C4	1.427 (3)	C9—C10	1.378 (3)
O2—C4	1.255 (2)	C10—H10	0.9500
O3—C8	1.362 (2)	C11—H11A	0.9800
O3—C11	1.433 (3)	C11—H11B	0.9800
C3—N3	1.353 (2)	C11—H11C	0.9800
N3—H3A	0.87 (2)		
C4—O1—H1	113.6 (19)	C10—C5—C6	120.09 (19)
C2—C1—H1A	123.4	C5—C6—H6	120.2
N2—C1—H1A	123.4	C7—C6—C5	119.65 (17)
N2—C1—C2	113.11 (18)	C7—C6—H6	120.2
N2—N1—C5	119.63 (15)	C6—C7—H7	119.8
C3—N1—N2	111.84 (16)	C6—C7—C8	120.44 (18)
C3—N1—C5	128.51 (15)	C8—C7—H7	119.8
C1—C2—C4	129.42 (19)	O3—C8—C7	115.24 (17)
C3—C2—C1	104.13 (18)	O3—C8—C9	125.16 (17)
C3—C2—C4	126.45 (18)	C9—C8—C7	119.60 (19)
C1—N2—N1	103.90 (16)	C8—C9—H9	120.2
C8—O3—C11	118.03 (17)	C10—C9—C8	119.65 (17)
N1—C3—C2	106.99 (16)	C10—C9—H9	120.2
N1—C3—N3	123.35 (18)	C5—C10—H10	119.7
N3—C3—C2	129.65 (19)	C9—C10—C5	120.54 (17)

C3—N3—H3A	114.1 (14)	C9—C10—H10	119.7
C3—N3—H3B	121.7 (15)	O3—C11—H11A	109.5
H3A—N3—H3B	124 (2)	O3—C11—H11B	109.5
O1—C4—C2	116.02 (18)	O3—C11—H11C	109.5
O2—C4—O1	121.64 (19)	H11A—C11—H11B	109.5
O2—C4—C2	122.34 (18)	H11A—C11—H11C	109.5
C6—C5—N1	120.85 (16)	H11B—C11—H11C	109.5
C10—C5—N1	119.05 (16)		

C1—C2—C3—N1	−1.5 (2)	C3—C2—C4—O1	−177.21 (18)
C1—C2—C3—N3	177.56 (19)	C3—C2—C4—O2	2.1 (3)
C1—C2—C4—O1	2.3 (3)	C4—C2—C3—N1	178.11 (18)
C1—C2—C4—O2	−178.46 (19)	C4—C2—C3—N3	−2.9 (3)
N1—C5—C6—C7	179.75 (16)	C5—N1—N2—C1	−179.45 (17)
N1—C5—C10—C9	−178.75 (16)	C5—N1—C3—C2	179.87 (16)
C2—C1—N2—N1	0.0 (2)	C5—N1—C3—N3	0.8 (3)
N2—C1—C2—C3	0.9 (2)	C5—C6—C7—C8	−0.2 (3)
N2—C1—C2—C4	−178.6 (2)	C6—C5—C10—C9	0.3 (3)
N2—N1—C3—C2	1.6 (2)	C6—C7—C8—O3	178.16 (17)
N2—N1—C3—N3	−177.50 (17)	C6—C7—C8—C9	−1.3 (3)
N2—N1—C5—C6	−127.58 (18)	C7—C8—C9—C10	2.3 (3)
N2—N1—C5—C10	51.4 (2)	C8—C9—C10—C5	−1.8 (3)
O3—C8—C9—C10	−177.11 (18)	C10—C5—C6—C7	0.8 (3)
C3—N1—N2—C1	−1.0 (2)	C11—O3—C8—C7	180.00 (19)
C3—N1—C5—C6	54.3 (3)	C11—O3—C8—C9	−0.5 (3)
C3—N1—C5—C10	−126.71 (19)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···O2	0.87 (2)	2.32 (2)	2.941 (3)	128.5 (18)
O1—H1···O2^i	0.90 (2)	1.75 (2)	2.649 (2)	176 (3)

Symmetry code: (i) −x+1, −y, −z+1.

5-Amino-3-(4-methoxyphenyl)isoxazole (II)

Crystal data

$C_{10}H_{10}N_2O_2$
$M_r = 190.20$
Orthorhombic, $P2_12_12_1$
$a = 7.6496$ (11) Å
$b = 8.7565$ (15) Å
$c = 14.128$ (2) Å
$V = 946.4$ (3) Å^3
$Z = 4$
$F(000) = 400$

$D_x = 1.335$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1405 reflections
$\theta = 2.7–22.5°$
$\mu = 0.10$ mm^{-1}
$T = 170$ K
Block, clear colourless
$0.4 \times 0.2 \times 0.2$ mm

Data collection

Rigaku XtaLAB mini diffractometer	$T_{min} = 0.757$, $T_{max} = 1.000$
Radiation source: fine-focus sealed X-ray tube, Rigaku (Mo) X-ray Source	6912 measured reflections
	2635 independent reflections
	1344 reflections with $I > 2\sigma(I)$
Graphite Monochromator monochromator	$R_{int} = 0.050$
Detector resolution: 13.6612 pixels mm^{-1}	$\theta_{max} = 29.6°$, $\theta_{min} = 2.7°$
profile data from ω–scans	$h = -10 \rightarrow 9$
Absorption correction: multi-scan (CrysalisPro; Rigaku OD, 2018)	$k = -11 \rightarrow 11$
	$l = -11 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.052$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.168$	$\Delta\rho_{max} = 0.17$ e Å^{-3}
$S = 1.02$	$\Delta\rho_{min} = -0.16$ e Å^{-3}
2635 reflections	Extinction correction: SHELXL2018/1 (Sheldrick 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
137 parameters	
2 restraints	Extinction coefficient: 0.037 (7)
Primary atom site location: dual	Absolute structure: Flack x determined using 385 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Hydrogen site location: mixed	
H atoms treated by a mixture of independent and constrained refinement	Absolute structure parameter: −0.7 (10)

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.

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

	x	*y*	*z*	$U_{iso}*/U_{eq}$
O1	0.5261 (3)	0.8179 (3)	0.69875 (17)	0.0617 (7)
C1	0.5966 (4)	0.6690 (4)	0.5813 (2)	0.0523 (8)
N1	0.4969 (4)	0.6710 (4)	0.6566 (2)	0.0632 (8)
O2	0.6029 (4)	0.1662 (3)	0.33196 (17)	0.0736 (8)
N2	0.6808 (5)	1.0370 (5)	0.6730 (3)	0.0718 (10)
C2	0.6906 (5)	0.8049 (4)	0.5699 (3)	0.0615 (10)
H2	0.770803	0.829616	0.520934	0.074*
C3	0.6421 (5)	0.8938 (4)	0.6445 (2)	0.0578 (9)
C4	0.5977 (4)	0.5345 (4)	0.5186 (2)	0.0516 (8)
C5	0.5115 (5)	0.4010 (4)	0.5422 (2)	0.0588 (9)
H5	0.452653	0.395103	0.601305	0.071*
C6	0.5081 (5)	0.2752 (5)	0.4821 (2)	0.0613 (10)
H6	0.446575	0.185365	0.499673	0.074*
C7	0.5963 (5)	0.2827 (5)	0.3959 (3)	0.0592 (10)
C8	0.6848 (5)	0.4147 (5)	0.3719 (2)	0.0629 (10)
H8	0.746554	0.419948	0.313670	0.076*
C9	0.6843 (5)	0.5390 (5)	0.4321 (2)	0.0606 (10)

H9	0.744260	0.629430	0.414044	0.073*
C10	0.5103 (6)	0.0287 (5)	0.3529 (3)	0.0887 (14)
H10A	0.533820	−0.047211	0.303518	0.133*
H10B	0.384640	0.049924	0.355305	0.133*
H10C	0.549038	−0.011138	0.414254	0.133*
H2A	0.635 (9)	1.074 (6)	0.726 (3)	0.17 (3)*
H2B	0.753 (5)	1.087 (5)	0.640 (3)	0.090 (17)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0673 (15)	0.0646 (17)	0.0531 (13)	−0.0011 (14)	0.0098 (11)	0.0035 (12)
C1	0.0433 (16)	0.065 (2)	0.0489 (17)	0.0065 (18)	0.0021 (14)	0.0079 (16)
N1	0.071 (2)	0.064 (2)	0.0551 (16)	−0.0038 (18)	0.0105 (15)	−0.0017 (15)
O2	0.0721 (17)	0.089 (2)	0.0600 (15)	−0.0106 (18)	0.0091 (13)	−0.0176 (14)
N2	0.080 (3)	0.065 (2)	0.071 (2)	−0.0054 (19)	0.0106 (19)	−0.0007 (18)
C2	0.056 (2)	0.070 (3)	0.058 (2)	−0.001 (2)	0.0137 (17)	0.0019 (19)
C3	0.056 (2)	0.063 (2)	0.0545 (19)	0.0013 (18)	−0.0014 (16)	0.0057 (18)
C4	0.0453 (17)	0.062 (2)	0.0477 (15)	0.0034 (17)	0.0009 (15)	0.0059 (15)
C5	0.057 (2)	0.070 (2)	0.0493 (18)	0.0015 (19)	0.0071 (16)	0.0024 (17)
C6	0.055 (2)	0.075 (2)	0.0539 (19)	−0.0026 (19)	0.0072 (18)	−0.0003 (18)
C7	0.0492 (18)	0.077 (3)	0.0512 (18)	0.0034 (19)	−0.0005 (17)	−0.0031 (17)
C8	0.055 (2)	0.083 (3)	0.0502 (19)	0.001 (2)	0.0097 (16)	0.0034 (19)
C9	0.056 (2)	0.073 (2)	0.0527 (19)	−0.001 (2)	0.0068 (16)	0.0096 (18)
C10	0.093 (3)	0.092 (3)	0.080 (3)	−0.019 (3)	0.015 (3)	−0.020 (3)

Geometric parameters (Å, º)

O1—N1	1.434 (4)	C4—C9	1.390 (5)
O1—C3	1.348 (4)	C5—H5	0.9500
C1—N1	1.310 (4)	C5—C6	1.391 (5)
C1—C2	1.399 (5)	C6—H6	0.9500
C1—C4	1.474 (5)	C6—C7	1.394 (5)
O2—C7	1.363 (5)	C7—C8	1.382 (6)
O2—C10	1.429 (5)	C8—H8	0.9500
N2—C3	1.350 (5)	C8—C9	1.381 (5)
N2—H2A	0.89 (3)	C9—H9	0.9500
N2—H2B	0.85 (2)	C10—H10A	0.9800
C2—H2	0.9500	C10—H10B	0.9800
C2—C3	1.362 (5)	C10—H10C	0.9800
C4—C5	1.383 (5)		

C3—O1—N1	108.0 (3)	C6—C5—H5	119.0
N1—C1—C2	112.4 (3)	C5—C6—H6	120.4
N1—C1—C4	120.2 (3)	C5—C6—C7	119.2 (4)
C2—C1—C4	127.4 (3)	C7—C6—H6	120.4
C1—N1—O1	105.0 (3)	O2—C7—C6	124.2 (4)
C7—O2—C10	118.4 (3)	O2—C7—C8	116.4 (3)

C3—N2—H2A	120 (4)	C8—C7—C6	119.3 (4)
C3—N2—H2B	117 (3)	C7—C8—H8	119.8
H2A—N2—H2B	122 (5)	C9—C8—C7	120.5 (3)
C1—C2—H2	127.5	C9—C8—H8	119.8
C3—C2—C1	104.9 (3)	C4—C9—H9	119.3
C3—C2—H2	127.5	C8—C9—C4	121.3 (4)
O1—C3—N2	115.7 (3)	C8—C9—H9	119.3
O1—C3—C2	109.7 (3)	O2—C10—H10A	109.5
N2—C3—C2	134.6 (4)	O2—C10—H10B	109.5
C5—C4—C1	121.8 (3)	O2—C10—H10C	109.5
C5—C4—C9	117.6 (3)	H10A—C10—H10B	109.5
C9—C4—C1	120.5 (3)	H10A—C10—H10C	109.5
C4—C5—H5	119.0	H10B—C10—H10C	109.5
C4—C5—C6	122.1 (3)		
C1—C2—C3—O1	0.2 (4)	C3—O1—N1—C1	0.2 (4)
C1—C2—C3—N2	−178.0 (4)	C4—C1—N1—O1	−178.9 (3)
C1—C4—C5—C6	178.2 (3)	C4—C1—C2—C3	178.6 (3)
C1—C4—C9—C8	−179.2 (3)	C4—C5—C6—C7	0.9 (6)
N1—O1—C3—N2	178.3 (3)	C5—C4—C9—C8	−0.2 (5)
N1—O1—C3—C2	−0.3 (4)	C5—C6—C7—O2	179.5 (4)
N1—C1—C2—C3	−0.1 (4)	C5—C6—C7—C8	0.0 (5)
N1—C1—C4—C5	−7.7 (5)	C6—C7—C8—C9	−0.9 (6)
N1—C1—C4—C9	171.3 (3)	C7—C8—C9—C4	1.0 (6)
O2—C7—C8—C9	179.5 (3)	C9—C4—C5—C6	−0.8 (5)
C2—C1—N1—O1	−0.1 (4)	C10—O2—C7—C6	1.7 (6)
C2—C1—C4—C5	173.7 (3)	C10—O2—C7—C8	−178.8 (4)
C2—C1—C4—C9	−7.3 (5)		

Hydrogen-bond geometry (Å, º)

*Cg*2 is the centroid of the C4–C9 ring.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N2—H2*A*⋯N1[i]	0.89 (3)	2.12 (3)	3.003 (5)	174 (6)
N2—H2*B*⋯*Cg*2[ii]	0.85 (2)	2.97 (4)	3.709 (4)	147 (4)

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