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

Chris J. Pintro, Analeece K. Long, Allison J. Amonette, James M. Lobue and Clifford W. Padgett*

Georgia Southern University, 11935 Abercorn St., Department of Chemistry and, Biochemistry, Savannah GA 30458, USA. *Correspondence e-mail: cpadgett@georgiasouthern.edu

The title compounds, C_{11}H_{11}N_{3}O_{3}, (I), and C_{10}H_{10}N_{2}O_{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···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).

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
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—C1/C1/C1 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/C1/C1/C1 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.

3. Supramolecular features

In the extended structure of (I), the molecules form centrosymmetric hydrogen-bonded dimers via the O1—H1/C1/C1/C1 O2i [symmetry code: (i) −x + 1, −y, −z + 1] link to generate an R(8) loop with O···O = 2.649 (2) Å, see Table 1 and Fig. 3. These dimers are linked via C25–C25 interactions, notably weak stacking interactions between the 4-methoxyphenyl rings [Cg1···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—H2A···N1i hydrogen bond [symmetry code: (i) −x + 1, y + 1/2, −z + 1/2] hydrogen bond forms a C(5) chain motif with an N···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...
Analysis of the two-dimensional fingerprint plots indicates centroids of the O1/N1/C1–C3 and C4–C9 rings, respectively. The crystal packing with C/H/C1/C1/C1 contributions of other weak interactions are: O/H/H (22.4%) interactions making the next highest contribution. The percentage contributions of other significant contacts are: C···H/H/C1/C1/C1 (13.1%) and N···H/H···N (8.7%).

Fig. 5 shows the $d_{\text{norm}}$ surface of compound (I). The most intense red spots on the $d_{\text{norm}}$ surface correspond to the O1–H1···O2 interactions. The red and blue triangles on the shape-index surface indicate that there are weak $\pi$-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/C1/C1/C1 (13.1%) and N···H/H···N (8.7%).

Fig. 6 shows the $d_{\text{norm}}$ 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 (2.97 (4) Å), C6–H6···Cg1 (2.86 Å) and C9–H9···Cg2 (2.86 Å) [symmetry codes: (i) $x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + 1$; (ii) $x - \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + 1$; 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-amino moiety. The four most closely related compounds are: 5-diacetylamino-3,4-diphenylisoxazole (CSD refcode ACPIXZ; Simon et al., 1974), 5-amino-1-phenyl-1H-pyrazole-4-carboxylic acid (GOLHEV; Zia-ur-Rehman et al., 2008), ethyl 5-amino-1-(2,4-dinitrophenyl)-1H-pyrazole-4-carboxylate (XUTZIX; Zia-ur-Rehman et al., 2008), and 2-ethoxyethyl 5-amino-1-(2,4-dimethylphenyl)-3-(methylthio)-1H-pyrazole-4-carboxylate (YOYHOK; Liu et al., 2009).

A similar search gave 14 hits for the 5-amino-1-phenyl-1Hpyrazole-4-carboxylic acid moiety. The seven most closely related compounds are: ethyl 1-(4-chloro-2-nitrophenyl)-5-nitro-4,5-dihydro-1H-pyrazole-4-carboxylate (GOLHEV; Zia-ur-Rehman et al., 2009), 5-amino-1-phenyl-3-(trifluoromethyl)-1H-pyrazole-4-carboxylic acid (HUDEQ; Caruso et al., 2009), 5-amino-1-phenyl-1H-pyrazole-4-carboxylic acid (KODXIL; Zia-ur-Rehman et al., 2008), ethyl 5-amino-1-(2,4-dinitrophenyl)-1H-pyrazole-4-carboxylate (QAHJER; Ghorab et al., 2016), ethyl 5-amino-1-phenyl-1H-pyrazole-4-carboxylate (RUVHUO; Soares et al., 2020), ethyl 5-amino-1-(4-sulfamoylphenyl)-1H-pyrazole-4-carboxylate (XUTZIX; Ibrahim et al., 2015) and 2-ethoxyethyl 5-amino-1-(2,4-dimethylphenyl)-3-(methylthio)-1H-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 $U_{\text{iso}}$(H) = 1.2$U_{\text{eq}}$(C) or 1.5$U_{\text{eq}}$(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 $U_{\text{iso}}$(H) = 1.5$U_{\text{eq}}$(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 $U_{\text{iso}}$(H) = 1.5$U_{\text{eq}}$(N). The absolute structure of (II) was indeterminate based on the present refinement.

Funding information
The authors would like to thank Georgia Southern University, Department of Chemistry and Biochemistry for the financial support of this work.
Table 3
Experimental details.

|     | (I)                                      | (II)                                      |
|-----|------------------------------------------|------------------------------------------|
| Crystal data |                                  |                                           |
| Chemical formula | C₁₁H₁₁N₃O₃                          | C₁₀H₁₀N₂O₂                               |
| M₁        | 233.23                                   | 190.20                                   |
| Crystal system, space group | Monoclinic, P2₁/n                  | Orthorhombic, P₂₁₂₂₁                  |
| 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 (Å³)     | 1067.0 (2)                               | 946.4 (3)                                |
| Z          | 4                                        | 4                                         |
| Radiation type | Mo K                                     | Mo K                                     |
| μ (mm⁻¹)   | 0.11                                     | 0.10                                     |
| Crystal size (mm) | 0.5 × 0.2 × 0.2 | 0.4 × 0.2 × 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) |
| Tmin, Tmax            | 0.975, 1.000                            | 0.757, 1.000                            |
| No. of measured, independent and observed | 8175, 2937, 1667 | 6912, 2635, 1344 |
| R(int) | 0.032                                    | 0.050                                    |
| (sin θ/λ)max (Å⁻¹) | 0.694                                   | 0.694                                   |

Refinement

|     |                                           |                                           |
| R(F² > 2σ(F²)), wR(F²), 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 |
| Δρmax, Δρmin (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)                               |

References

Caruso, F., Raimondi, M. V., Daidone, G., Pettinari, C. & Rossi, M. (2009). Acta Cryst. E65, o2175.
Chen, C. & Cui, S. (2013). J. Org. Chem. 84, 12157–12164.
Dobson, A. J. & Gerkin, R. E. (1996). Acta Cryst. C52, 1512–1514.
Dobson, A. J. & Gerkin, R. E. (1998). Acta Cryst. B54, 1503–1505.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339–341.
Ghorab, M. M., Alsaid, M. S. & Ghabbour, H. A. (2016). Z. Kristallogr. New Cryst. Struct. 231, 699–701.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.
Li, H., You, L., Zhang, X., Johnson, W. L., Figueroa, R. & Hsung, R. P. (2007). Heterocycles, 74, 553–568.
Ibrahim, H. S., Abou-Seri, S. M., Tane, M., Elasser, M. M., Abdel-Aziz, H. A. & Supuran, C. T. (2015). Eur. J. Med. Chem. 103, 583–593.
Liu, Y., Liu, S., Li, Y., Song, H. & Wang, Q. (2009). Bioorg. Med. Chem. Lett. 19, 2953–2956.
McKinnon, I. J., Jayatilaka, D. & Spackman, M. A. (2007). Chem. Commun. pp. 3814–3816.
Mikhailov, K. I., Galenko, E. E., Galenko, A. V., Novikov, M. S., Ivanov, A. Y., Starova, G. L. & Khlebnikov, A. F. (2018). J. Org. Chem. 83, 3177–3187.
Nunez, L., Brown, J. D., Donnelly, A. M., Whitlock, C. R. & Dobson, A. J. (2004). Acta Cryst. E60, 2076–2078.
Parsons, S., Flack, H. D. & Wagner, T. (2013). Acta Cryst. B69, 249–259.
Rigaku OD (2018). CrysAlis PRO. Rigaku Oxford Diffraction, Yarnton, England.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Simon, K., Sasvári, K., Dvortsák, P., Horváth, K. & Harsányi, K. (1974). J. Chem. Soc. Perkin Trans. 2, pp. 1409–1412.
Soares, I. C., Junior, H. C. S., de Almeida, P. S. V. B., Alves, O. C., Soriano, S., Ferreira, G. F. & Guedes, G. P. (2020). Inorg. Chem. Commun. 121, 108201.
Spackman, M. A. & Jayatilaka, D. (2009). CrystEngComm, 11, 19–32.
Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). Crystal Explorer 17. University of Western Australia. http://hirshfeldsurfacingResearch.net.
Zia-ur-Rehman, M., Elsegoud, M. R. J., Akbar, N. & Shah Zaib Saleem, R. (2008). Acta Cryst. E64, o1312–o1313.
Zia-ur-Rehman, M., Elsegoud, M. R. J., Choudary, J. A., Fasih Ullah, M. & Siddiqui, H. L. (2009). Acta Cryst. E65, o275–o276.
Crystal structures and Hirshfeld surface analysis of 5-amino-1-(4-methoxyphenyl)pyrazole-4-carboxylic acid and 5-amino-3-(4-methoxyphenyl)isoxazole

Chris J. Pintro, Analeece K. Long, Allison J. Amonette, James M. Lobue and Clifford W. Padgett

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_{3}O_{3}
Mr = 233.23
Monoclinic, P2_1/n
a = 3.9608 (4) Å
b = 24.104 (3) Å
c = 11.1762 (10) Å
β = 90.189 (9)°
V = 1067.0 (2) Å³
Z = 4

F(000) = 488
D_x = 1.452 Mg m⁻³
Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 1271 reflections
θ = 2.0–23.7°
µ = 0.11 mm⁻¹
T = 170 K
Block, clear colourless
0.5 × 0.2 × 0.2 mm

Data collection
Rigaku XtaLAB mini diffractometer
Radiation source: Sealed Tube, Rigaku (Mo) X-ray Source
Graphite Monochromator monochromator
Detector resolution: 13.6612 pixels mm⁻¹
profile data from ω–scans
Absorption correction: multi-scan
(CrystalisPro; Rigaku OD, 2018)

T_{min} = 0.975, T_{max} = 1.000
8175 measured reflections
2937 independent reflections
1667 reflections with I > 2σ(I)
R_{int} = 0.032
θ_{max} = 29.6°, θ_{min} = 2.0°
h = −5→5
k = −33→33
l = −15→14

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.049
wR(F²) = 0.155
S = 1.03
2937 reflections
168 parameters
1 restraint
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(Fo²) + (0.060P)² + 0.1763P]
where P = (Fo² + 2Fc²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.16 e Å⁻³

Acta Cryst. (2022). E78, 336-339
Δρ_{min} = −0.19 e Å⁻³

Extinction correction: SHELXL2018/1
(Sheldrick, 2015b),
F_c^* = kF_c[1+0.001xF_c^2λ^3/sin(2θ)]^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 (Å²)**

| Atom | x     | y     | z     | Uiso*/Ueq |
|------|-------|-------|-------|-----------|
| 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 (Å²)**

| U₁₁ | U₂₂ | U₃₃ | U₁₂ | U₁₃ | U₂₃ |
|-----|-----|-----|-----|-----|-----|
| 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) |

*Acta Cryst. (2022), E78, 336-339*
|   |     |     |     |     |     |     |
|---|-----|-----|-----|-----|-----|-----|
| 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, °)**

|   |     |     |     |     |     |
|---|-----|-----|-----|-----|-----|
| 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) |
Supporting Information

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—C3—C2 179.87 (16)
N1—C5—C10—C9 −178.75 (16) C5—N1—C3—N3 0.8 (3)
C2—C1—C2—C3 0.9 (2) C5—N1—N2—C1 −179.45 (17)
C2—C1—C2—C4 −178.6 (2) C5—N1—N2—C1 −179.45 (17)
N2—C1—C2—C3 1.6 (2) C6—C5—C10—C9 0.3 (3)
N2—C1—C2—C4 −177.50 (17) C6—C5—C10—C9 0.3 (3)
N2—N1—C3—C2 −127.58 (18) C7—C8—C9—C10 2.3 (3)
N2—N1—C3—N3 51.4 (2) C8—C9—C10—C5 −1.8 (3)
N2—N1—C5—C6 51.4 (2) C9—C8—C9—C10 −1.8 (3)
N2—N1—C5—C10 −177.11 (18) O3—C9—C8—C7 0.8 (3)
O3—C8—C9—C10 0.0 (2) C11—O3—C8—C7 180.00 (19)
O3—C8—C9—C10 −177.11 (18) C11—O3—C8—C7 −0.5 (3)
C3—N1—N2—C1 −1.0 (2) C11—O3—C8—C7 −0.5 (3)
C3—N1—C5—C6 54.3 (3) C11—O3—C8—C7 180.00 (19)
C3—N1—C5—C10 −126.71 (19)

Hydrogen-bond geometry (Å, °)

| 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···O2i | 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

C10H10N2O2

$D_\text{c} = 1.335 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ Å}$

Cell parameters from 1405 reflections

$\theta = 2.7–22.5^\circ$

$\mu = 0.10 \text{ mm}^{-1}$

$T = 170 \text{ K}$

Block, clear colourless

$0.4 \times 0.2 \times 0.2 \text{ mm}$

Acta Cryst. (2022). E78, 336-339 sup-4
Data collection

Rigaku XtaLAB mini diffractometer
Radiation source: fine-focus sealed X-ray tube, Rigaku (Mo) X-ray Source
Graphite Monochromator monochromator
Detector resolution: 13.6612 pixels mm\(^{-1}\)
profile data from \(\omega\)–scans
Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2018)

\(T_{\text{min}} = 0.757, T_{\text{max}} = 1.000\)
6912 measured reflections
2635 independent reflections
1344 reflections with \(I > 2\sigma(I)\)

Refinement

Refinement on \(F^2\)
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.052\)
\(wR(F^2) = 0.168\)
\(S = 1.02\)
2635 reflections
137 parameters
2 restraints

Primary atom site location: dual
Hydrogen site location: mixed
\(H\) atoms treated by a mixture of independent and constrained refinement

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(9) |
| 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) |
**Atomic displacement parameters (Å²)**

|    | \(U_11\)     | \(U_22\)     | \(U_33\)     | \(U_{12}\) | \(U_{13}\) | \(U_{23}\) |
|----|---------------|---------------|---------------|------------|------------|------------|
| 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, °)**

|     | 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, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|-------|---------|
| N2—H2A···N1'i | 0.89 (3) | 2.12 (3) | 3.003 (5) | 174 (6) |
| N2—H2B···Cg2ii | 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.