Synthesis and crystal structures of three Schiff bases derived from 3-formylacetylacetone and o-, m- and p-aminobenzoic acid

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Treatment of 3-formylacetylacetone with the isomeric o-, m- and p-aminobenzoic acids led to the formation of the corresponding Schiff bases, namely, 3-[(2-carboxyphenylamino)methylidene]pentane-2,4-dione, 1, 3-[(3-carboxyphenylamino)methylidene]pentane-2,4-dione, 2, and 3-[(4-carboxyphenylamino)methylidene]pentane-2,4-dione, 3, all C_{13}H_{13}NO_{4}, that contain a planar amino-methylene-pentane-2,4-dione core with a strong intramolecular N-H···O hydrogen bridge. The carboxyphenyl groups attached to the nitrogen atom are almost coplanar to the central molecular fragment. Depending on the position of the carboxyl unit, different supramolecular structures with hydrogen-bonding networks are formed in the three title structures.

1. Chemical context

The reaction of 3-formylacetylacetone with primary amines RNH_{2} provides easy access to enamines with an amino-methylene-pentane-2,4-dione core. This approach was used for the first time as early as 1966 by Jäger’s group in order to synthesize salen-type ligands from 3-formylacetylacetone and ethylenediamine (Wolf & Jäger, 1966). Recently, this type of ligand was applied successfully for the preparation of Fe^{II} complexes that exhibit spin-crossover effects (Dankhoff & Weber, 2019). In a previous study, we were interested in the preparation of chiral N,O,O-ketiminate ligands from 3-formylacetylacetone and naturally occuring aminoacids (Hentsch et al., 2014) and recently, we reported on N,O,P-ketiminates with additional PPh_{2} functionalities (Halz et al., 2021). In this context, we studied the synthesis of Schiff bases derived from 3-formylacetylacetone and the isomeric o-, m- and p-aminobenzoic acids. The corresponding crystal structures of 1, 2 and 3 are reported here.
2. Structural commentary

The ortho derivative compound 1 crystallizes in the monoclinic system, space group C2/c with Z = 8. Compound 2 (meta derivative) forms orthorhombic crystals, space group Pnma, Z = 4, and compound 3 (para derivative) crystallizes in the monoclinic space group P21/c, Z = 4. Each of the three isomers 1–3 exists as the enamine tautomer with a central amino-methylene-pentane-2,4-dione structure (Figs. 1–3). The molecular structures of compounds 1 and 3 exhibit nearly planar amino-methylene-pentane-2,4-dione units, and in the case of compound 2 exact planarity is observed as the molecule resides on a crystallographic mirror plane perpendicular to the crystallographic b axis. In the case of compounds 1 and 3, there is a small torsion of the phenyl groups [1: 12.16 (6)°, 3:

30.76 (8)°] with respect to the amino-methylene-pentane-2,4-dione unit.

Regarding the central amino-methylene-pentane-2,4-dione part, the geometric parameters for isomers 1–3 are very similar (Tables 1–3). The lengths of the enamine double bonds C3=C6 range from 1.379 (2) Å in the ortho derivative to 1.394 (3) Å in the case of the meta derivative. The remaining C—C bonds at the central C3 atom are 1.443 (3)–1.482 (3) Å. In the parent compound amino-methylene-pentane-2,4-dione, which may serve as a reference, the corresponding C—C distances at the central C atom are 1.397 (2) Å and 1.456 (2)–1.464 (2) Å, respectively (Gröf et al., 2006). The enamine C–N bond lengths in compounds 1–3 are 1.333 (3)–1.379 (2) Å and thus practically identical. Generally, in this type of enamine, the C–N bond lengths for the parent amino [1.305 (2) Å] and related N-alkyl derivatives (e.g. N–CH3: 1.308 Å) are marginally shorter than those of N-aryl derivatives [e.g. N(o-NH2-Ph): 1.324 (2) Å] (Svensson et al., 1982).

Table 1

| Bond          | Length (Å)   | Bond          | Length (Å)   |
|---------------|--------------|---------------|--------------|
| O1—C2         | 1.2380 (18)  | C2—C3        | 1.473 (2)    |
| O2—C4         | 1.239 (2)    | C3—C4        | 1.4621 (18)  |
| N—C6          | 1.3344 (18)  | C3—C6        | 1.383 (2)    |
| C1—C2         | 1.501 (2)    | C4—C5        | 1.513 (5)    |
| C6—N—C7—C8   | −167.19 (14) | C6—C3—C4—O2  | 176.05 (14)  |

Table 2

| Bond          | Length (Å)   | Bond          | Length (Å)   |
|---------------|--------------|---------------|--------------|
| O1—C2         | 1.243 (3)    | C2—C3        | 1.443 (3)    |
| O2—C4         | 1.226 (3)    | C3—C4        | 1.482 (3)    |
| N—C6          | 1.337 (3)    | C3—C6        | 1.394 (3)    |
| C1—C2         | 1.496 (3)    | C4—C5        | 1.503 (3)    |
| C6—N—C7—C8   | 180.000 (1)  | C6—C3—C4—O2  | 180.000 (1)  |

Table 3

| Bond          | Length (Å)   | Bond          | Length (Å)   |
|---------------|--------------|---------------|--------------|
| O1—C2         | 1.2401 (19)  | C2—C3        | 1.475 (2)    |
| O2—C4         | 1.233 (2)    | C3—C4        | 1.470 (2)    |
| N—C6          | 1.333 (2)    | C3—C6        | 1.379 (2)    |
| C1—C2         | 1.487 (3)    | C4—C5        | 1.503 (2)    |
| C6—N—C7—C8   | −27.4 (2)    | C6—C3—C4—O2  | 176.88 (17)  |
Table 4
Hydrogen-bond geometry (Å, °) for 1.

| D—H···A     | D—H | H···A | D···A | D—H···A |
|-------------|------|-------|-------|---------|
| O3—H13···O2i | 0.82 | 1.83  | 2.613 (15) | 160 |
| N—H8···O1   | 0.86 | 2.00  | 2.6308 (18) | 129 |
| N—H8···O4   | 0.86 | 2.06  | 2.7266 (16) | 133 |
| C5—H6···O3   | 0.96 | 2.62  | 3.330 (2) | 131 |
| C11—H11···O1ii | 0.93 | 2.56  | 3.2891 (19) | 136 |

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

Table 5
Hydrogen-bond geometry (Å, °) for 2.

| D—H···A     | D—H | H···A | D···A | D—H···A |
|-------------|------|-------|-------|---------|
| O3—H11···O1i | 0.83 (4) | 1.84 (4) | 2.656 (2) | 166 (3) |
| N—H6···O1   | 0.86 | 1.96  | 2.598 (2) | 130 |
| C8—H7···O4i  | 0.93 | 2.44  | 3.327 (2) | 160 |

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

Table 6
Hydrogen-bond geometry (Å, °) for 3.

| D—H···A     | D—H | H···A | D···A | D—H···A |
|-------------|------|-------|-------|---------|
| O3—H13···O4i | 1.12 (3) | 1.49 (3) | 2.6098 (18) | 173 (3) |
| N—H8···O1   | 0.86 | 1.91  | 2.5792 (18) | 133 |
| C8—H9···O3i  | 0.93 | 2.65  | 3.4832 (18) | 150 |
| C9—H10···O4i | 0.93 | 2.65  | 3.3252 (18) | 130 |
| C11—H11···O1ii | 0.93 | 2.68  | 3.3612 (19) | 131 |

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

The structural differences between compounds 1–3 are mainly due to individual hydrogen-bonding patterns (Tables 4–6). The presence of intramolecular N—H···O-type hydrogen bonds with the amine group as hydrogen donor and the acetyl oxygen atom as acceptor is typical for amino-methylene-pentane-2,4-dione derivatives. However, as a result of the participation of the carboxyl groups, additional hydrogen-bonding patterns are formed.

In the case of the ortho derivative 1, the intramolecular S\(^1\(6\)) type hydrogen bond between the amino group and acetyl oxygen atom O1 is extended to a bifurcated hydrogen bridge with the carbonyl oxygen atom O4 as additional acceptor. The presence of the second hydrogen bridge leads to a significant elongation of the N···O(acetyl) distance [2.631 (2) Å] in comparison with the \( m\) and \( p\)-derivatives 2 and 3 [2.598 (2) and 2.573 (2) Å, respectively].

3. Supramolecular features

For all three derivatives 1–3 the supramolecular structures in the solid state are clearly governed by the presence of intramolecular hydrogen bonds.

For compound 1, the carboxyl hydrogen atom H13 forms a moderately strong hydrogen bond (Bu et al., 2019; Desiraju, 2002) to the acetyl oxygen atom O2i of a neighbouring molecule with an O3···O2 distance of 2.613 (2) Å (Fig. 4). The presence of this hydrogen bond is also clearly evident from the Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) carried out using CrystalExplorer (Turner et al., 2017; version 17).

As a result of these C\(^2\)(10)-type hydrogen-bonding motifs, the Schiff base molecules are linked into infinite chains propagating along [101]. One translational unit of the chain has the dimension of 20.1 Å and consists of two planar molecular units, which are mutually tilted by around 51° (Fig. 6).
Furthermore, the Hirshfeld surface plot hints at a weak C—H⋯O hydrogen bond between the phenylene hydrogen atom H11 and the keto group oxygen atom O1 of a neighbouring chain.

As in the case of compound 1, the meta derivative 2 displays a supramolecular chain structure. The link between the Schiff base units is provided by the hydrogen atom H11 of the carboxyl group and the acetyl oxygen atom O1 of the adjacent molecule with an O3⋯O1 distance of 2.656 (2) Å. This connection leads to $C_1(10)$-type chains in the $a$-axis direction (Fig. 7). The translational unit of the chain comprises two molecular units and the repeat distance is identical to the length of the crystallographic $a$ axis [11.4880 (4) Å]. In contrast to the ortho derivative, compound 2 exhibits exactly planar chains because of crystallographically imposed mirror symmetry (Fig. 8). Obviously, the planar arrangement is further stabilized by a weak C—H⋯O hydrogen bond between the phenylene hydrogen atom H7 and the carboxyl oxygen atom O4 of an adjacent Schiff base unit, which is emphasized in the Hirshfeld surface plot (Fig. 9).

The para derivative 3 displays typical carboxylic acid dimers with an $R_2^2(8)$ motif (Fig. 10). The dimers exhibit crystallographic $T$ symmetry with an O3⋯O4 distance of 2.6098 (18) Å that indicates a strong hydrogen bridge. Furthermore, the Hirshfeld surface plot reveals the participation of phenylene hydrogen atoms in C—H⋯O hydrogen bonds (Fig. 11). Two weak C—H⋯O hydrogen bonds [C8—H8⋯O3, symmetry code: (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; C9—H9⋯O4, symmetry code: (iii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$] are formed between phenylene H atoms and neighbouring carboxyl oxygen atoms, and a third intermolecular hydrogen bond is observed...
Among the total of 53 compounds, 24 exhibit supramolecular interactions (13 from benzoic acid derivatives, 17 out of 19 compounds display hydrogen bridges, predominately in the case of the "m" form. Moreover, there are 19 Schiff base compounds derived from o-aminobenzoic acid (6 as enamine tautomers, 13 as imines), 13 from m-aminobenzoic acid (4 enamines, 9 imines) and 24 from p-aminobenzoic acid (3 enamines, 21 imines). Among the total of 53 compounds, 24 exhibit supramolecular structures based on carboxylic acid dimers with R2(8) type hydrogen bonds, predominately in the case of the m- and p-aminobenzoic acid derivatives. In the case of the o-aminobenzoic acid derivatives, 17 out of 19 compounds display intramolecular N—H···O or O—H···N hydrogen bridges with an S2(6) topology. Additionally, there are reports on ketoimines derived from 2,4-pentanedione and aminobenzoic acids. The corresponding o- and p-aminobenzoic acid derivatives exist as enamines with intramolecular N—H···O hydrogen bridges (Murugavel et al., 2012; Joshi et al., 2005). The crystal structure of the m-derivative has not yet been determined. Deprotonation of the aminobenzoic acid derivatives was used to generate carboxylates that have been applied as ligands in transition-metal complexes (Shi & Hu, 2007) and organotin compounds (Chen et al., 2020; Baul et al., 2008, 2009).

4. Database survey

The Cambridge Structural Database (CSD, Version 2020.3, Groom et al., 2016) lists 22 Schiff base derivatives of 3-formylacetylacetone, all of which crystallize in the enamine form. Moreover, there are 19 Schiff base compounds derived from o-aminobenzoic acid (6 as enamine tautomers, 13 as imines), 13 from m-aminobenzoic acid (4 enamines, 9 imines) and 24 from p-aminobenzoic acid (3 enamines, 21 imines). Among the total of 53 compounds, 24 exhibit supramolecular structures based on carboxylic acid dimers with R2(8) type hydrogen bonds, predominately in the case of the m- and p-aminobenzoic acid derivatives. In the case of the o-aminobenzoic acid derivatives, 17 out of 19 compounds display intramolecular N—H···O or O—H···N hydrogen bridges with an S2(6) topology. Additionally, there are reports on ketoimines derived from 2,4-pentanedione and aminobenzoic acids. The corresponding o- and p-aminobenzoic acid derivatives exist as enamines with intramolecular N—H···O hydrogen bridges (Murugavel et al., 2012; Joshi et al., 2005). The crystal structure of the m-derivative has not yet been determined. Deprotonation of the aminobenzoic acid derivatives was used to generate carboxylates that have been applied as ligands in transition-metal complexes (Shi & Hu, 2007) and organotin compounds (Chen et al., 2020; Baul et al., 2008, 2009).

5. Synthesis and crystallization

3-Formylacetylacetone (3.0 g, 23.4 mmol) and the corresponding aminobenzoic acid (3.3 g, 24.0 mmol) were dissolved in methanol (50 ml) and stirred at room temperature for 3 h. The solid products 1-3 were isolated by filtration, washed with methanol and dried in vacuo.

Yield: 2.7 g (47%) for 1, 3.1 g (54%) for 2 and 3.1 g (74%) for 3 based on 3-formylacetylacetone.

Crystals suitable for single crystal X-ray diffraction of 3 were obtained from the mother liquor. In the case of compounds 1 and 2, single crystals were obtained from a slow reaction (around three days of reaction time) of a suspension of copper(II) o- or p-aminobenzoate (1.5 g in 3 ml of water) and a solution of 3-formylacetylacetone (1.0 g in 5 ml of diethyl ether).

1: white powder, air stable, soluble in DMF and DMSO, hardly soluble in methanol, water, diethyl ether, THF.

C13H13NO4: 63.07% C (calc. 63.16%), 5.30% H (calc. 5.26%), 5.41% N (calc. 5.67%), IR: 2864 (br), 2586 (w), 1696 (w), 1647 (m), 1552 (s), 1492 (m), 1405 (m), 1325 (s), 1144 (m), 1077 (w), 978 (m), 935 (m), 789 (m), 759 (s), 695 (m), 652 (m), 634 (s), 584 (s), 544 (s), 470 (m), 405 (m), 326 (m) cm⁻¹. 1H NMR(DMSO-d6): 2.35 (s, 3 H, CO—CH3), 2.39 (s, 3 H, CO—CH3), 7.25–7.97 (m, 4 H, CHromatic), 8.39 [d (J = 12.8 Hz), 1 H, C==CH—N=H], 13.49 [d (J =12.8 Hz), 1 H, C==CH—N=H], 13C NMR(DMSO-d6): 27.4 ppm (–CH3), 31.4 (–CH3), 114.3 (C(O)—C—C(O)), 117.0 (CHromatic), 118.4 (CHromatic), 124.0 (CHromatic), 131.4 (CHromatic), 134.1 (CHromatic), 140.6 (CHromatic), 150.6 (CHromatic), 167.4 (COOH), 195.7 (CO) ppm.

2: off-white powder, air stable, soluble in DMF and DMSO, hardly soluble in methanol, water, diethyl ether, THF.

C13H13NO4: 62.74% C (calc. 63.16%), 5.26% H (calc. 5.26%), 5.68% N (calc. 5.67%), IR: 2929 (br), 1704 (s), 1656 (w), 1632 (s), 1557 (s), 1497 (w), 1405 (s), 1347 (m), 1308 (s), 1032 (w), 979 (m), 877 (s), 802 (m), 749 (m), 679 (s), 641 (s), 593 (w), 537 (m), 475 (w), 280 (m), 232 (m) cm⁻¹. 1H NMR(DMSO-d6): 2.37 (s, 3 H, CO—CH3), 2.38 (s, 3 H, CO—CH3), 7.52–7.94 (m, 4 H, CHromatic), 8.34 [d (J = 12.8 Hz), 1 H, C==CH—N=H], 12.53 [d (J =12.8 Hz), 1 H, C==CH—N=H], 13C NMR(DMSO-d6): 27.5 ppm (–CH3), 31.4 (–CH3), 112.8 (C(O)—C—C(O)), 118.5 (CHromatic), 122.5 (CHromatic), 125.7 (CHromatic), 129.8 (CHromatic), 132.2 (CHromatic), 139.4 (CHromatic), 152.6 (CHromatic), 166.6 (COOH), 195.2 (CO) ppm.

3: yellow powder, air stable, soluble in DMF and DMSO, hardly soluble in methanol, water, diethyl ether, THF.

C13H13NO4: 62.79% C (calc. 63.16%), 5.27% H (calc. 5.26%), 5.53% N (calc. 5.67%), IR: 2820 (br), 1674 (s), 1628 (s), 1586 (s), 1564 (s), 1433 (w), 1390 (s), 1314 (w), 1285 (s), 1249 (s), 1206 (m), 1175 (m), 929 (s), 864 (m), 845 (m), 793 (m), 771 (s), 694 (m), 646 (m), 613 (s), 550 (m), 510 (s), 471 (w), 424 (w), 275 (m), 214 (s) cm⁻¹. 1H NMR(DMSO-d6): 2.37 (s, 3 H, CO—CH3), 2.38 (s, 3 H, CO—CH3), 7.57 [m, 2 H, NHFacac—C—(CHromatic)2], 8.44 [d (J = 12.6 Hz), 1 H, C==CH—N=H], 12.64 [d (J =12.8 Hz), 1 H, C==CH—N=H], 12.86 (s, 1H, OH).
Table 7

|                  | 1                     | 2                     | 3                     |
|------------------|-----------------------|-----------------------|-----------------------|
| Crystal data     |                       |                       |                       |
| Chemical formula | C_{13}H_{13}NO_{4}    | C_{13}H_{13}NO_{4}    | C_{13}H_{13}NO_{4}    |
| M, g mol⁻¹       | 247.24                | 247.24                | 247.24                |
| Crystal system, space group | Monoclinic, C2/c | Orthorhombic, Pnma | Monoclinic, P2₁/c |
| Temperature (K)  | 170                   | 170                   | 170                   |
| a, b, c (Å)      | 10.6287 (5), 12.3740 (4), 17.5419 (7) | 11.4880 (4), 6.4726 (3), 15.2012 (5) | 10.8649 (6), 10.6185 (5), 11.3616 (6) |
| α, β, γ (°)      | 90, 92.836 (3), 90 | 90, 90, 90 | 90, 118.422 (4), 90 |
| V (Å³)           | 2304.28 (16)          | 1130.32 (8)          | 1152.78 (11)          |
| Z                 | 8                     | 4                    | 4                     |
| D₀ (Mg m⁻³)      | 1.425                 | 1.453                | 1.425                 |
| Radiation type   | Mo K                  | Mo K                 | Mo K                 |
| μ (mm⁻¹)         | 0.11                  | 0.11                 | 0.11                  |
| Crystal size (mm)| 0.32 × 0.23 × 0.14    | 0.16 × 0.07 × 0.07   | 0.54 × 0.25 × 0.08    |

Data collection

|                  | 1                     | 2                     | 3                     |
|------------------|-----------------------|-----------------------|-----------------------|
| Diffractometer   | Stoe IPDS 2T          | Stoe IPDS 2T          | Stoe IPDS 2T          |
| No. of measured, independent and observed | 5925, 2242, 2041      | 4667, 1346, 1118     | 5836, 2225, 1796      |
| R_{int}          | 0.051                 | 0.039                 | 0.036                 |
| (sin θ/λ)max (Å⁻¹) | 0.617                | 0.639                 | 0.617                 |
| Refinement       |                       |                       |                       |
| R(F² > 2σ(F²))   | 0.046, 0.127, 1.06    | 0.044, 0.128, 1.08   | 0.045, 0.129, 1.06   |
| S                 | 2242                  | 1346                  | 2225                 |
| No. of reflections | 166                  | 126                   | 169                 |
| No. of parameters | 166                  | 126                   | 169                 |
| H-atom treatment | H-atom parameters constrained | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement |
| Δρ_{max}, Δρ_{min} (e Å⁻³) | 0.20, −0.25           | 0.35, −0.25          | 0.27, −0.19          |

Computer programs: X-AREA (Stoe, 2016), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b), DIAMOND (Brandenburg et al., 2019) and OLEX2 (Dolomanov et al., 2009).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 7. The methyl group hydrogen atoms of compound 2 and the carboxyl hydrogen atoms of compounds 2 and 3 were located from difference-Fourier maps and were refined freely. The remaining hydrogen atoms were positioned geometrically and refined using a riding model.

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References

Baul, T. S. B., Masharing, C., Basu, S., Pettinari, C., Rivarola, E., Chantarapromma, S. & Fun, H.-K. (2008). Appl. Organomet. Chem. 22, 114–121.
Baul, T. S. B., Masharing, C., Ruisi, G., Pettinari, C. & Linden, A. (2009). J. Inorg. Organomet. Polym. 19, 395–400.
Brandenburg, K. (2019). DIAMOND. Crystal Impact GbR, Bonn, Germany.
Bu, R., Xiong, Y., Wei, X., Li, H. & Zhang, C. (2019). Cryst. Growth Des. 19, 5981–5997.
Chen, L., Wang, Z., Qiu, T., Sun, R., Zhao, Z., Tian, L. & Liu, X. (2020). Appl. Organomet. Chem. 34, 5790–5801.
Dankhoff, K. & Weber, B. (2019). Dalton Trans. 48, 15376–15380.
Desiraju, G. R. (2002). Acc. Chem. Res. 35, 565–573.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339–341.
Groß, M., Milata, V. & Kožíšek, J. (2006). Acta Cryst. E62, o4464–o4465.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.
Halz, J. H., Hentsch, A., Wagner, C. & Merzweiker, K. (2021). Z. Anorg. Allg. Chem. 647, 922–930.
Hentsch, A., Wagner, C. & Merzweiker, K. (2014). Z. Anorg. Allg. Chem. 640, 339–346.
Joshi, K. A., Deshpande, M. S., Kumbhar, A. S., Butcher, R. J. & Geiji, S. P. (2005). J. Mol. Struct. Theoc. 722, 57–63.
Murugavel, R., Singh, M. P. & Nethaji, M. (2012). J. Chem. Crystallogr. 42, 12–17.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Shi, S.-M. & Hu, Z.-Q. (2007). Acta Cryst. E63, m426–m428.
Spackman, M. A. & Jayatilaka, D. (2009). CrystEngComm, 11, 19–32.
Stoe (2016). X-AREA. Stoe & Cie, Darmstadt, Germany.
Svensson, C., Ymén, I. & Yom-Tov, B. (1982). Acta Cryst. Scand. 36B, 71–76.
Turner, M. J., Mckinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). CrystalExplorer. Version 17. University of Western Australia.
Wolf, L. & Jäger, E.-G. (1966). Z. Anorg. Allg. Chem. 346, 76–91.

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Computing details
For all structures, data collection: \( X \)-AREA (Stoe, 2016); cell refinement: \( X \)-AREA (Stoe, 2016); data reduction: \( X \)-AREA (Stoe, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: DIAMOND (Brandenburg et al., 2019); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

\( \text{2-[(2-Acetyl-3-oxobut-1-en-1-yl)amino]benzoic acid (1)} \)

Crystal data
\( \text{C}_{13}\text{H}_{13}\text{NO}_{4} \)
\( M_r = 247.24 \)
Monoclinic, \( \text{C}_2/c \)
\( a = 10.6287 (5) \, \text{Å} \)
\( b = 12.3740 (4) \, \text{Å} \)
\( c = 17.5419 (7) \, \text{Å} \)
\( \beta = 92.836 (3)° \)
\( V = 2304.28 (16) \, \text{Å}^3 \)
\( Z = 8 \)

Data collection
Stoe IPDS 2T diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus, Incoatec I\( \mu \)s
Plane graphite monochromator
Detector resolution: 6.67 pixels mm\(^{-1}\)
rotation method, \( \omega \) scans
5925 measured reflections
2242 independent reflections
2041 reflections with \( I > 2\sigma(I) \)

Refinement
Refinement on \( F^2 \)
Least-squares matrix: full
\( R[F^2 > 2\sigma(F^2)] = 0.046 \)
\( wR(F^2) = 0.127 \)
\( S = 1.06 \)
2242 reflections
166 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
\( w = 1/[\sigma^2(F_c^2) + (0.0676P)^2 + 1.813P] \)
where \( P = (F_c^2 + 2F_s^2)/3 \)
\( (\Delta\sigma)_{\text{max}} < 0.001 \)
\( \Delta\rho_{\text{max}} = 0.20 \, \text{e} \, \text{Å}^{-3} \)
\( \Delta\rho_{\text{min}} = -0.25 \, \text{e} \, \text{Å}^{-3} \)
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)

|     | x       | y       | z       | U(eq) |
|-----|---------|---------|---------|-------|
| O1  | 0.45960 (11)| 0.15997 (10) | 0.47933 (6) | 0.0356 (3) |
| O2  | 0.27859 (11)| 0.16211 (10) | 0.26411 (6) | 0.0358 (3) |
| O3  | 0.61428 (11)| 0.44676 (10) | 0.67913 (7) | 0.0359 (3) |
| H13 | 0.6590   | 0.4003   | 0.6999   | 0.054*   |
| O4  | 0.53453 (11)| 0.30520 (10) | 0.61407 (6) | 0.0339 (3) |
| N   | 0.36984 (11)| 0.35634 (11) | 0.49544 (7) | 0.0239 (3) |
| H8  | 0.4164   | 0.3073   | 0.5171   | 0.029*   |
| C1  | 0.45492 (18)| 0.06191 (16) | 0.36409 (10) | 0.0401 (4) |
| H1  | 0.5001   | 0.0099   | 0.3955   | 0.060*   |
| H2  | 0.5079   | 0.0872   | 0.3250   | 0.060*   |
| H3  | 0.3809   | 0.0288   | 0.3409   | 0.060*   |
| C2  | 0.41727 (14)| 0.15556 (13) | 0.41238 (9) | 0.0285 (4) |
| C3  | 0.33393 (13)| 0.24280 (13) | 0.38304 (8) | 0.0245 (3) |
| C4  | 0.26485 (13)| 0.23812 (13) | 0.30893 (8) | 0.0259 (3) |
| C5  | 0.17366 (15)| 0.32733 (15) | 0.28533 (9) | 0.0320 (4) |
| H4  | 0.1318   | 0.3093   | 0.2373   | 0.048*   |
| H5  | 0.2189   | 0.3939   | 0.2804   | 0.048*   |
| H6  | 0.1124   | 0.3354   | 0.3233   | 0.048*   |
| C6  | 0.31739 (13)| 0.33454 (13) | 0.42647 (8) | 0.0245 (3) |
| H7  | 0.2636   | 0.3869   | 0.4052   | 0.029*   |
| C7  | 0.35433 (13)| 0.45398 (13) | 0.53529 (8) | 0.0232 (3) |
| C8  | 0.43310 (13)| 0.47785 (13) | 0.60039 (7) | 0.0233 (3) |
| C9  | 0.41800 (14)| 0.57606 (13) | 0.63783 (8) | 0.0277 (4) |
| H9  | 0.4699   | 0.5919   | 0.6806   | 0.033*   |
| C10 | 0.32814 (15)| 0.65050 (14) | 0.61313 (9) | 0.0303 (4) |
| H10 | 0.3205   | 0.7161   | 0.6383   | 0.036*   |
| C11 | 0.24927 (15)| 0.62563 (14) | 0.54998 (9) | 0.0316 (4) |
| H11 | 0.1872   | 0.6744   | 0.5334   | 0.038*   |
| C12 | 0.26238 (14)| 0.52931 (14) | 0.51180 (8) | 0.0297 (4) |
| H12 | 0.2090   | 0.5141   | 0.4696   | 0.036*   |
| C13 | 0.53074 (14)| 0.40013 (13) | 0.63058 (8) | 0.0250 (3) |

Atomic displacement parameters (Å²)

|     | U¹¹ | U²² | U³³ | U¹² | U¹³ | U²³ |
|-----|-----|-----|-----|-----|-----|-----|
| O1  | 0.0409 (7) | 0.0372 (7) | 0.0267 (6) | 0.0043 (5) | −0.0176 (5) | −0.0039 (5) |
| O2  | 0.0406 (7) | 0.0404 (7) | 0.0248 (6) | 0.0031 (5) | −0.0151 (5) | −0.0082 (5) |
| O3  | 0.0385 (6) | 0.0341 (7) | 0.0329 (6) | −0.0001 (5) | −0.0221 (5) | −0.0002 (5) |
| O4  | 0.0402 (6) | 0.0316 (7) | 0.0284 (6) | 0.0033 (5) | −0.0147 (5) | −0.0024 (5) |

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N 0.0246 (6) 0.0291 (7) 0.0173 (6) −0.0004 (5) −0.0070 (5) −0.0010 (5)  
C1 0.0417 (9) 0.0459 (11) 0.0315 (9) 0.0119 (8) −0.0111 (7) −0.0077 (8)  
C2 0.0265 (7) 0.0350 (9) 0.0230 (7) −0.0033 (6) −0.0074 (6) −0.0009 (6)  
C3 0.0225 (7) 0.0325 (8) 0.0180 (7) −0.0041 (6) −0.0060 (5) −0.0005 (6)  
C4 0.0242 (7) 0.0337 (9) 0.0190 (7) −0.0058 (6) −0.0058 (5) 0.0006 (6)  
C5 0.0305 (8) 0.0419 (10) 0.0223 (7) 0.0004 (7) −0.0110 (6) −0.0010 (7)  
C6 0.0224 (7) 0.0329 (8) 0.0176 (7) −0.0029 (6) −0.0056 (5) 0.0027 (6)  
C7 0.0225 (7) 0.0296 (8) 0.0171 (6) −0.0026 (6) −0.0026 (5) 0.0003 (6)  
C8 0.0242 (7) 0.0298 (8) 0.0156 (6) −0.0035 (6) −0.0032 (5) 0.0016 (6)  
C9 0.0298 (8) 0.0345 (9) 0.0184 (7) −0.0037 (6) −0.0029 (6) −0.0009 (6)  
C10 0.0329 (8) 0.0310 (8) 0.0269 (8) −0.0002 (6) 0.0009 (6) −0.0033 (6)  
C11 0.0296 (8) 0.0342 (9) 0.0306 (8) 0.0052 (7) −0.0030 (6) 0.0023 (7)  
C12 0.0275 (7) 0.0372 (9) 0.0234 (7) 0.0014 (6) −0.0084 (6) 0.0004 (6)  
C13 0.0283 (7) 0.0314 (9) 0.0145 (6) −0.0034 (6) −0.0054 (5) 0.0016 (6)  

Geometric parameters (Å, º)

| Bond (Å) | Bond (º) |
|----------|----------|
| O1—C2 | 1.2380 (18) |
| O2—C4 | 1.239 (2) |
| O3—H13 | 0.8200 |
| O3—C13 | 1.3312 (17) |
| O4—C13 | 1.211 (2) |
| N—H8 | 0.8600 |
| N—C6 | 1.3344 (18) |
| N—C7 | 1.410 (2) |
| C1—H1 | 0.9600 |
| C1—H2 | 0.9600 |
| C1—H3 | 0.9600 |
| C1—C2 | 1.501 (2) |
| C2—C3 | 1.473 (2) |
| C3—C4 | 1.4621 (18) |
| C3—C6 | 1.383 (2) |
| C4—C5 | 1.513 (2) |
| C13—O3—H13 | 109.5 |
| C6—N—H8 | 117.7 |
| C6—N—C7 | 124.68 (13) |
| C7—N—H8 | 117.7 |
| H1—C1—H2 | 109.5 |
| H1—C1—H3 | 109.5 |
| H2—C1—H3 | 109.5 |
| C2—C1—H1 | 109.5 |
| C2—C1—H2 | 109.5 |
| C2—C1—H3 | 109.5 |
| O1—C2—C1 | 118.34 (14) |
| O1—C2—C3 | 118.90 (14) |
| C3—C2—C1 | 122.75 (13) |
| C4—C3—C2 | 123.26 (14) |

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C6—C3—C2 119.98 (12) C11—C10—H10 120.6
C6—C3—C4 116.76 (13) C10—C11—H11 119.8
O2—C4—C3 121.63 (14) C12—C11—C10 120.49 (15)
O2—C4—C5 118.30 (13) C12—C11—H11 119.8
C3—C4—C5 120.07 (14) C7—C12—H12 119.3
C4—C5—H4 109.5 C11—C12—C7 121.31 (14)
C4—C5—H5 109.5 C11—C12—H12 119.3
C4—C5—H6 109.5 O3—C13—C8 121.20 (13)
H4—C5—H5 109.5 O4—C13—O3 122.99 (14)
H4—C5—H6 109.5 O4—C13—C8 124.81 (13)
H5—C5—H6 109.5

Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H | H···A | D···A    | D—H···A |
|-----------|------|-------|----------|---------|
| O3—H13···O2i | 0.82 | 1.83  | 2.6132 (15) | 160 |
| N—H8···O1   | 0.86 | 2.00  | 2.6308 (18) | 129 |
| N—H8···O4   | 0.86 | 2.06  | 2.7266 (16) | 133 |
| C5—H6···O4ii| 0.96 | 2.62  | 3.330 (2)   | 131 |
| C11—H11···O1iii | 0.93 | 2.56  | 3.2891 (19) | 136 |

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

3-[(2-Acetyl-3-oxobut-1-en-1-yl)amino]benzoic acid (2)

Crystal data

C_{13}H_{13}NO_{4} \hspace{1cm} D_{\ell} = 1.453 \text{ Mg m}^{-3} \\
M_{r} = 247.24 \hspace{1cm} \text{Mo K\(\alpha\) radiation, } \lambda = 0.71073 \text{ Å} \\
Orthorhombic, Pnma \hspace{1cm} \text{Cell parameters from 10416 reflections} \\
a = 11.4880 (4) \text{ Å} \hspace{1cm} \theta = 2.7–29.7^\circ \\
b = 6.4726 (3) \text{ Å} \hspace{1cm} \mu = 0.11 \text{ mm}^{-1} \\
c = 15.2012 (5) \text{ Å} \hspace{1cm} T = 170 \text{ K} \\
V = 1130.32 (8) \text{ Å}^3 \hspace{1cm} \text{Needle, clear yellow} \\
Z = 4 \hspace{1cm} 0.16 \times 0.07 \times 0.07 \text{ mm} \\
F(000) = 520

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sup-4
Data collection

Stoe IPDS 2T diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus, Incoatec Iµs Plane graphite monochromator
Detector resolution: 6.67 pixels mm\(^{-1}\)
rotation method, \(\omega\) scans
4667 measured reflections
1346 independent reflections
1118 reflections with \(I > 2\sigma(I)\)
\(R_{int} = 0.039\)
\(\theta_{max} = 27.0^\circ, \theta_{min} = 2.7^\circ\)

Refinement

Refinement on \(F^2\)
Least-squares matrix: full
\[R(F^2 > 2\sigma(F^2)) = 0.044\]
\(wR(F^2) = 0.128\)
\(S = 1.08\)
1346 reflections
126 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
\[w = 1/[\sigma^2(F_o^2) + (0.0692P)^2 + 0.4804P]\]
where \(P = (F_o^2 + 2F_c^2)/3\)
\((\Delta\sigma)_{max} < 0.001\)
\(\Delta\rho_{max} = 0.35\ \text{e} \cdot \text{Å}^{-3}\)
\(\Delta\rho_{min} = -0.25\ \text{e} \cdot \text{Å}^{-3}\)

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 | 0.95570 (13) | 0.2500 | 0.53720 (10) | 0.0312 (4) |
| O2 | 1.00391 (13) | 0.2500 | 0.26645 (10) | 0.0337 (4) |
| O3 | 0.55070 (12) | 0.2500 | 0.80351 (10) | 0.0272 (4) |
| H11 | 0.532 (3) | 0.2500 | 0.856 (2) | 0.060 (11)* |
| O4 | 0.35794 (13) | 0.2500 | 0.78224 (10) | 0.0362 (5) |
| N  | 0.73322 (14) | 0.2500 | 0.50635 (11) | 0.0204 (4) |
| H6 | 0.7858 | 0.2500 | 0.5466 | 0.025* |
| C1 | 1.10424 (19) | 0.2500 | 0.43063 (16) | 0.0359 (6) |
| H1 | 1.146 (3) | 0.2500 | 0.487 (2) | 0.046 (8)* |
| H2 | 1.1236 (17) | 0.134 (3) | 0.3925 (15) | 0.049 (6)* |
| C2 | 0.97887 (18) | 0.2500 | 0.45735 (13) | 0.0236 (5) |
| C3 | 0.88505 (17) | 0.2500 | 0.39425 (13) | 0.0210 (4) |
| C4 | 0.90572 (18) | 0.2500 | 0.29799 (13) | 0.0251 (5) |
| C5 | 0.8029 (2) | 0.2500 | 0.23691 (15) | 0.0422 (7) |
| H3 | 0.829 (3) | 0.2500 | 0.175 (3) | 0.069 (11)* |
| H4 | 0.7490 (18) | 0.124 (4) | 0.2474 (14) | 0.058 (6)* |
| C6 | 0.76977 (17) | 0.2500 | 0.42287 (13) | 0.0209 (4) |
| H5 | 0.7126 | 0.2500 | 0.3796 | 0.025* |
| C7 | 0.61523 (17) | 0.2500 | 0.53461 (13) | 0.0190 (4) |
| C8 | 0.59563 (16) | 0.2500 | 0.62497 (13) | 0.0195 (4) |
| H7 | 0.6581 | 0.2500 | 0.6638 | 0.023* |
### Geometric parameters (Å, °)

|       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|
| O1—C2 | 1.243 (3) |      | C5—H3 | 0.98 (4) |      |       |
| O2—C4 | 1.226 (3) |      | C5—H4 | 1.03 (2) |      |       |
| O3—H11 | 0.83 (4) |      | C6—H5 | 0.9300 |      |       |
| O3—C13 | 1.330 (2) |      | C7—C8 | 1.392 (3) |      |       |
| O4—C13 | 1.210 (2) |      | C7—C12 | 1.392 (3) |      |       |
| N—H6 | 0.8600 |      | C8—H7 | 0.9300 |      |       |
| N—C6 | 1.337 (3) |      | C8—C9 | 1.398 (3) |      |       |
| N—C7 | 1.422 (2) |      | C9—C10 | 1.395 (3) |      |       |
| C1—H1 | 0.98 (3) |      | C9—C13 | 1.490 (3) |      |       |
| C1—H2 | 0.97 (2) |      | C10—H8 | 0.9300 |      |       |
| C1—C2 | 1.496 (3) |      | C10—C11 | 1.388 (3) |      |       |
| C2—C3 | 1.443 (3) |      | C11—H9 | 0.9300 |      |       |
| C3—C4 | 1.482 (3) |      | C11—C12 | 1.387 (3) |      |       |
| C3—C6 | 1.394 (3) |      | C12—H10 | 0.9300 |      |       |
| C4—C5 | 1.503 (3) |      |       |       |      |       |

### Atomic displacement parameters (Å²)

|       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|
| O1    | 0.0188 (7) | 0.0604 (12) | 0.0144 (7) | 0.000 | ~0.0007 (6) | 0.000 |
| O2    | 0.0226 (8) | 0.0580 (12) | 0.0205 (8) | 0.000 | 0.0054 (6) | 0.000 |
| O3    | 0.0191 (8) | 0.0479 (10) | 0.0147 (7) | 0.000 | 0.0015 (5) | 0.000 |
| O4    | 0.0184 (7) | 0.0686 (13) | 0.0217 (7) | 0.000 | 0.0057 (6) | 0.000 |
| N     | 0.0136 (7) | 0.0315 (10) | 0.0162 (8) | 0.000 | 0.0014 (6) | 0.000 |
| C1    | 0.0161 (10) | 0.0687 (19) | 0.0227 (11) | 0.000 | ~0.0002 (8) | 0.000 |
| C2    | 0.0200 (9) | 0.0341 (12) | 0.0167 (9) | 0.000 | ~0.0001 (8) | 0.000 |
| C3    | 0.0157 (8) | 0.0307 (11) | 0.0165 (9) | 0.000 | 0.0020 (7) | 0.000 |
| C4    | 0.0221 (10) | 0.0373 (12) | 0.0159 (9) | 0.000 | 0.0014 (8) | 0.000 |
| C5    | 0.0256 (11) | 0.085 (2) | 0.0156 (10) | 0.000 | ~0.0019 (9) | 0.000 |
| C6    | 0.0178 (9) | 0.0288 (11) | 0.0160 (9) | 0.000 | 0.0002 (7) | 0.000 |
| C7    | 0.0153 (9) | 0.0226 (10) | 0.0192 (9) | 0.000 | 0.0032 (7) | 0.000 |
| C8    | 0.0156 (9) | 0.0266 (10) | 0.0164 (9) | 0.000 | ~0.0009 (7) | 0.000 |
| C9    | 0.0180 (9) | 0.0277 (11) | 0.0161 (9) | 0.000 | 0.0024 (7) | 0.000 |
| C10   | 0.0132 (8) | 0.0307 (11) | 0.0235 (10) | 0.000 | 0.0020 (7) | 0.000 |
| C11   | 0.0170 (10) | 0.0320 (12) | 0.0225 (10) | 0.000 | ~0.0043 (8) | 0.000 |
| C12   | 0.0198 (10) | 0.0290 (11) | 0.0151 (9) | 0.000 | ~0.0005 (7) | 0.000 |
| C13   | 0.0170 (9) | 0.0347 (11) | 0.0178 (9) | 0.000 | 0.0019 (7) | 0.000 |
### Hydrogen-bond geometry (Å, °)

|        | D—H | H···A | D···A | D—H···A |
|--------|-----|------|-------|---------|
| O3—H11···O1<sup>1</sup> | 0.83 (4) | 1.84 (4) | 2.656 (2) | 166 (3) |
| N—H6···O1<sup>2</sup> | 0.86 | 1.96 | 2.598 (2) | 130 |
| C8—H7···O4<sup>a</sup> | 0.93 | 2.44 | 3.327 (2) | 160 |

Symmetry codes: (i) x−1/2, y, −z+3/2; (ii) x+1/2, y, −z+3/2.
4-[(2-Acetyl-3-oxobut-1-en-1-yl)amino]benzoic acid (3)

Crystal data

C₁₃H₁₁NO₄

Mᵣ = 247.24

Monoclinic, P₂₁/c

a = 10.8649 (6) Å

b = 10.6185 (5) Å

V = 1152.78 (11) Å³

Z = 4

F(000) = 520

Dᵣ = 1.425 Mg m⁻³

Cell parameters from 6441 reflections

θ = 1.9–29.6°

µ = 0.11 mm⁻¹

T = 170 K

Plate, clear yellowish colourless

0.54 × 0.25 × 0.08 mm

Data collection

Stoe IPDS 2T
diffractometer

1796 reflections with I > 2σ(I)

R(int) = 0.036

Detector resolution: 6.67 pixels mm⁻¹

rotation method, ω scans

5856 measured reflections

2225 independent reflections

Refinement

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.045

wR(F²) = 0.129

S = 1.06

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(Fo²) + (0.0728P)² + 0.2229P]

where P = (Fo² + 2Fc²)/3

(Δ/σ)max < 0.001

Δρmax = 0.27 e Å⁻³

Δρmin = −0.18 e Å⁻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)

|     | x      | y      | z      | U₁₁* / Ueq |
|-----|--------|--------|--------|------------|
| O1  | 0.26870 (14) | 0.40034 (11) | 0.95427 (13) | 0.0496 (4) |
| O2  | 0.47787 (18) | 0.71853 (13) | 1.16675 (13) | 0.0659 (5) |
| O3  | 0.05035 (12) | 0.60892 (10) | 0.12974 (12) | 0.0429 (3) |
| H13 | 0.010 (3) | 0.600 (3) | 0.019 (3) | 0.132 (14)* |
| O4  | 0.02909 (13) | 0.39969 (10) | 0.12604 (12) | 0.0457 (3) |
| N   | 0.25034 (14) | 0.51162 (11) | 0.74534 (14) | 0.0372 (3) |
| H8  | 0.2356 | 0.4443 | 0.7789 | 0.045* |
| C1  | 0.3680 (2) | 0.48695 (16) | 1.16943 (19) | 0.0471 (4) |
| H3  | 0.4676 | 0.4951 | 1.2227 | 0.071* |
| H1  | 0.3385 | 0.4078 | 1.1884 | 0.071* |
| H2  | 0.3228 | 0.5544 | 1.1903 | 0.071* |
| C2  | 0.32935 (16) | 0.49262 (14) | 1.02514 (18) | 0.0392 (4) |
### Atomic displacement parameters (Å²)

|       | $U_{11}$  | $U_{22}$  | $U_{33}$  | $U_{12}$  | $U_{13}$  | $U_{23}$  |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| O1    | 0.0581 (7)| 0.0358 (6)| 0.0532 (7)| −0.0088 (5)| 0.0249 (6)| −0.0014 (5)|
| O2    | 0.0992 (11)| 0.0492 (8)| 0.0403 (7)| −0.0221 (7)| 0.0259 (7)| −0.0058 (6)|
| O3    | 0.0523 (7)| 0.0300 (6)| 0.0431 (7)| −0.0037 (5)| 0.0199 (5)| 0.0013 (4)  |
| O4    | 0.0624 (7)| 0.0301 (6)| 0.0440 (7)| −0.0095 (5)| 0.0250 (6)| −0.0070 (4)|
| N     | 0.0399 (7)| 0.0308 (7)| 0.0398 (8)| −0.0021 (5)| 0.0181 (6)| −0.0014 (5)|
| C1    | 0.0529 (10)| 0.0405 (9)| 0.0499 (10)| −0.0014 (7)| 0.0262 (8)| 0.0035 (7)  |
| C2    | 0.0365 (8)| 0.0314 (8)| 0.0497 (10)| 0.0023 (6)| 0.0204 (7)| 0.0011 (6)  |
| C3    | 0.0361 (8)| 0.0301 (7)| 0.0429 (9)| 0.0022 (6)| 0.0174 (7)| 0.0005 (6)  |
| C4    | 0.0459 (9)| 0.0336 (8)| 0.0426 (9)| −0.0002 (6)| 0.0184 (7)| 0.0001 (6)  |
| C5    | 0.0519 (10)| 0.0359 (9)| 0.0462 (9)| −0.0080 (7)| 0.0212 (8)| −0.0034 (7)|
| C6    | 0.0358 (8)| 0.0296 (7)| 0.0460 (9)| 0.0014 (6)| 0.0197 (7)| 0.0006 (6)  |
| C7    | 0.0307 (7)| 0.0330 (8)| 0.0414 (9)| −0.0009 (6)| 0.0171 (6)| −0.0015 (6)|
| C8    | 0.0397 (8)| 0.0275 (7)| 0.0443 (9)| 0.0019 (6)| 0.0182 (7)| −0.0057 (6)|
| C9    | 0.0387 (8)| 0.0266 (7)| 0.0446 (9)| 0.0022 (6)| 0.0184 (7)| 0.0009 (6)  |
| C10   | 0.0312 (7)| 0.0279 (7)| 0.0419 (9)| −0.0017 (5)| 0.0177 (6)| −0.0024 (6)|
| C11   | 0.0423 (8)| 0.0263 (7)| 0.0441 (9)| −0.0025 (6)| 0.0198 (7)| −0.0038 (6)|
| C12   | 0.0436 (8)| 0.0266 (7)| 0.0453 (9)| −0.0015 (6)| 0.0194 (7)| 0.0003 (6)  |
| C13   | 0.0343 (7)| 0.0283 (7)| 0.0444 (9)| −0.0015 (6)| 0.0180 (7)| −0.0010 (6)|

### Geometric parameters (Å, °)

|        | O1—C2  | C5—H6  | C5—H4  | C5—H5  | C6—H7  |
|--------|--------|--------|--------|--------|--------|
| O1—C2  | 1.2401 (19)|        |        |        |        |
| O2—C4  | 1.223 (2) |        |        |        |        |
| O3—H13 | 1.12 (3) |        |        |        |        |
| O3—C13 | 1.2863 (18)|        |        |        |        |

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| Bond          | Distance (Å) | Bond          | Distance (Å) | Bond          | Distance (Å) |
|--------------|--------------|--------------|--------------|--------------|--------------|
| O4—C13       | 1.2584 (18)  | C7—C8        | 1.392 (2)    |              |              |
| N—H8         | 0.8600       | C7—C12       | 1.398 (2)    |              |              |
| N—C6         | 1.333 (2)    | C8—H9        | 0.9300       |              |              |
| N—C7         | 1.402 (2)    | C8—C9        | 1.373 (2)    |              |              |
| C1—H3        | 0.9600       | C9—H10       | 0.9300       |              |              |
| C1—H1        | 0.9600       | C9—C10       | 1.394 (2)    |              |              |
| C1—H2        | 0.9600       | C10—C11      | 1.399 (2)    |              |              |
| C1—C2        | 1.487 (3)    | C10—C13      | 1.470 (2)    |              |              |
| C2—C3        | 1.475 (2)    | C11—H11      | 0.9300       |              |              |
| C3—C4        | 1.470 (2)    | C11—C12      | 1.369 (2)    |              |              |
| C3—C6        | 1.379 (2)    | C12—H12      | 0.9300       |              |              |
| C4—C5        | 1.503 (2)    |              |              |              |              |
| C13—O3—H13   | 113.3 (17)   | N—C6—C3      | 125.17 (15)  |              |              |
| C6—N—H8      | 116.9        | N—C6—H7      | 117.4        |              |              |
| C6—N—C7      | 126.30 (13)  | C3—C6—H7     | 117.4        |              |              |
| C7—N—H8      | 116.9        | C8—C7—N      | 121.74 (13)  |              |              |
| H3—C1—H1     | 109.5        | C8—C7—C12    | 119.78 (15)  |              |              |
| H3—C1—H2     | 109.5        | C12—C7—N     | 118.48 (13)  |              |              |
| H1—C1—H2     | 109.5        | C7—C8—H9     | 120.0        |              |              |
| C2—C1—H3     | 109.5        | C9—C8—C7     | 119.92 (14)  |              |              |
| C2—C1—H1     | 109.5        | C9—C8—H9     | 120.0        |              |              |
| C2—C1—H2     | 109.5        | C8—C9—H10    | 119.7        |              |              |
| O1—C2—C1     | 117.89 (14)  | C8—C9—C10    | 120.63 (14)  |              |              |
| O1—C2—C3     | 119.97 (16)  | C10—C9—H10   | 119.7        |              |              |
| C3—C2—C1     | 122.14 (14)  | C9—C10—C11   | 119.16 (16)  |              |              |
| C4—C3—C2     | 121.99 (15)  | C9—C10—C13   | 120.39 (13)  |              |              |
| C6—C3—C2     | 119.45 (14)  | C11—C10—C13  | 120.45 (13)  |              |              |
| C6—C3—C4     | 118.54 (14)  | C10—C11—H11  | 119.8        |              |              |
| O2—C4—C3     | 122.13 (15)  | C12—C11—C10  | 120.44 (14)  |              |              |
| O2—C4—C5     | 118.41 (15)  | C12—C11—H11  | 119.8        |              |              |
| C3—C4—C5     | 119.46 (15)  | C7—C12—H12   | 120.0        |              |              |
| C4—C5—H6     | 109.5        | C11—C12—C7   | 120.05 (14)  |              |              |
| C4—C5—H4     | 109.5        | C11—C12—H12  | 120.0        |              |              |
| C4—C5—H5     | 109.5        | O3—C13—C10   | 117.16 (13)  |              |              |
| H6—C5—H4     | 109.5        | O4—C13—O3    | 122.59 (15)  |              |              |
| H6—C5—H5     | 109.5        | O4—C13—C10   | 120.23 (13)  |              |              |
| H4—C5—H5     | 109.5        |              |              |              |              |
| O1—C2—C3     | −175.84 (16) | C7—N—C6—C3   | 178.50 (15)  |              |              |
| O1—C2—C3     | 2.8 (2)      | C7—N—C6—C3   | 1.1 (2)      |              |              |
| N—C7—C8—C9   | 179.62 (14)  | C8—C7—C12—C11| 0.7 (2)      |              |              |
| N—C7—C12—C11 | 179.51 (14)  | C8—C9—C10—C11| 0.2 (2)      |              |              |
| C1—C2—C3     | 4.2 (2)      | C8—C9—C10—C13| −179.41 (14) |              |              |
| C1—C2—C3     | −177.18 (15) | C9—C10—C11—C12| −1.1 (2)    |              |              |
| C2—C3—C4     | −4.5 (3)     | C9—C10—C13—O3| 10.8 (2)     |              |              |
| C2—C3—C4     | 175.83 (15)  | C9—C10—C13—O4| −170.75 (15) |              |              |
| C2—C3—C6     | −2.4 (2)     | C10—C11—C12—C7| 0.7 (3)     |              |              |
C4—C3—C6—N  176.29 (15)  C11—C10—C13—O3  -168.83 (14)
C6—N—C7—C8  -27.4 (2)       C11—C10—C13—O4  9.7 (2)
C6—N—C7—C12  153.77 (15)   C12—C7—C8—C9  -1.6 (2)
C6—C3—C4—O2  176.88 (17)   C13—C10—C11—C12  178.49 (15)
C6—C3—C4—C5  -2.8 (2)

Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H | H···A | D···A | D—H···A |
|-----------|------|-------|-------|---------|
| O3—H13···O4i | 1.12 (3) | 1.49 (3) | 2.6098 (18) | 173 (3) |
| N—H8···O1   | 0.86 | 1.91  | 2.5729 (18) | 133     |
| C8—H9···O3ii| 0.93 | 2.65  | 3.4832 (18) | 150     |
| C9—H10···O4iii| 0.93 | 2.65  | 3.3252 (18) | 130     |
| C11—H11···O1iv | 0.93 | 2.68  | 3.3612 (19) | 131     |

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