research communications

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-amino-benzoic acids led to the formation of the corresponding Schiff bases, namely, 3-[(2-carboxyphenylamino)methylidene]pentane-2,4-dione, **1**, 3-[(3-carboxy-phenylamino)methylidene]pentane-2,4-dione, **2**, and 3-[(4-carboxyphenyl-amino)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.

Table 1
Selected geometric parameters (Å, °) for **1**.

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 (2)
C6—N—C7—C8	−167.19 (14)	C6—C3—C4—O2	176.05 (14)

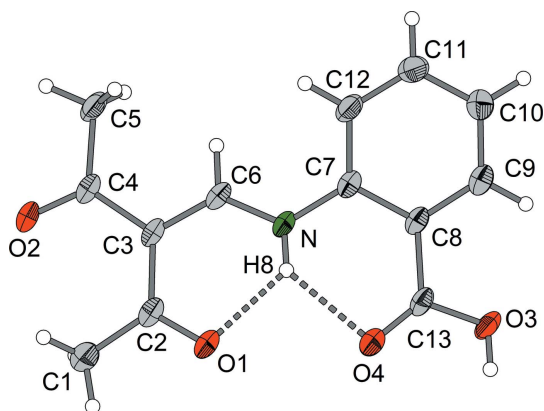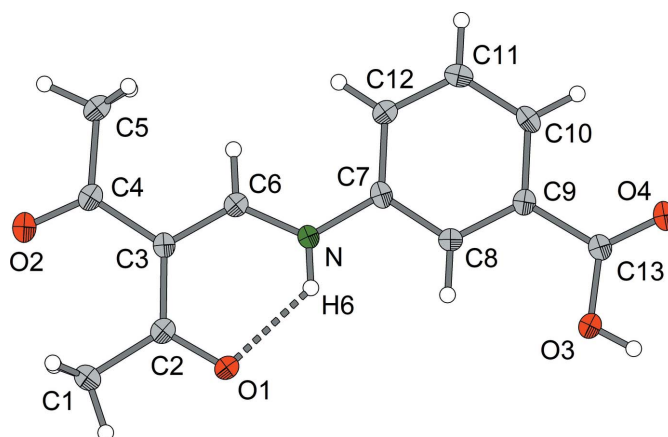**Table 2**
Selected geometric parameters (Å, °) for **2**.

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
Selected geometric parameters (Å, °) for **3**.

O1—C2	1.2401 (19)	C2—C3	1.475 (2)
O2—C4	1.223 (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)

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 $P2_1/c$, $Z = 4$. 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**:

Figure 2
Molecular structure of enamine **2** showing the labelling scheme. The hydrogen bond is shown as a dashed line; displacement ellipsoids are drawn at the 50% probability level.

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 (Gróf *et al.*, 2006). The enamine C—N bond lengths in compounds **1**–**3** are 1.333 (3)–1.337 (3) 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).

Figure 1
Molecular structure of enamine **1** showing the labelling scheme. Hydrogen bonds are shown as dashed lines; displacement ellipsoids are drawn at the 50% probability level.
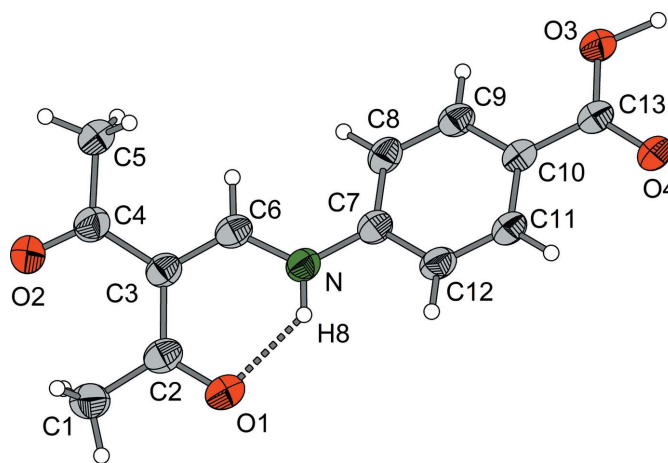
Figure 3
Molecular structure of enamine **3** showing the labelling scheme. The hydrogen bond is shown as a dashed line; displacement ellipsoids are drawn at the 50% probability level.

Table 4
Hydrogen-bond geometry (Å, °) for **1**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H13$\cdots$O2^{i}	0.82	1.83	2.6132 (15)	160
N—H8$\cdots$O1	0.86	2.00	2.6308 (18)	129
N—H8$\cdots$O4	0.86	2.06	2.7266 (16)	133
C5—H6$\cdots$O4^{ii}	0.96	2.62	3.330 (2)	131
C11—H11$\cdots$O1^{iii}	0.93	2.56	3.2891 (19)	136

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H11$\cdots$O1^{i}	0.83 (4)	1.84 (4)	2.656 (2)	166 (3)
N—H6$\cdots$O1	0.86	1.96	2.598 (2)	130
C8—H7$\cdots$O4^{ii}	0.93	2.44	3.327 (2)	160

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H13$\cdots$O4^{i}	1.12 (3)	1.49 (3)	2.6098 (18)	173 (3)
N—H8$\cdots$O1	0.86	1.91	2.5729 (18)	133
C8—H9$\cdots$O3^{ii}	0.93	2.65	3.4832 (18)	150
C9—H10$\cdots$O4^{iii}	0.93	2.65	3.3252 (18)	130
C11—H11$\cdots$O1^{iv}	0.93	2.68	3.3612 (19)	131

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (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$\cdots$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 $S_1^1(6)$ 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$\cdots$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].
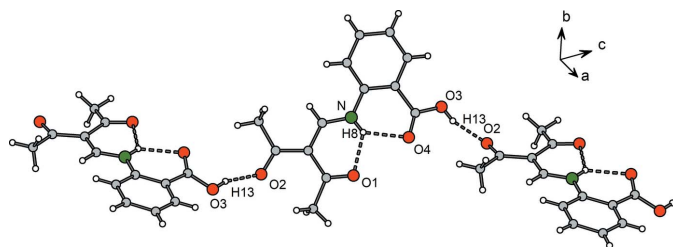

Figure 4
Section of the crystal structure of **1** showing the hydrogen-bonding pattern (dashed lines). Symmetry codes refer to Table 4.

Figure 5
View of the Hirshfeld surface of **1** mapped over d_{norm} in the range −0.712 to 0.973 au showing intermolecular hydrogen bonds as green dashed lines.

3. Supramolecular features

For all three derivatives **1–3** the supramolecular structures in the solid state are clearly governed by the presence of intermolecular 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 O2^{i} of a neighbouring molecule with an O3$\cdots$O2^{i} distance of 2.613 (2) Å (Fig. 4). The presence of this hydrogen bond is also clearly evident from the Hirshfeld surface plot (Fig. 5). Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) was carried out using *CrystalExplorer* (Turner *et al.* 2017; version 17).

As a result of these $C_1^1(10)$-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).

Figure 6
Molecular packing of **1** in the crystal, in a view along [110].

Figure 7
Section of the crystal structure of **2** showing the hydrogen-bonding pattern (dashed lines). Symmetry codes refer to Table 5.

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 $O1^{iii}$ of a neighbouring chain.

Figure 8
Molecular packing of **2** in the crystal, (*a*) in a view along the *b* axis and (*b*) in a view along the *a* axis.
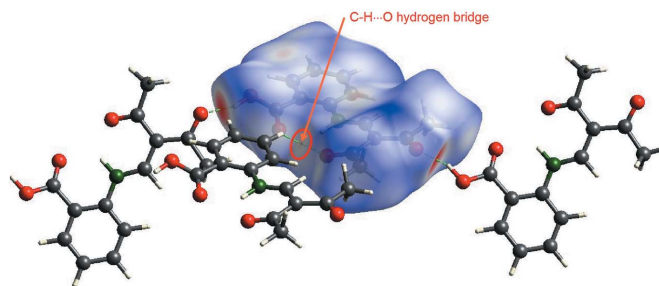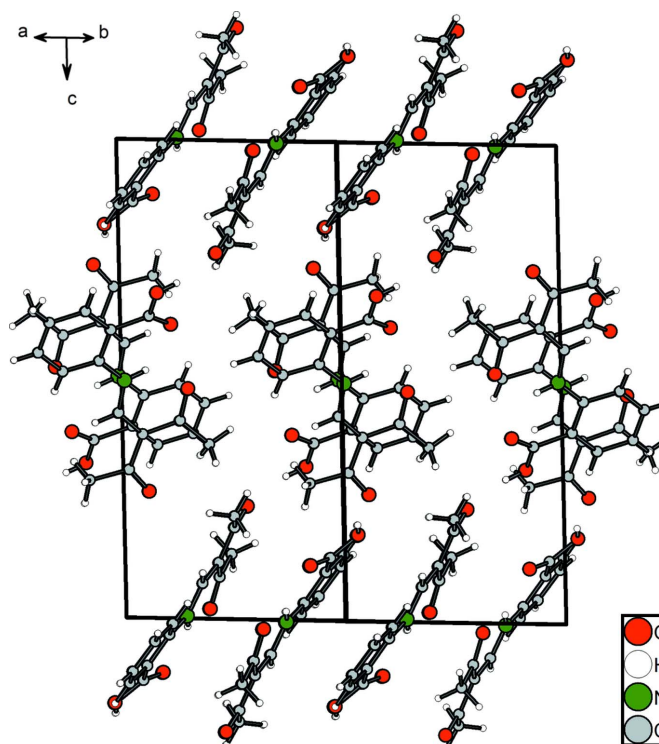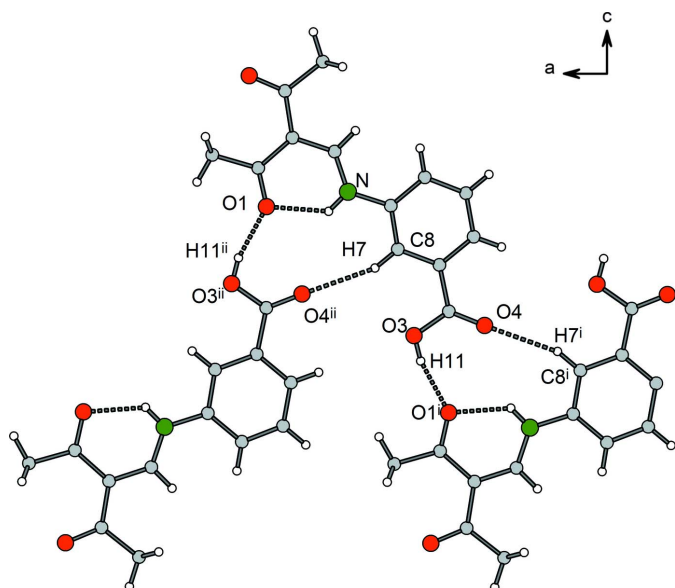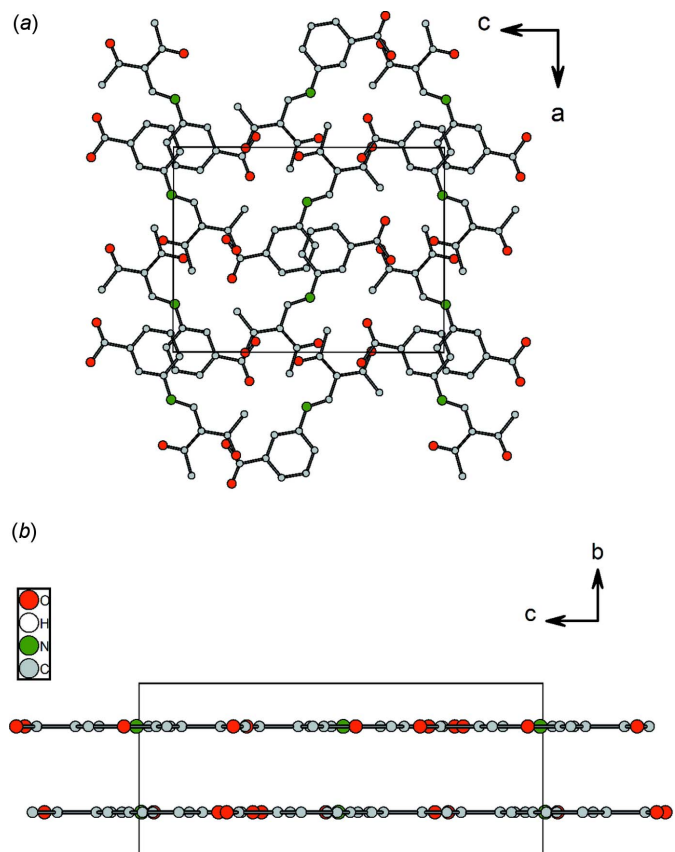

Figure 9
View of the Hirshfeld surface of **2** mapped over d_{norm} in the range −0.712 to 0.973 au showing intermolecular hydrogen bonds as green dashed lines.

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 $O1^{i}$ of the adjacent molecule with an $O3···O1^{i}$ distance of 2.656 (2) Å. This connection leads to $C_1^1(10)$-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 $O4^{ii}$ 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 $\bar{1}$ symmetry with an $O3···O4^{i}$ 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^{ii}, symmetry code: (ii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; C9—H9···O4^{iii}, 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

Figure 10
Section of the crystal structure of **3** showing the hydrogen-bonding pattern (dashed lines). Symmetry codes refer to Table 6.
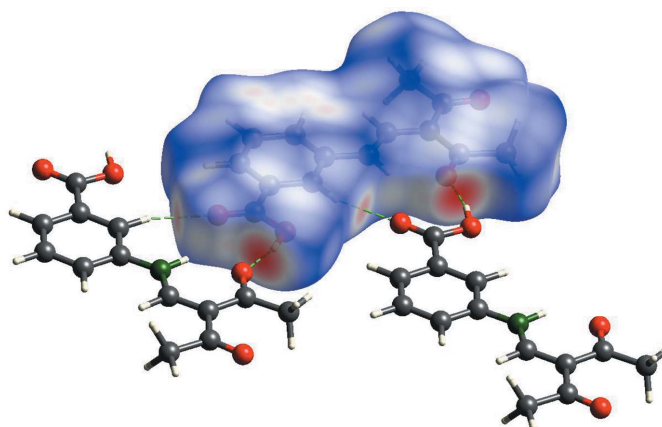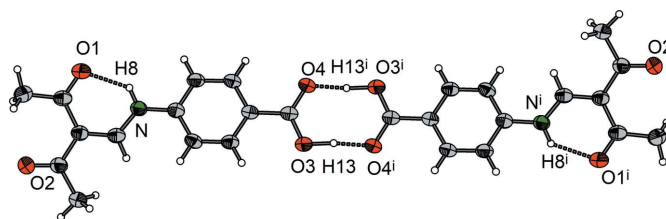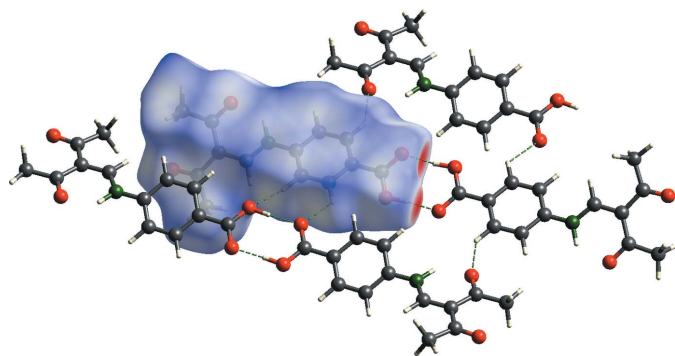
Figure 11
View of the Hirshfeld surface of **3** mapped over d_{norm} in the range -0.761 to 1.366 au showing intermolecular hydrogen bonds as green dashed lines.

between H11 and the keto group oxygen atom O1^{iv}. Overall, this cross-linking leads to a layer structure that extends parallel to (100). The crystal packing is shown in Fig. 12.

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 $R_2^2(8)$-type hydrogen bridges, predominately in the case of the *m*- and *p*-amimobenzoic 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 $S_1^1(6)$ topology. Additionally, there are reports on ketoimines derived from 2,4-pentanedione and aminobenzoic acids. The corresponding *o*- and the *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 derivates 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),
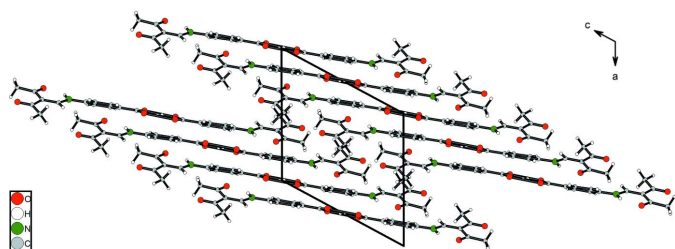

Figure 12
Molecular packing of **3** in the crystal in a view along the *b* axis.

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.

$C_{13}H_{13}NO_4$: 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 (*m*), 470 (*m*), 405 (*m*), 326 (*m*) cm^{-1}, ^{1}H NMR(DMSO-d_6): 2.35 (*s*, 3 H, CO—CH$_3$), 2.39 (*s*, 3 H, CO—CH$_3$), 7.25–7.97 (*m*, 4 H, CH$_{aromatic}$), 8.39 [*d* (^3J = 12.8 Hz), 1 H, C=CH—-NH], 13.49 [*d* (^3J =12.8 Hz), 1 H, C=CH—N*H*], ^{13}C NMR(DMSO-d_6): 27.4 ppm (–CH$_3$), 31.4 (–CH$_3$), 114.3 (C(O)—C—C(O)), 117.0 (CH$_{aromatic}$), 118.4 (CH$_{aromatic}$), 124.0 (CH$_{aromatic}$), 131.4 (CH$_{aromatic}$), 134.1 (CH$_{aromatic}$), 140.6 (CH$_{aromatic}$), 150.6 (CH—NH), 167.4 (COOH), 195.7 (CO) 198.2 (CO) ppm.

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

$C_{13}H_{13}NO_4$: 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 (*s*), 679 (*s*), 641 (*s*), 593 (*w*), 537 (*m*), 475 (*w*), 280 (*m*), 232 (*m*) cm^{-1}, ^{1}H NMR(DMSO-d_6): 2.37 (*s*, 3 H, CO—CH$_3$), 2.38 (*s*, 3 H, CO–CH$_3$), 7.52–7.94 (*m*, 4 H, CH$_{aromatic}$), 8.34 [*d* (^3J = 12.8 Hz), 1 H, C=CH—NH], 12.53 [*d* (^3J =12.8 Hz), 1 H, C=CH—N*H*], ^{13}C NMR(DMSO-d_6): 27.5 ppm (–CH$_3$), 31.4 (–CH$_3$), 112.8 (C(O)—C–-C(O)), 118.5 (CH$_{aromatic}$), 122.5 (CH$_{aromatic}$), 125.7 (CH$_{aromatic}$), 129.8 (CH$_{aromatic}$), 132.2 (CH$_{aromatic}$), 139.4 (CH$_{aromatic}$), 152.6 (CH—NH), 166.6 (COOH), 195.2 (CO) 199.4 (CO) ppm.

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

$C_{13}H_{13}NO_4$: 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}, ^{1}H NMR(DMSO-d_6): 2.37 (*s*, 3 H, CO—CH$_3$), 2.38 (*s*, 3 H, CO—CH$_3$), 7.57 [*m*, 2 H, NHFacac-C–(CH$_{aromatic}$)$_2$)], 8.44 [*d* (^3J = 12.6 Hz), 1 H, C=CH—NH], 12.64 [*d* (^3J =12.8 Hz), 1 H, C=CH—N*H*], 12.86 (*s*, 1H,

Table 7
Experimental details.

	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_r	247.24	247.24	247.24
Crystal system, space group	Monoclinic, $C2/c$	Orthorhombic, $Pnma$	Monoclinic, $P2_1/c$
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 (Å^3)	2304.28 (16)	1130.32 (8)	1152.78 (11)
Z	8	4	4
D_x (Mg m^{-3})	1.425	1.453	1.425
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.11	0.11	0.11
Crystal size (mm)	$0.32 \times 0.23 \times 0.14$	$0.16 \times 0.07 \times 0.07$	$0.54 \times 0.25 \times 0.08$
Data collection			
Diffractometer	Stoe IPDS 2T	Stoe IPDS 2T	Stoe IPDS 2T
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5925, 2242, 2041	4667, 1346, 1118	5856, 2225, 1796
R_{int}	0.051	0.039	0.036
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617	0.639	0.617
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.127, 1.06	0.044, 0.128, 1.08	0.045, 0.129, 1.06
No. of reflections	2242	1346	2225
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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (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).

COO*H*), ^{13}C NMR(DMSO-d_6): 27.5 ppm (−CH_3), 31.5 (−CH_3), 113.4 [C(O)−C−C(O)], 117.7 ($CH_{aromatic}$), 126.9 ($CH_{aromatic}$), 130.8 ($CH_{aromatic}$), 142.7 ($CH_{aromatic}$), 151.7 (CH−NH), 166.5 (COOH), 195.4 (CO) 199.7 (CO) ppm.

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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supporting information

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

Jan Henrik Halz, Andreas Hentsch, Christoph Wagner and Kurt Merzweiler

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).

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

Crystal data

$C_{13}H_{13}NO_4$	$F(000) = 1040$
$M_r = 247.24$	$D_x = 1.425$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.6287$ (5) Å	Cell parameters from 22415 reflections
$b = 12.3740$ (4) Å	$\theta = 2.5–29.6°$
$c = 17.5419$ (7) Å	$\mu = 0.11$ mm^{-1}
$\beta = 92.836$ (3)°	$T = 170$ K
$V = 2304.28$ (16) Å^3	Block, clear colourless
$Z = 8$	$0.32 \times 0.23 \times 0.14$ mm

Data collection

Stoe IPDS 2T diffractometer	2242 independent reflections
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus, Incoatec Iμs	2041 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.051$
Plane graphite monochromator	$\theta_{max} = 26.0°$, $\theta_{min} = 2.5°$
Detector resolution: 6.67 pixels mm^{-1}	$h = -10 \rightarrow 13$
rotation method, ω scans	$k = -13 \rightarrow 15$
5925 measured reflections	$l = -21 \rightarrow 21$

Refinement

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

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_{iso}*/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)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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)

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)

O1—C2	1.2380 (18)	C5—H4	0.9600
O2—C4	1.239 (2)	C5—H5	0.9600
O3—H13	0.8200	C5—H6	0.9600
O3—C13	1.3312 (17)	C6—H7	0.9300
O4—C13	1.211 (2)	C7—C8	1.4135 (19)
N—H8	0.8600	C7—C12	1.398 (2)
N—C6	1.3344 (18)	C8—C9	1.394 (2)
N—C7	1.410 (2)	C8—C13	1.493 (2)
C1—H1	0.9600	C9—H9	0.9300
C1—H2	0.9600	C9—C10	1.381 (2)
C1—H3	0.9600	C10—H10	0.9300
C1—C2	1.501 (2)	C10—C11	1.390 (2)
C2—C3	1.473 (2)	C11—H11	0.9300
C3—C4	1.4621 (18)	C11—C12	1.378 (2)
C3—C6	1.383 (2)	C12—H12	0.9300
C4—C5	1.513 (2)		
C13—O3—H13	109.5	N—C6—C3	127.34 (14)
C6—N—H8	117.7	N—C6—H7	116.3
C6—N—C7	124.68 (13)	C3—C6—H7	116.3
C7—N—H8	117.7	N—C7—C8	120.04 (13)
H1—C1—H2	109.5	C12—C7—N	121.51 (13)
H1—C1—H3	109.5	C12—C7—C8	118.45 (14)
H2—C1—H3	109.5	C7—C8—C13	121.72 (14)
C2—C1—H1	109.5	C9—C8—C7	119.03 (14)
C2—C1—H2	109.5	C9—C8—C13	119.25 (12)
C2—C1—H3	109.5	C8—C9—H9	119.1
O1—C2—C1	118.34 (14)	C10—C9—C8	121.83 (14)
O1—C2—C3	118.90 (14)	C10—C9—H9	119.1
C3—C2—C1	122.75 (13)	C9—C10—H10	120.6
C4—C3—C2	123.26 (14)	C9—C10—C11	118.86 (15)

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	112.20 (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		
O1—C2—C3—C4	−171.05 (14)	C6—C3—C4—C5	−4.1 (2)
O1—C2—C3—C6	8.5 (2)	C7—N—C6—C3	176.56 (14)
N—C7—C8—C9	178.50 (13)	C7—C8—C9—C10	0.1 (2)
N—C7—C8—C13	−2.3 (2)	C7—C8—C13—O3	164.41 (13)
N—C7—C12—C11	−178.64 (14)	C7—C8—C13—O4	−16.2 (2)
C1—C2—C3—C4	9.9 (2)	C8—C7—C12—C11	1.1 (2)
C1—C2—C3—C6	−170.53 (15)	C8—C9—C10—C11	1.2 (2)
C2—C3—C4—O2	−4.4 (2)	C9—C8—C13—O3	−16.39 (19)
C2—C3—C4—C5	175.49 (14)	C9—C8—C13—O4	163.00 (15)
C2—C3—C6—N	0.1 (2)	C9—C10—C11—C12	−1.3 (2)
C4—C3—C6—N	179.70 (14)	C10—C11—C12—C7	0.2 (2)
C6—N—C7—C8	−167.19 (14)	C12—C7—C8—C9	−1.2 (2)
C6—N—C7—C12	12.5 (2)	C12—C7—C8—C13	178.00 (13)
C6—C3—C4—O2	176.05 (14)	C13—C8—C9—C10	−179.13 (14)

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H13⋯O2^i	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⋯O4^{ii}	0.96	2.62	3.330 (2)	131
C11—H11⋯O1^{iii}	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

$C_{13}H_{13}NO_4$	$D_x = 1.453$ Mg m^{-3}
$M_r = 247.24$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $Pnma$	Cell parameters from 10416 reflections
$a = 11.4880$ (4) Å	$\theta = 2.7–29.7°$
$b = 6.4726$ (3) Å	$\mu = 0.11$ mm^{-1}
$c = 15.2012$ (5) Å	$T = 170$ K
$V = 1130.32$ (8) Å^3	Needle, clear yellow
$Z = 4$	$0.16 \times 0.07 \times 0.07$ mm
$F(000) = 520$	

Data collection

Stoe IPDS 2T diffractometer	1346 independent reflections
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus, Incoatec Iμs	1118 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.039$
Plane graphite monochromator	$\theta_{max} = 27.0°$, $\theta_{min} = 2.7°$
Detector resolution: 6.67 pixels mm^{-1}	$h = -14 \rightarrow 13$
rotation method, ω scans	$k = -8 \rightarrow 7$
4667 measured reflections	$l = -18 \rightarrow 19$

Refinement

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

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*

C9	0.48160 (17)	0.2500	0.65704 (13)	0.0206 (4)
C10	0.38808 (17)	0.2500	0.59853 (14)	0.0225 (5)
H8	0.3121	0.2500	0.6196	0.027*
C11	0.40940 (17)	0.2500	0.50868 (14)	0.0238 (5)
H9	0.3470	0.2500	0.4697	0.029*
C12	0.52216 (18)	0.2500	0.47599 (13)	0.0213 (4)
H10	0.5354	0.2500	0.4156	0.026*
C13	0.45603 (17)	0.2500	0.75316 (14)	0.0232 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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

Geometric parameters (Å, º)

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)		

C13—O3—H11	110 (2)	C8—C7—N	116.89 (17)
C6—N—H6	117.1	C12—C7—N	122.60 (18)
C6—N—C7	125.89 (17)	C12—C7—C8	120.50 (18)
C7—N—H6	117.1	C7—C8—H7	120.1
H1—C1—H2	114.2 (15)	C7—C8—C9	119.73 (18)
C2—C1—H1	103.3 (18)	C9—C8—H7	120.1
C2—C1—H2	112.4 (12)	C8—C9—C13	121.79 (18)
O1—C2—C1	118.12 (19)	C10—C9—C8	119.96 (18)
O1—C2—C3	119.29 (19)	C10—C9—C13	118.25 (17)
C3—C2—C1	122.58 (18)	C9—C10—H8	120.3
C2—C3—C4	122.45 (17)	C11—C10—C9	119.45 (18)
C6—C3—C2	120.15 (18)	C11—C10—H8	120.3
C6—C3—C4	117.40 (18)	C10—C11—H9	119.4
O2—C4—C3	122.24 (18)	C12—C11—C10	121.16 (19)
O2—C4—C5	118.81 (19)	C12—C11—H9	119.4
C3—C4—C5	118.94 (18)	C7—C12—H10	120.4
C4—C5—H3	111 (2)	C11—C12—C7	119.20 (18)
C4—C5—H4	112.0 (12)	C11—C12—H10	120.4
H3—C5—H4	109.1 (17)	O3—C13—C9	113.76 (16)
N—C6—C3	126.50 (19)	O4—C13—O3	123.45 (19)
N—C6—H5	116.8	O4—C13—C9	122.79 (19)
C3—C6—H5	116.8		
O1—C2—C3—C4	180.000 (1)	C7—N—C6—C3	180.000 (1)
O1—C2—C3—C6	0.000 (1)	C7—C8—C9—C10	0.000 (1)
N—C7—C8—C9	180.000 (1)	C7—C8—C9—C13	180.000 (1)
N—C7—C12—C11	180.000 (1)	C8—C7—C12—C11	0.000 (1)
C1—C2—C3—C4	0.000 (1)	C8—C9—C10—C11	0.000 (1)
C1—C2—C3—C6	180.000 (1)	C8—C9—C13—O3	0.000 (1)
C2—C3—C4—O2	0.000 (1)	C8—C9—C13—O4	180.000 (1)
C2—C3—C4—C5	180.000 (1)	C9—C10—C11—C12	0.000 (1)
C2—C3—C6—N	0.000 (1)	C10—C9—C13—O3	180.000 (1)
C4—C3—C6—N	180.000 (1)	C10—C9—C13—O4	0.000 (1)
C6—N—C7—C8	180.000 (1)	C10—C11—C12—C7	0.000 (1)
C6—N—C7—C12	0.000 (1)	C12—C7—C8—C9	0.000 (1)
C6—C3—C4—O2	180.000 (1)	C13—C9—C10—C11	180.000 (1)
C6—C3—C4—C5	0.000 (1)		

Hydrogen-bond geometry (Å, º)

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···O4ii	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

$C_{13}H_{13}NO_4$	$F(000) = 520$
$M_r = 247.24$	$D_x = 1.425$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.8649$ (6) Å	Cell parameters from 6441 reflections
$b = 10.6185$ (5) Å	$\theta = 1.9–29.6°$
$c = 11.3616$ (6) Å	$\mu = 0.11$ mm^{-1}
$\beta = 118.422$ (4)°	$T = 170$ K
$V = 1152.78$ (11) Å^3	Plate, clear yellowish colourless
$Z = 4$	$0.54 \times 0.25 \times 0.08$ mm

Data collection

Stoe IPDS 2T diffractometer	1796 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm^{-1}	$R_{int} = 0.036$
rotation method, ω scans	$\theta_{max} = 26.0°$, $\theta_{min} = 2.1°$
5856 measured reflections	$h = -12 \rightarrow 13$
2225 independent reflections	$k = -12 \rightarrow 13$
	$l = -14 \rightarrow 13$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.045$	
$wR(F^2) = 0.129$	$w = 1/[\sigma^2(F_o^2) + (0.0728P)^2 + 0.2229P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
2225 reflections	$(\Delta/\sigma)_{max} < 0.001$
169 parameters	$\Delta\rho_{max} = 0.27$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.18$ 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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
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)

C3	0.36077 (16)	0.60332 (14)	0.96565 (16)	0.0366 (4)
C4	0.44066 (17)	0.71139 (15)	1.04708 (16)	0.0418 (4)
C5	0.47780 (19)	0.81748 (16)	0.98209 (17)	0.0455 (4)
H6	0.5200	0.7839	0.9314	0.068*
H4	0.5425	0.8732	1.0498	0.068*
H5	0.3946	0.8631	0.9236	0.068*
C6	0.31691 (16)	0.60528 (14)	0.83010 (16)	0.0370 (4)
H7	0.3352	0.6777	0.7950	0.044*
C7	0.20199 (15)	0.51226 (14)	0.60687 (16)	0.0350 (4)
C8	0.16521 (16)	0.62357 (14)	0.53318 (16)	0.0379 (4)
H9	0.1719	0.7001	0.5756	0.046*
C9	0.11906 (16)	0.62019 (14)	0.39778 (16)	0.0372 (4)
H10	0.0962	0.6949	0.3492	0.045*
C10	0.10618 (15)	0.50592 (13)	0.33249 (17)	0.0335 (3)
C11	0.14053 (17)	0.39422 (14)	0.40664 (16)	0.0378 (4)
H11	0.1307	0.3174	0.3637	0.045*
C12	0.18846 (17)	0.39721 (14)	0.54199 (17)	0.0392 (4)
H12	0.2120	0.3226	0.5908	0.047*
C13	0.05802 (15)	0.50298 (13)	0.18776 (17)	0.0360 (4)

Atomic displacement parameters (Å^2)

	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)	0.0421 (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, º)

O1—C2	1.2401 (19)	C5—H6	0.9600
O2—C4	1.223 (2)	C5—H4	0.9600
O3—H13	1.12 (3)	C5—H5	0.9600
O3—C13	1.2863 (18)	C6—H7	0.9300

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—C4	−175.84 (16)	C7—N—C6—C3	178.50 (15)
O1—C2—C3—C6	2.8 (2)	C7—C8—C9—C10	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—C4	4.2 (2)	C8—C9—C10—C13	−179.41 (14)
C1—C2—C3—C6	−177.18 (15)	C9—C10—C11—C12	−1.1 (2)
C2—C3—C4—O2	−4.5 (3)	C9—C10—C13—O3	10.8 (2)
C2—C3—C4—C5	175.83 (15)	C9—C10—C13—O4	−170.75 (15)
C2—C3—C6—N	−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···O4[i]	1.12 (3)	1.49 (3)	2.6098 (18)	173 (3)
N—H8···O1	0.86	1.91	2.5729 (18)	133
C8—H9···O3[ii]	0.93	2.65	3.4832 (18)	150
C9—H10···O4[iii]	0.93	2.65	3.3252 (18)	130
C11—H11···O1[iv]	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.