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Two closely related 2-(benzofuran-2-yl)-2-oxoethyl benzoates: structural differences and C—H···O hydrogen-bonded supramolecular assemblies

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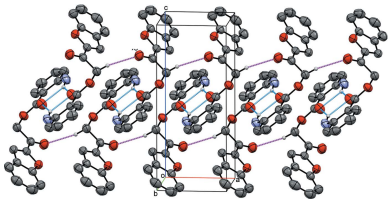
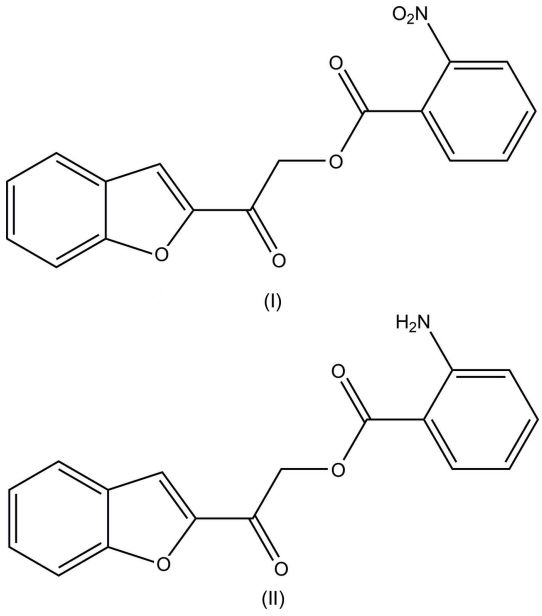
The compounds 2-(1-benzofuran-2-yl)-2-oxoethyl 2-nitrobenzoate, $C_{17}H_{11}NO_6$ (I), and 2-(1-benzofuran-2-yl)-2-oxoethyl 2-aminobenzoate, $C_{17}H_{13}NO_4$ (II), were synthesized under mild conditions. Their molecular structures were characterized by both spectroscopic and single-crystal X-ray diffraction analysis. The molecular conformations of both title compounds are generally similar. However, different *ortho*-substituted moieties at the phenyl ring of the two compounds cause deviations in the torsion angles between the carbonyl group and the attached phenyl ring. In compound (I), the *ortho*-nitrophenyl ring is twisted away from the adjacent carbonyl group whereas in compound (II), the *ortho*-aminophenyl ring is almost co-planar with the carbonyl group. In the crystal of compound (I), two C—H···O hydrogen bonds link the molecules into chains propagating along the *c*-axis direction and the chains are interdigitated, forming sheets parallel to [20$\bar{1}$]. Conversely, pairs of N—H···O hydrogen bonds in compound (II) link inversion-related molecules into dimers, which are further extended by C—H···O hydrogen bonds into dimer chains. These chains are interconnected by π–π interactions involving the furan rings, forming sheets parallel to the *ac* plane.

1. Chemical context

Oxygen-containing heterocycles are the basic cores of many bioactive structures. Among these, benzofuran and its derivatives occur frequently in nature because of their stability and ease of generation. Those with substitution(s) at their C-2 and/or C-3 positions are important. Important biological activity such as anticancer (Swamy *et al.*, 2015), anti-acetylcholinesterase (Zhou *et al.*, 2010), antimicrobial (Ugale *et al.*, 2012) and antioxidant (Naik *et al.*, 2013) actions exhibited by this scaffold have attracted the attention of synthetic chemists. Some of the biological and medicinal significance of benzofuran derivatives (Nevagi *et al.*, 2015) have been discussed in review reports. The known potential of benzofuran derivatives has motivated us to synthesise some new compounds incorporating this core structure and we herein report the synthesis and crystal structures of 2-(1-benzofuran-2-yl)-2-oxoethyl 2-nitrobenzoate (I) and 2-(1-benzofuran-2-yl)-2-oxoethyl 2-aminobenzoate (II).





2. Structural commentary

The molecular structures of the title compounds (Fig. 1) contain a benzofuran ring and an *ortho*-substituted [nitro- for compound (I) and amino- for compound (II)] phenyl ring, joined by a C—C(=O)—O—C(=O) carbonyl-connecting bridge. Their molecular conformations can be characterized by three degrees of freedom, as indicated by the O1—C8—C9—O3 (τ1), C9—C10—O2—C11 (τ2) and O4—C11—C12—C13 (τ3) torsion angles, respectively (Fig. 2). The torsion angle τ1 for compounds (I) and (II) is close to 0°, showing that the benzofuran ring is nearly coplanar with the C—C(=O)—O—C(=O) carbonyl bridge. Torsion angle τ2 adopts a *syn*-clinal conformation, as both carbonyl groups at the connecting bridges are twisted away from each other forming torsion angles of −71.43 (3)° in (I) and −70.85 (18)° in (II). For compound (I), the substituted *ortho*-nitrophenyl moiety is perpendicular to the adjacent carbonyl group with a τ3 torsion angle of −90.2 (4)°; this may arise from a steric repulsion force between the nitro group and carbonyl group. In contrast, the *ortho*-aminophenyl ring in compound (II) is almost coplanar with its adjacent carbonyl group due to the intramolecular hydrogen bond (N1—H1*A*···O4, Table 2) between the amino and carbonyl groups, which generates an *S*(6) ring.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10*A*···O3^{i}	0.99	2.59	3.471 (4)	148
C15—H15*A*···O5^{ii}	0.95	2.58	3.380 (3)	142

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O4	0.91 (2)	2.05 (2)	2.700 (3)	127.7 (18)
N1—H1*A*···O4^{i}	0.91 (2)	2.49 (2)	3.246 (2)	141.4 (18)
C10—H10*A*···O3^{ii}	0.97	2.50	3.444 (2)	165

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y, z$.

3. Supramolecular features

The crystal packing of compound (I) depends mainly on two weak intermolecular hydrogen bonds. Molecules are joined into infinite chains propagating along the *c*-axis by C10—H10*A*···O3 hydrogen bonds (Table 1, Fig. 3), meanwhile those chains are interdigitated into a fishbone sheet extending along the [20$\bar{1}$] direction through C15—H15*A*···O5 hydrogen bonds. The fishbone sheets alternate in an up–down manner along the *ab* plane as shown in Fig. 4.

In compound (II), the molecular interactions are more abundant than in (I) because of the *ortho*-substituted amino

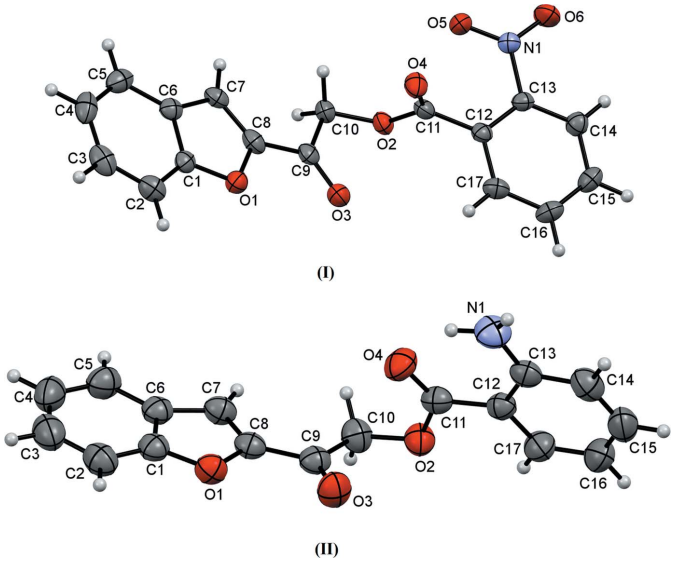


Figure 1
ORTEP diagram of the title compounds, with ellipsoids drawn at the 50% probability level, showing the atomic labelling scheme.

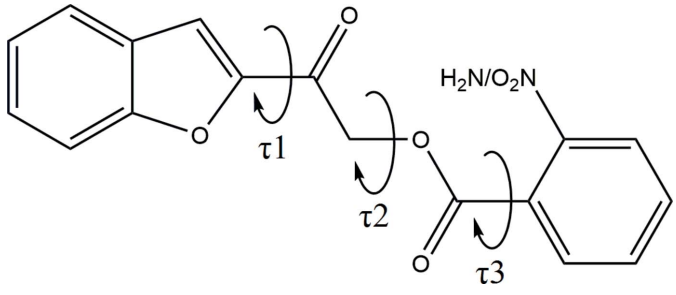


Figure 2
General chemical diagram showing torsion angles τ1, τ2 and τ3 in compounds (I) and (II).

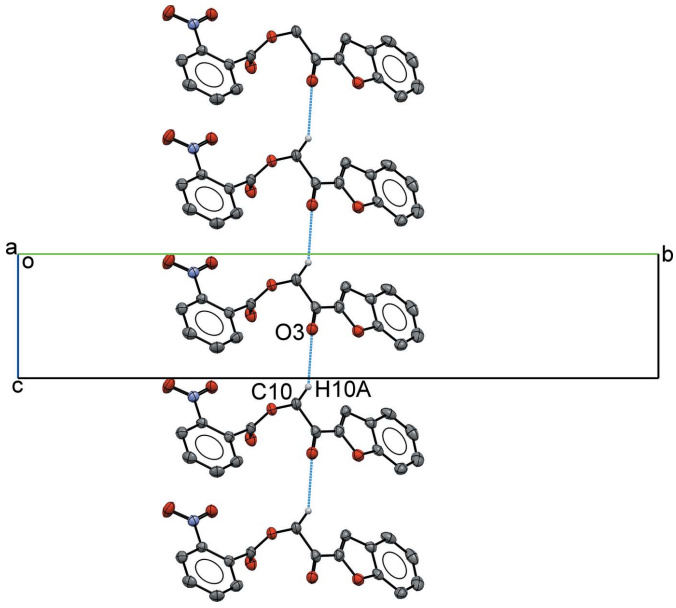


Figure 3
Molecules in compound (I) joined by intermolecular hydrogen bonds, forming a fishbone chain.

group at its phenyl ring. Pairs of N1—H1*A*···O4 hydrogen bonds link molecules into inversion dimers with an $R_2^2(12)$ graph-set motif (Fig. 5). These dimers are further expanded by C10—H10*A*···O3 hydrogen bonds into infinite chains along the [100] direction (Fig. 6). In addition, neighbouring chains are interconnected by π–π interactions involving adjacent furan rings [centroid–centroid distance = 3.7982 (15) Å; symmetry code: $-x$, $-y+1$, $-z$), forming a sheet parallel to the *ac* plane (Fig. 7).

4. Database survey

A survey of the Cambridge Structural Database (Groom *et al.*, 2016) revealed five benzofuran structures (Kumar *et al.*, 2015) similar to the title compounds: ITAXUY, ITAYAF, ITAYEJ, ITAYIN and ITAYOT. The molecular structures of the studied and previous compounds differ only at their substituted phenyl rings. By comparing their torsion angles at the

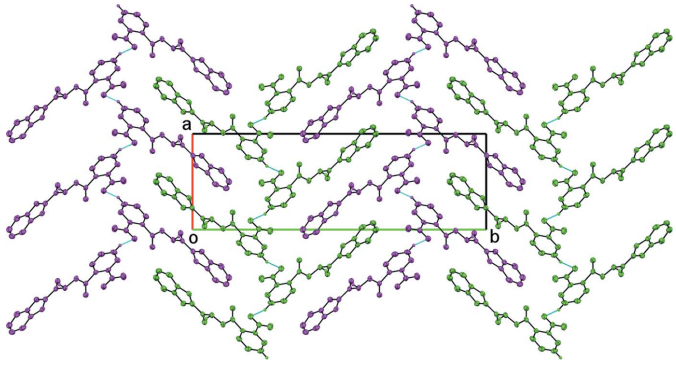


Figure 4
Fishbone chains in an up–down manner are shown in different colours.

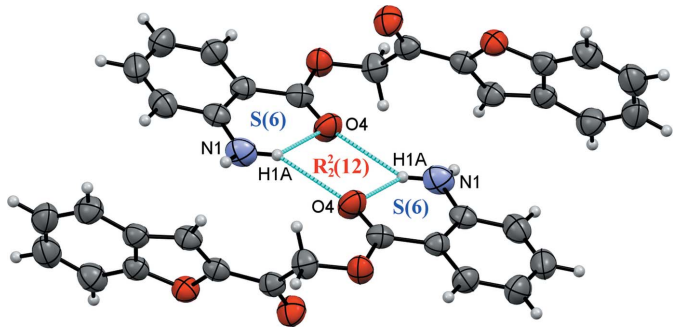


Figure 5
Intramolecular and intermolecular N1—H1*A*···O4 hydrogen bonds.

C(=O)—O—C(=O) carbonyl bridges, the title compounds exhibit a *syn*-clinal conformation similar to ITAXUY, ITAYEJ and ITAYIN with respect to their torsion angles which range from 75 to 80°.

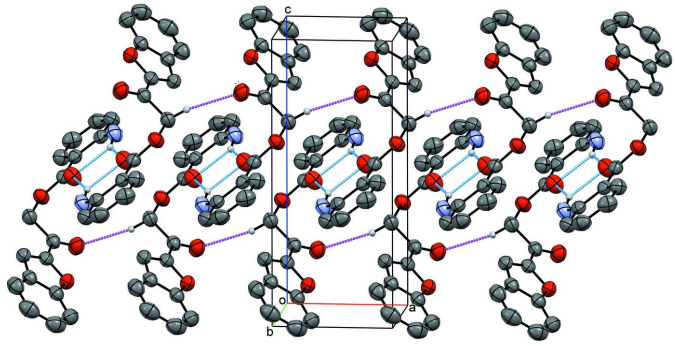


Figure 6
Interactions in the crystal structure of compound (II), showing hydrogen bonds (cyan dotted lines) and $\pi\cdots\pi$ interactions (red dotted lines).

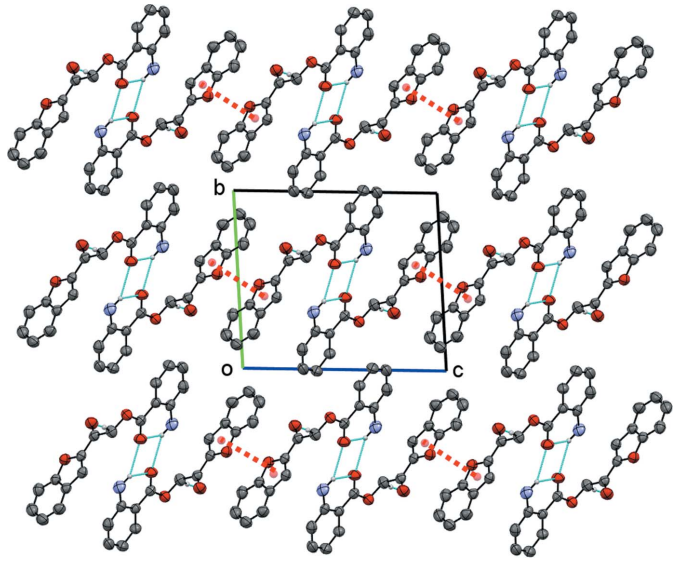


Figure 7
The packing of compound (II), showing the hydrogen bonds (cyan dotted lines) and π–π interactions (red dotted lines).

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{17}H_{11}NO_6$	$C_{17}H_{13}NO_4$
M_r	325.27	295.28
Crystal system, space group	Orthorhombic, $Pna2_1$	Triclinic, $P\overline{1}$
Temperature (K)	100	297
a, b, c (Å)	9.3022 (10), 28.482 (3), 5.5208 (6)	5.1839 (12), 10.853 (3), 12.269 (3)
α, β, γ (°)	90, 90, 90	93.562 (3), 91.167 (3), 98.714 (3)
V (Å^3)	1462.7 (3)	680.6 (3)
Z	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.11	0.10
Crystal size (mm)	0.27 × 0.16 × 0.13	0.40 × 0.32 × 0.21
Data collection		
Diffractometer	Bruker APEXII DUO CCD area-detector	Bruker APEXII DUO CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.933, 0.985	0.871, 0.978
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15875, 3358, 2915	17052, 3105, 2214
R_{int}	0.037	0.037
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.651	0.650
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.085, 1.08	0.046, 0.123, 1.08
No. of reflections	3358	3105
No. of parameters	217	207
No. of restraints	1	0
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.17	0.18, −0.18

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXT2013* (Sheldrick, 2015*a*), *SHELXL2013* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2009).

5. Synthesis and crystallization

The synthesis was carried out by reacting 1-(benzofuran-2-yl)-2-bromoethan-1-one (1 mmol) with 2-nitrobenzoic acid (1 mmol) for compound (I) and 2-aminobenzoic acid (1 mmol) for compound (II) in 8 ml of *N*,*N*-dimethylformamide in the presence of a catalytic amount of anhydrous potassium carbonate at room temperature. The reaction solution was stirred for about two h and monitored by thin-layer chromatography (TLC). After the reaction was complete, the resultant mixture was then added to a beaker of ice-cooled water to form a precipitate. The precipitate was then filtered, rinsed with distilled water and dried. Crystals suitable for X-ray analysis were obtained by slow evaporation using a suitable solvent.

2-(Benzofuran-2-yl)-2-oxoethyl 2-nitrobenzoate (I):

Solvents used to grow crystal: acetone + methanol 1:1 *v*/*v*); yield: 80%, m.p. 381–383 K; ^{1}H NMR (500MHz, $CDCl_3$) in ppm: δ 8.041–8.025 (*d*, 1H, *J* = 7.9Hz, ^{14}CH), 7.995–7.980 (*d*, 1H, *J* = 7.9Hz, ^{17}CH), 7.796–7.763 (*m*, 2H, ^{2}CH, ^{3}CH), 7.726–7.695 (*t*, 1H, *J* = 7.9Hz, ^{15}CH), 7.673 (*s*, 1H, ^{7}CH), 7.644–7.627 (*d*, 1H, *J* = 8.4Hz, ^{5}CH), 7.578–7.544 (*t*, 1H, *J* = 8.4Hz, ^{4}CH), 7.398–7.366 (*t*, 1H, *J* = 7.9Hz, ^{16}CH), 5.609 (*s*, 2H, $^{10}CH_2$). ^{13}C NMR (125 MHz, $CDCl_3$) in ppm: 182.94 (C9), 165.67 (C11), 155.80 (C1), 150.25 (C13), 133.31 (C16), 132.04 (C15), 130.39 (C17), 130.10 (C8), 128.97 (C3), 127.23 (C12), 126.70 (C6), 124.34 (C5), 124.11 (C4), 123.60 (C14), 113.75 (C7), 112.57 (C2), 67.10 (C10). FT–IR (ATR (solid) cm^{-1}): 3089 (Ar C—H, *v*), 2953 (C—H, *v*), 1744, 1686 (C═O, *v*), 1612 (C═C, *v*), 1554, 1422 (Ar C═C, *v*), 1529, 1344 (N═O, *v*), 1278, 1123 (C—O, *v*).

2-(Benzofuran-2-yl)-2-oxoethyl 2-aminobenzoate (II):

Solvents used to grow crystal: acetone + acetonitrile (1:1 *v*/*v*); yield: 83%; m.p. 432–434 K; ^{1}H NMR (500 MHz, DMSO) in ppm: δ 8.083 (*s*, 1H, ^{7}CH), 7.907–7.891 (*d*, 1H, *J* = 8.1Hz, ^{17}CH), 7.848–7.832 (*d*, 1H, *J* = 8.1Hz, ^{14}CH), 7.787–7.770 (*d*, 1H, *J* = 8.5Hz, ^{2}CH), 7.617–7.583 (*t*, 1H, *J* = 8.5Hz, ^{3}CH), 7.437–7.405 (*t*, 1H, *J* = 8.1Hz, ^{15}CH), 7.329–7.295 (*t*, 1H, *J* = 8.5Hz, ^{4}CH), 6.824–6.807 (*d*, 1H, *J* = 8.5Hz, ^{5}CH), 6.669 (*br*–*s*, 2H, $^1NH_2$), 6.607–6.574 (*t*, 1H, *J* = 8.1Hz, ^{16}CH), 5.591 (*s*, 2H, $^{10}CH_2$). ^{13}C NMR (125MHz, DMSO) in ppm: 184.08 (C9), 166.60 (C11), 154.96 (C1), 151.62 (C15), 149.63 (C13), 134.49 (C8), 130.78 (C17), 128.88 (C3), 126.49 (C6), 124.28 (C5), 123.84 (C4), 116.63 (C14), 114.84 (C16), 114.66 (C7), 112.31 (C2), 107.87 (C2), 65.63 (C10). FT–IR (ATR (solid) cm^{-1}): 3473, 3360 (N—H, *v*), 3078 (Ar C—H, *v*), 2942 (C—H, *v*), 1697, 1676 (C═O, *v*), 1615 (C═C, *v*), 1583, 1487 (Ar C═C, *v*), 1244, 1112 (C—O, *v*).

6. Refinement

Crystal data, data collection and structure refinement details for both compounds are summarized in Table 3. All C-bound H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and refined using a riding model with U_{iso}(H) = 1.2U_{eq}(parent

atom). The N-bound H atoms of compound (II) were located in a difference-Fourier map and refined freely.

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References

Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Kumar, C., Then, L., Chia, T., Chandraju, S., Win, Y.-F., Sulaiman, S., Hashim, N., Ooi, K., Quah, C. & Fun, H.-K. (2015). *Molecules*, **20**, 16566–16581.

Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.

Naik, N., Vijay, K., Dias, S. M. & Ranga, S. (2013). *Int. J. Pharm. Pharm. Sci.* **5**, 242–247.

Nevagi, R. J., Dighe, S. N. & Dighe, S. N. (2015). *Eur. J. Med. Chem.* **97**, 561–581.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Swamy, P. M. G., Prasad, Y. R., Ashvini, H. M., Giles, D., Shashidhar, B. V. & Agasimundin, Y. S. (2015). *Med. Chem. Res.* **24**, 3437–3452.

Ugale, V., Patel, H., Patel, B. & Bari, S. (2012). *Arab. J. Chem.* **10**, S389–A396.

Zhou, X., Li, M., Wang, X.-B., Wang, T. & Kong, L.-Y. (2010). *Molecules*, **15**, 8593–8601.

supporting information

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Two closely related 2-(benzofuran-2-yl)-2-oxoethyl benzoates: structural differences and C—H···O hydrogen-bonded supramolecular assemblies

Li Yee Then, C. S. Chidan Kumar, Huey Chong Kwong, Yip-Foo Win, Siau Hui Mah, Ching Kheng Quah, S. Naveen and Ismail Warad

Computing details

For both compounds, data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: SHELXT2013 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015b). Molecular graphics: *SHELXL2013* (Sheldrick, 2015b) and *Mercury* (Macrae *et al.*, 2006) for (I); *SHELXL2013* (Sheldrick, 2015b) for (II). For both compounds, software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2015b) and *PLATON* (Spek, 2009).

(I) 2-(1*H*-1-Benzofuran-2-yl)-2-oxoethyl 2-nitrobenzoate

Crystal data

$C_{17}H_{11}NO_6$
M_r = 325.27
Orthorhombic, $Pna2_1$
a = 9.3022 (10) Å
b = 28.482 (3) Å
c = 5.5208 (6) Å
V = 1462.7 (3) Å^3
Z = 4
$F(000)$ = 672
D_x = 1.477 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3687 reflections
θ = 2.3–25.3°
μ = 0.11 mm^{-1}
T = 100 K
Block, colourless
0.27 × 0.16 × 0.13 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2009)
T_{min} = 0.933, T_{max} = 0.985
15875 measured reflections
3358 independent reflections
2915 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 27.6°, θ_{min} = 1.4°
h = −12→12
k = −36→37
l = −7→7

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.085
S = 1.08
3358 reflections
217 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2 + 0.279P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ 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*	U_{iso}*/U_{eq}
N1	0.5075 (2)	0.27391 (8)	0.1493 (4)	0.0290 (5)
O1	0.72961 (19)	0.53112 (6)	0.6220 (3)	0.0309 (4)
O2	0.51143 (18)	0.39614 (6)	0.2506 (3)	0.0289 (4)
O3	0.5376 (2)	0.45933 (6)	0.6044 (4)	0.0328 (4)
O4	0.6811 (2)	0.36342 (6)	0.4887 (4)	0.0350 (5)
O5	0.5946 (2)	0.30243 (6)	0.0721 (4)	0.0343 (4)
O6	0.4877 (2)	0.23524 (7)	0.0592 (4)	0.0460 (6)
C1	0.8415 (3)	0.56187 (8)	0.5803 (5)	0.0270 (6)
C2	0.8830 (3)	0.59794 (10)	0.7294 (6)	0.0362 (6)
H2A	0.8343	0.6045	0.8768	0.043*
C3	0.9982 (3)	0.62384 (10)	0.6543 (6)	0.0412 (7)
H3A	1.0313	0.6488	0.7539	0.049*
C4	1.0686 (3)	0.61491 (10)	0.4372 (6)	0.0413 (8)
H4A	1.1475	0.6341	0.3910	0.050*
C5	1.0259 (3)	0.57859 (11)	0.2866 (6)	0.0380 (7)
H5A	1.0743	0.5725	0.1385	0.046*
C6	0.9074 (3)	0.55093 (9)	0.3613 (5)	0.0278 (6)
C7	0.8303 (3)	0.51167 (9)	0.2669 (5)	0.0284 (6)
H7A	0.8489	0.4958	0.1187	0.034*
C8	0.7272 (3)	0.50142 (9)	0.4259 (5)	0.0312 (6)
C9	0.6161 (3)	0.46488 (9)	0.4317 (5)	0.0286 (6)
C10	0.6080 (3)	0.43440 (9)	0.2082 (5)	0.0299 (6)
H10A	0.5737	0.4533	0.0691	0.036*
H10B	0.7047	0.4221	0.1685	0.036*
C11	0.5621 (3)	0.36359 (9)	0.4045 (5)	0.0272 (6)
C12	0.4463 (3)	0.32984 (8)	0.4742 (5)	0.0250 (5)
C13	0.4219 (3)	0.28707 (9)	0.3614 (4)	0.0247 (5)
C14	0.3186 (3)	0.25567 (9)	0.4415 (5)	0.0307 (6)
H14A	0.3052	0.2264	0.3622	0.037*
C15	0.2354 (3)	0.26790 (10)	0.6397 (5)	0.0345 (6)
H15A	0.1640	0.2469	0.6979	0.041*
C16	0.2562 (3)	0.31066 (10)	0.7531 (5)	0.0348 (6)
H16A	0.1978	0.3191	0.8874	0.042*
C17	0.3614 (3)	0.34129 (10)	0.6725 (5)	0.0319 (6)
H17A	0.3755	0.3704	0.7535	0.038*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0311 (11)	0.0268 (11)	0.0292 (12)	0.0017 (9)	0.0055 (10)	−0.0006 (10)
O1	0.0304 (10)	0.0307 (9)	0.0316 (9)	0.0006 (8)	0.0030 (8)	0.0025 (8)
O2	0.0337 (10)	0.0216 (9)	0.0314 (9)	0.0024 (7)	−0.0008 (9)	0.0025 (8)
O3	0.0371 (10)	0.0267 (9)	0.0346 (10)	0.0017 (8)	0.0038 (9)	−0.0001 (8)
O4	0.0278 (10)	0.0305 (10)	0.0467 (12)	0.0005 (8)	−0.0025 (9)	0.0064 (9)
O5	0.0374 (10)	0.0291 (9)	0.0364 (11)	0.0010 (8)	0.0133 (9)	0.0021 (9)
O6	0.0516 (13)	0.0338 (11)	0.0527 (13)	−0.0047 (10)	0.0184 (11)	−0.0161 (10)
C1	0.0267 (13)	0.0262 (12)	0.0280 (13)	0.0043 (10)	−0.0017 (11)	0.0067 (11)
C2	0.0419 (16)	0.0360 (16)	0.0307 (14)	0.0065 (13)	−0.0075 (13)	−0.0020 (12)
C3	0.0426 (17)	0.0341 (15)	0.0470 (18)	0.0033 (13)	−0.0196 (15)	0.0017 (14)
C4	0.0293 (15)	0.0395 (17)	0.055 (2)	−0.0040 (13)	−0.0109 (15)	0.0193 (15)
C5	0.0326 (15)	0.0502 (18)	0.0312 (15)	0.0123 (13)	0.0035 (13)	0.0142 (13)
C6	0.0281 (13)	0.0299 (14)	0.0256 (13)	0.0072 (11)	−0.0027 (11)	0.0043 (11)
C7	0.0316 (14)	0.0247 (13)	0.0289 (13)	0.0081 (11)	−0.0035 (12)	−0.0022 (11)
C8	0.0349 (14)	0.0230 (12)	0.0357 (15)	0.0058 (11)	−0.0062 (13)	−0.0002 (11)
C9	0.0293 (13)	0.0222 (12)	0.0342 (14)	0.0065 (11)	−0.0007 (12)	0.0042 (11)
C10	0.0343 (14)	0.0208 (12)	0.0345 (15)	0.0017 (11)	0.0044 (12)	0.0032 (11)
C11	0.0299 (14)	0.0217 (12)	0.0299 (14)	0.0059 (11)	0.0028 (12)	−0.0010 (11)
C12	0.0234 (12)	0.0244 (12)	0.0273 (13)	0.0056 (10)	0.0004 (11)	0.0021 (11)
C13	0.0233 (12)	0.0281 (13)	0.0227 (12)	0.0052 (10)	0.0021 (10)	0.0008 (11)
C14	0.0301 (13)	0.0308 (14)	0.0313 (13)	−0.0033 (11)	−0.0001 (12)	−0.0007 (12)
C15	0.0275 (13)	0.0436 (16)	0.0324 (14)	−0.0054 (12)	0.0042 (12)	0.0049 (13)
C16	0.0289 (14)	0.0471 (17)	0.0286 (13)	0.0011 (13)	0.0069 (12)	−0.0014 (14)
C17	0.0320 (14)	0.0343 (15)	0.0295 (14)	0.0050 (12)	0.0012 (12)	−0.0051 (12)

Geometric parameters (Å, º)

N1—O6	1.223 (3)	C6—C7	1.427 (4)
N1—O5	1.224 (3)	C7—C8	1.333 (4)
N1—C13	1.465 (3)	C7—H7A	0.9500
O1—C8	1.374 (3)	C8—C9	1.467 (4)
O1—C1	1.380 (3)	C9—C10	1.511 (4)
O2—C11	1.343 (3)	C10—H10A	0.9900
O2—C10	1.431 (3)	C10—H10B	0.9900
O3—C9	1.211 (3)	C11—C12	1.494 (4)
O4—C11	1.201 (3)	C12—C13	1.387 (3)
C1—C2	1.372 (4)	C12—C17	1.389 (4)
C1—C6	1.391 (4)	C13—C14	1.385 (4)
C2—C3	1.365 (4)	C14—C15	1.385 (4)
C2—H2A	0.9500	C14—H14A	0.9500
C3—C4	1.389 (5)	C15—C16	1.383 (4)
C3—H3A	0.9500	C15—H15A	0.9500
C4—C5	1.385 (4)	C16—C17	1.384 (4)
C4—H4A	0.9500	C16—H16A	0.9500
C5—C6	1.416 (4)	C17—H17A	0.9500

C5—H5A	0.9500

O6—N1—O5	123.8 (2)	O3—C9—C10	122.6 (2)
O6—N1—C13	118.3 (2)	C8—C9—C10	115.1 (2)
O5—N1—C13	117.9 (2)	O2—C10—C9	109.6 (2)
C8—O1—C1	105.8 (2)	O2—C10—H10A	109.8
C11—O2—C10	114.1 (2)	C9—C10—H10A	109.8
C2—C1—O1	126.0 (3)	O2—C10—H10B	109.8
C2—C1—C6	124.4 (3)	C9—C10—H10B	109.8
O1—C1—C6	109.6 (2)	H10A—C10—H10B	108.2
C3—C2—C1	116.3 (3)	O4—C11—O2	124.9 (2)
C3—C2—H2A	121.8	O4—C11—C12	124.2 (2)
C1—C2—H2A	121.8	O2—C11—C12	110.7 (2)
C2—C3—C4	122.2 (3)	C13—C12—C17	117.8 (2)
C2—C3—H3A	118.9	C13—C12—C11	124.6 (2)
C4—C3—H3A	118.9	C17—C12—C11	117.5 (2)
C5—C4—C3	121.3 (3)	C14—C13—C12	122.5 (2)
C5—C4—H4A	119.4	C14—C13—N1	117.8 (2)
C3—C4—H4A	119.4	C12—C13—N1	119.7 (2)
C4—C5—C6	117.6 (3)	C13—C14—C15	118.5 (3)
C4—C5—H5A	121.2	C13—C14—H14A	120.7
C6—C5—H5A	121.2	C15—C14—H14A	120.7
C1—C6—C5	118.1 (3)	C16—C15—C14	120.1 (3)
C1—C6—C7	105.7 (2)	C16—C15—H15A	120.0
C5—C6—C7	136.1 (3)	C14—C15—H15A	120.0
C8—C7—C6	107.0 (2)	C15—C16—C17	120.6 (3)
C8—C7—H7A	126.5	C15—C16—H16A	119.7
C6—C7—H7A	126.5	C17—C16—H16A	119.7
C7—C8—O1	111.9 (2)	C16—C17—C12	120.5 (3)
C7—C8—C9	132.6 (3)	C16—C17—H17A	119.8
O1—C8—C9	115.5 (2)	C12—C17—H17A	119.8
O3—C9—C8	122.3 (3)		

C8—O1—C1—C2	179.6 (2)	O3—C9—C10—O2	−7.9 (3)
C8—O1—C1—C6	−0.3 (3)	C8—C9—C10—O2	171.4 (2)
O1—C1—C2—C3	179.2 (2)	C10—O2—C11—O4	−5.4 (4)
C6—C1—C2—C3	−0.8 (4)	C10—O2—C11—C12	169.6 (2)
C1—C2—C3—C4	1.1 (4)	O4—C11—C12—C13	−90.2 (4)
C2—C3—C4—C5	−0.8 (4)	O2—C11—C12—C13	94.7 (3)
C3—C4—C5—C6	0.3 (4)	O4—C11—C12—C17	86.9 (3)
C2—C1—C6—C5	0.3 (4)	O2—C11—C12—C17	−88.2 (3)
O1—C1—C6—C5	−179.7 (2)	C17—C12—C13—C14	−1.0 (4)
C2—C1—C6—C7	−179.7 (2)	C11—C12—C13—C14	176.1 (2)
O1—C1—C6—C7	0.3 (3)	C17—C12—C13—N1	179.1 (2)
C4—C5—C6—C1	0.0 (4)	C11—C12—C13—N1	−3.8 (4)
C4—C5—C6—C7	−180.0 (3)	O6—N1—C13—C14	−2.8 (3)
C1—C6—C7—C8	−0.1 (3)	O5—N1—C13—C14	177.0 (2)
C5—C6—C7—C8	179.9 (3)	O6—N1—C13—C12	177.1 (2)

C6—C7—C8—O1	−0.1 (3)	O5—N1—C13—C12	−3.1 (3)
C6—C7—C8—C9	−179.1 (3)	C12—C13—C14—C15	1.0 (4)
C1—O1—C8—C7	0.3 (3)	N1—C13—C14—C15	−179.1 (2)
C1—O1—C8—C9	179.4 (2)	C13—C14—C15—C16	0.0 (4)
C7—C8—C9—O3	174.5 (3)	C14—C15—C16—C17	−1.0 (4)
O1—C8—C9—O3	−4.5 (3)	C15—C16—C17—C12	1.0 (4)
C7—C8—C9—C10	−4.9 (4)	C13—C12—C17—C16	0.1 (4)
O1—C8—C9—C10	176.2 (2)	C11—C12—C17—C16	−177.3 (2)
C11—O2—C10—C9	−71.4 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10*A*···O3^{i}	0.99	2.59	3.471 (4)	148
C15—H15*A*···O5^{ii}	0.95	2.58	3.380 (3)	142

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

(II) 2-(1*H*-1-Benzofuran-2-yl)-2-oxoethyl 2-aminobenzoate

Crystal data

$C_{17}H_{13}NO_4$
M_r = 295.28
Triclinic, $P\overline{1}$
a = 5.1839 (12) Å
b = 10.853 (3) Å
c = 12.269 (3) Å
α = 93.562 (3)°
β = 91.167 (3)°
γ = 98.714 (3)°
V = 680.6 (3) Å^3
Z = 2
F(000) = 308
D_x = 1.441 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 5796 reflections
θ = 2.4–27.9°
μ = 0.10 mm^{-1}
T = 297 K
Block, orange
0.40 × 0.32 × 0.21 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and *ω* scans
Absorption correction: multi-scan (SADABS; Bruker, 2009)
T_{min} = 0.871, T_{max} = 0.978
17052 measured reflections
3105 independent reflections
2214 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 27.5°, θ_{min} = 1.7°
h = −6→6
k = −14→14
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.123
S = 1.08
3105 reflections
207 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.1899P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.6563 (4)	0.67887 (18)	0.63733 (16)	0.0583 (4)
H1A	0.611 (4)	0.617 (2)	0.5840 (19)	0.069 (7)*
H1B	0.797 (5)	0.682 (2)	0.6702 (19)	0.074 (7)*
O1	0.2314 (2)	0.47254 (11)	0.10178 (9)	0.0478 (3)
O2	0.0514 (2)	0.72867 (11)	0.41702 (9)	0.0500 (3)
O3	0.3365 (3)	0.67869 (12)	0.24247 (11)	0.0587 (4)
O4	0.2949 (3)	0.59366 (11)	0.47797 (11)	0.0579 (4)
C1	0.1297 (3)	0.35882 (16)	0.05120 (14)	0.0448 (4)
C2	0.2360 (4)	0.3001 (2)	−0.03521 (16)	0.0581 (5)
H2A	0.3890	0.3356	−0.0667	0.070*
C3	0.1032 (5)	0.1866 (2)	−0.07204 (17)	0.0677 (6)
H3A	0.1669	0.1434	−0.1309	0.081*
C4	−0.1240 (5)	0.1334 (2)	−0.02449 (18)	0.0672 (6)
H4A	−0.2072	0.0551	−0.0514	0.081*
C5	−0.2283 (4)	0.19380 (18)	0.06135 (17)	0.0585 (5)
H5A	−0.3814	0.1581	0.0926	0.070*
C6	−0.0976 (3)	0.31045 (16)	0.10033 (14)	0.0452 (4)
C7	−0.1376 (3)	0.40069 (16)	0.18454 (14)	0.0453 (4)
H7A	−0.2762	0.3957	0.2318	0.054*
C8	0.0625 (3)	0.49452 (16)	0.18298 (13)	0.0429 (4)
C9	0.1355 (3)	0.60838 (16)	0.25240 (14)	0.0439 (4)
C10	−0.0582 (3)	0.63287 (18)	0.33799 (14)	0.0507 (4)
H10A	−0.2107	0.6571	0.3031	0.061*
H10B	−0.1141	0.5567	0.3741	0.061*
C11	0.2338 (3)	0.69697 (16)	0.48521 (13)	0.0431 (4)
C12	0.3415 (3)	0.79867 (15)	0.56403 (13)	0.0407 (4)
C13	0.5539 (3)	0.78708 (16)	0.63365 (13)	0.0441 (4)
C14	0.6573 (4)	0.89064 (19)	0.70265 (15)	0.0567 (5)
H14A	0.7996	0.8855	0.7486	0.068*
C15	0.5549 (4)	0.9990 (2)	0.70424 (16)	0.0611 (5)
H15A	0.6289	1.0667	0.7506	0.073*
C16	0.3431 (4)	1.00947 (18)	0.63798 (16)	0.0603 (5)
H16A	0.2715	1.0831	0.6403	0.072*
C17	0.2401 (4)	0.91065 (17)	0.56910 (15)	0.0515 (4)
H17A	0.0976	0.9179	0.5240	0.062*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0538 (10)	0.0643 (11)	0.0604 (11)	0.0199 (9)	−0.0078 (8)	0.0097 (9)
O1	0.0432 (7)	0.0505 (7)	0.0489 (7)	0.0035 (5)	0.0037 (5)	0.0054 (5)
O2	0.0511 (7)	0.0514 (7)	0.0492 (7)	0.0158 (6)	−0.0066 (6)	−0.0011 (6)
O3	0.0505 (8)	0.0579 (8)	0.0635 (8)	−0.0041 (6)	0.0051 (6)	−0.0002 (6)
O4	0.0647 (8)	0.0426 (7)	0.0680 (8)	0.0158 (6)	−0.0080 (7)	0.0023 (6)
C1	0.0456 (9)	0.0457 (10)	0.0441 (9)	0.0097 (8)	−0.0051 (7)	0.0072 (8)
C2	0.0588 (12)	0.0676 (13)	0.0508 (11)	0.0174 (10)	0.0053 (9)	0.0058 (9)
C3	0.0846 (16)	0.0697 (14)	0.0532 (12)	0.0292 (12)	−0.0042 (11)	−0.0027 (10)
C4	0.0846 (16)	0.0519 (12)	0.0630 (13)	0.0095 (11)	−0.0195 (12)	−0.0043 (10)
C5	0.0565 (11)	0.0540 (11)	0.0622 (12)	−0.0018 (9)	−0.0073 (9)	0.0083 (10)
C6	0.0457 (9)	0.0462 (10)	0.0442 (9)	0.0075 (8)	−0.0060 (7)	0.0081 (8)
C7	0.0399 (9)	0.0523 (10)	0.0438 (9)	0.0047 (8)	0.0017 (7)	0.0087 (8)
C8	0.0408 (9)	0.0489 (10)	0.0409 (9)	0.0105 (7)	−0.0014 (7)	0.0093 (7)
C9	0.0405 (9)	0.0458 (10)	0.0458 (9)	0.0065 (8)	−0.0051 (7)	0.0080 (7)
C10	0.0432 (10)	0.0576 (11)	0.0508 (10)	0.0083 (8)	−0.0033 (8)	−0.0008 (8)
C11	0.0422 (9)	0.0447 (10)	0.0444 (9)	0.0098 (7)	0.0042 (7)	0.0093 (7)
C12	0.0416 (9)	0.0414 (9)	0.0403 (8)	0.0078 (7)	0.0058 (7)	0.0064 (7)
C13	0.0417 (9)	0.0511 (10)	0.0404 (9)	0.0064 (8)	0.0069 (7)	0.0104 (7)
C14	0.0538 (11)	0.0684 (13)	0.0461 (10)	0.0039 (10)	−0.0026 (8)	0.0032 (9)
C15	0.0724 (13)	0.0573 (12)	0.0488 (11)	−0.0023 (10)	0.0052 (9)	−0.0049 (9)
C16	0.0776 (14)	0.0471 (11)	0.0579 (11)	0.0156 (10)	0.0074 (10)	−0.0006 (9)
C17	0.0565 (11)	0.0482 (10)	0.0520 (10)	0.0152 (9)	0.0008 (8)	0.0034 (8)

Geometric parameters (Å, º)

N1—C13	1.363 (2)	C6—C7	1.419 (2)
N1—H1A	0.91 (2)	C7—C8	1.340 (2)
N1—H1B	0.82 (2)	C7—H7A	0.9300
O1—C1	1.371 (2)	C8—C9	1.453 (2)
O1—C8	1.373 (2)	C9—C10	1.507 (3)
O2—C11	1.3469 (19)	C10—H10A	0.9700
O2—C10	1.420 (2)	C10—H10B	0.9700
O3—C9	1.208 (2)	C11—C12	1.457 (2)
O4—C11	1.209 (2)	C12—C17	1.394 (2)
C1—C2	1.371 (3)	C12—C13	1.405 (2)
C1—C6	1.382 (2)	C13—C14	1.396 (3)
C2—C3	1.363 (3)	C14—C15	1.361 (3)
C2—H2A	0.9300	C14—H14A	0.9300
C3—C4	1.387 (3)	C15—C16	1.376 (3)
C3—H3A	0.9300	C15—H15A	0.9300
C4—C5	1.370 (3)	C16—C17	1.358 (3)
C4—H4A	0.9300	C16—H16A	0.9300
C5—C6	1.393 (3)	C17—H17A	0.9300
C5—H5A	0.9300		

C13—N1—H1A	119.3 (14)	O3—C9—C10	122.21 (16)
C13—N1—H1B	117.8 (16)	C8—C9—C10	115.14 (15)
H1A—N1—H1B	118 (2)	O2—C10—C9	111.46 (14)
C1—O1—C8	105.72 (13)	O2—C10—H10A	109.3
C11—O2—C10	115.04 (13)	C9—C10—H10A	109.3
C2—C1—O1	125.63 (17)	O2—C10—H10B	109.3
C2—C1—C6	124.29 (18)	C9—C10—H10B	109.3
O1—C1—C6	110.08 (15)	H10A—C10—H10B	108.0
C3—C2—C1	115.8 (2)	O4—C11—O2	121.09 (16)
C3—C2—H2A	122.1	O4—C11—C12	126.02 (15)
C1—C2—H2A	122.1	O2—C11—C12	112.89 (14)
C2—C3—C4	122.1 (2)	C17—C12—C13	118.93 (16)
C2—C3—H3A	119.0	C17—C12—C11	120.32 (15)
C4—C3—H3A	119.0	C13—C12—C11	120.72 (15)
C5—C4—C3	121.3 (2)	N1—C13—C14	119.72 (17)
C5—C4—H4A	119.3	N1—C13—C12	122.51 (17)
C3—C4—H4A	119.3	C14—C13—C12	117.76 (16)
C4—C5—C6	117.9 (2)	C15—C14—C13	121.56 (18)
C4—C5—H5A	121.1	C15—C14—H14A	119.2
C6—C5—H5A	121.1	C13—C14—H14A	119.2
C1—C6—C5	118.65 (17)	C14—C15—C16	120.74 (19)
C1—C6—C7	105.84 (15)	C14—C15—H15A	119.6
C5—C6—C7	135.50 (18)	C16—C15—H15A	119.6
C8—C7—C6	106.96 (16)	C17—C16—C15	119.00 (18)
C8—C7—H7A	126.5	C17—C16—H16A	120.5
C6—C7—H7A	126.5	C15—C16—H16A	120.5
C7—C8—O1	111.38 (15)	C16—C17—C12	121.99 (18)
C7—C8—C9	132.36 (17)	C16—C17—H17A	119.0
O1—C8—C9	116.19 (14)	C12—C17—H17A	119.0
O3—C9—C8	122.65 (17)		

C8—O1—C1—C2	179.91 (16)	O1—C8—C9—C10	177.70 (13)
C8—O1—C1—C6	−0.32 (16)	C11—O2—C10—C9	−70.85 (18)
O1—C1—C2—C3	179.33 (15)	O3—C9—C10—O2	−13.3 (2)
C6—C1—C2—C3	−0.4 (3)	C8—C9—C10—O2	166.80 (13)
C1—C2—C3—C4	−0.5 (3)	C10—O2—C11—O4	−0.3 (2)
C2—C3—C4—C5	1.0 (3)	C10—O2—C11—C12	179.52 (14)
C3—C4—C5—C6	−0.5 (3)	O4—C11—C12—C17	−175.17 (17)
C2—C1—C6—C5	0.8 (3)	O2—C11—C12—C17	5.1 (2)
O1—C1—C6—C5	−178.95 (14)	O4—C11—C12—C13	6.8 (3)
C2—C1—C6—C7	−179.49 (16)	O2—C11—C12—C13	−172.97 (14)
O1—C1—C6—C7	0.74 (17)	C17—C12—C13—N1	176.84 (17)
C4—C5—C6—C1	−0.3 (2)	C11—C12—C13—N1	−5.1 (2)
C4—C5—C6—C7	−179.90 (18)	C17—C12—C13—C14	−1.8 (2)
C1—C6—C7—C8	−0.87 (18)	C11—C12—C13—C14	176.29 (15)
C5—C6—C7—C8	178.74 (18)	N1—C13—C14—C15	−177.67 (18)
C6—C7—C8—O1	0.71 (18)	C12—C13—C14—C15	1.0 (3)
C6—C7—C8—C9	−176.21 (16)	C13—C14—C15—C16	0.6 (3)

C1—O1—C8—C7	−0.26 (17)	C14—C15—C16—C17	−1.3 (3)
C1—O1—C8—C9	177.21 (13)	C15—C16—C17—C12	0.4 (3)
C7—C8—C9—O3	174.59 (17)	C13—C12—C17—C16	1.1 (3)
O1—C8—C9—O3	−2.2 (2)	C11—C12—C17—C16	−176.94 (17)
C7—C8—C9—C10	−5.5 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O4	0.91 (2)	2.05 (2)	2.700 (3)	127.7 (18)
N1—H1*A*···O4^{i}	0.91 (2)	2.49 (2)	3.246 (2)	141.4 (18)
C10—H10*A*···O3^{ii}	0.97	2.50	3.444 (2)	165
C17—H17*A*···O2	0.93	2.35	2.687 (2)	101

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