organic compounds

1-(2-Hydroxy-4,5-dimethoxyphenyl)-ethanone

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The molecular structure of the title compound, $C_{10}H_{12}O_4$, contains an intramolecular hydrogen bond between the phenol and acetyl substituents. In the crystal, C—H$\cdots\pi$ interactions act between the molecules in a cyclic manner to stabilize stacks of molecules along the b axis. Several C—H$\cdots$O interactions are present between the stacks.

Related literature

For a review on lamellarin alkaloids, see: Fan *et al.* (2008). The experimental procedure of Combes *et al.* (2002) for a related Fries rearrangement was adapted for the synthesis of the title compound. For alternative syntheses of the title compound by Fries rearrangement, see: Ploypradith *et al.* (2003); Nolan *et al.* (2009).
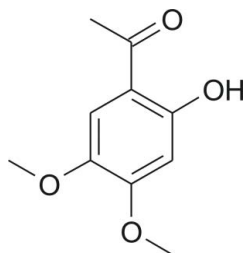
Experimental

Crystal data

$C_{10}H_{12}O_4$	V = 949.10 (9) Å³
M_r = 196.20	Z = 4
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation
a = 19.1740 (12) Å	μ = 0.11 mm⁻¹
b = 5.5026 (3) Å	T = 173 K
c = 8.9956 (5) Å	0.41 × 0.32 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer	1214 independent reflections
4718 measured reflections	1106 reflections with $I > 2\sigma(I)$
	R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.085	
S = 1.06	$\Delta\rho_{max}$ = 0.20 e Å⁻³
1214 reflections	$\Delta\rho_{min}$ = −0.18 e Å⁻³
134 parameters	
1 restraint	

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

$Cg1$ is the centroid of the C1–C6 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O4	0.93 (3)	1.71 (3)	2.549 (2)	150 (2)
C8—H8$C\cdots$O3[i]	0.98	2.40	3.365 (2)	168
C9—H9$B\cdots$O3[ii]	0.98	2.57	3.513 (3)	162
C10—H10$C\cdots$O2[i]	0.98	2.53	3.334 (3)	139
C8—H8$B\cdots Cg1$[iii]	0.98	2.80	3.738 (3)	160
C9—H9$A\cdots Cg1$[iv]	0.98	2.90	3.828 (3)	158

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *SCHAKAL99* (Keller, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NK2196).

References

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supporting information

1-(2-Hydroxy-4,5-dimethoxyphenyl)ethanone

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S1. Comment

The title organic compound (Fig. 1), required as an intermediate in the synthesis of lamellarin alkaloids (Fan *et al.*, 2008), was prepared by Fries rearrangement of 3,4-dimethoxyphenyl acetate with boron trifluoride etherate. Syntheses of the same compound by related Fries rearrangements have been reported by Ploypradith *et al.* (2003) and Nolan *et al.* (2009).

The compound crystallizes in the polar space group $Pca2_1$. An intramolecular hydrogen bond exists between the phenol and acetyl groups (Fig. 1). Molecules related by translation along the *b* axis interact through two C—H···π interactions which act between the molecules in a cyclic manner. These stabilize stacks of molecules along the *b* axis (Fig. 2). Several C—H···O interactions exist in the structure, the most significant being listed in Table 1. These act between the stacks to stabilize the structure (Fig. 3).

S2. Experimental

The experimental procedure of Combes *et al.*. (2002) for a related Fries rearrangement was adapted for the synthesis of the title compound. Boron trifloride etherate (20 ml, 23.1 g, 163 mmol) was cautiously added to ice-cooled 3,4-dimeth-oxyphenyl acetate (7.99 g, 40.7 mmol). The mixture was warmed to room temperature, then heated to 383 K for 5 h before being cooled again to room temperature and stirred for an additional 18 h. Water (50 ml) was added, resulting in the precipitation of a brown solid. This was filtered off, washed with a copious amount of water, then recrystallized from methanol to afford 1-(2-hydroxy-4,5-dimethoxyphenyl)ethanone (4.90 g, 61%) as dark yellow blocks, m.p. 385–386 K.

S3. Refinement

All H atoms attached to carbon were positioned geometrically, and allowed to ride on their parent atoms, with C—H bond lengths of 0.95 Å (CH) or 0.98 Å (CH₃), and isotropic displacement parameters set to 1.2 (CH) or 1.5 times (CH₃) the U_{eq} of the parent atom. Friedel pairs were merged during final refinement.
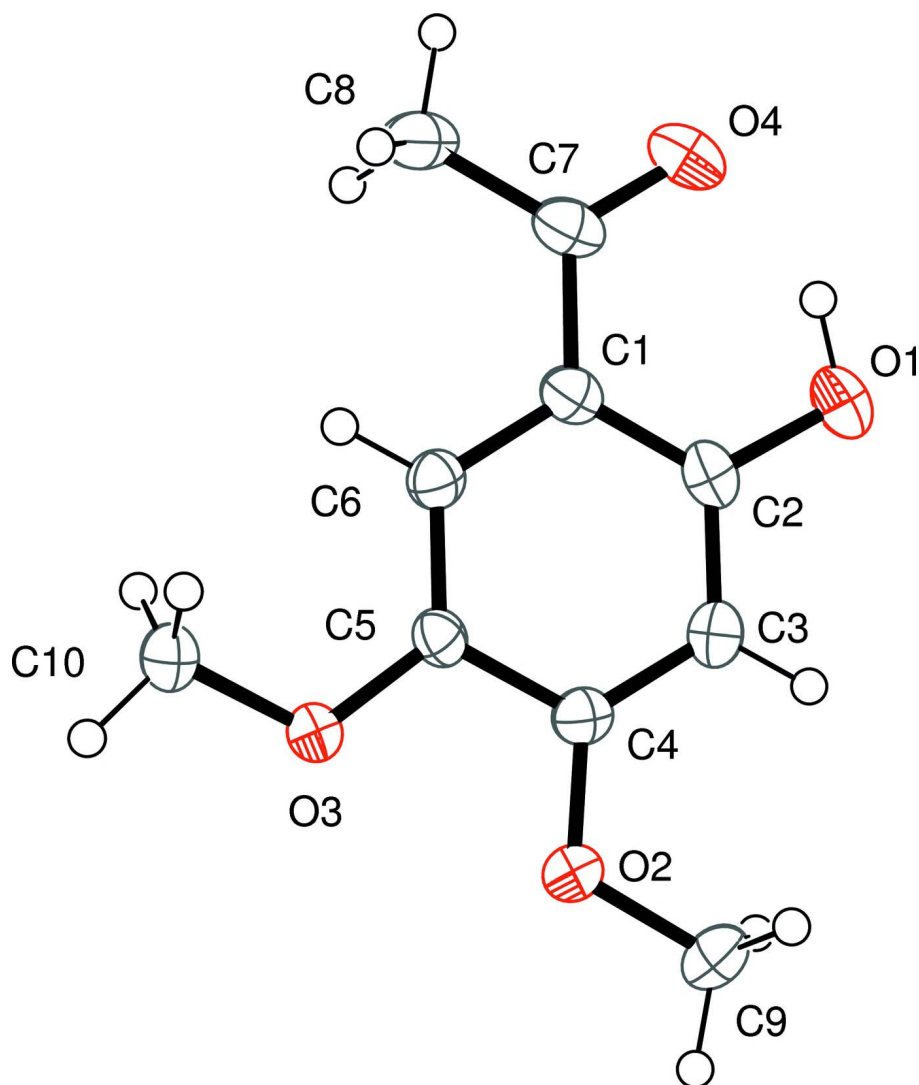
Figure 1

The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Figure 2

C-H···π interactions in the structure of (I) stabilising stacks of molecules along the *b* axis. [Symmetry codes: (i) x, y, z; (ii) x, -1+y, z; (iii) x, 1+y, z.]

Figure 3

C-H···O interactions between the stacks of molecules in the structure of (I). [Symmetry codes: (i) x, y, z; (ii) 1/2-x, 1+y, 1/2+z; (iii) 1-x, 1-y, 1/2+z; (iv) 1/2+x, -y, z; (v) 1-x, -y, -1/2+z.]

1-(2-Hydroxy-4,5-dimethoxyphenyl)ethanone

Crystal data

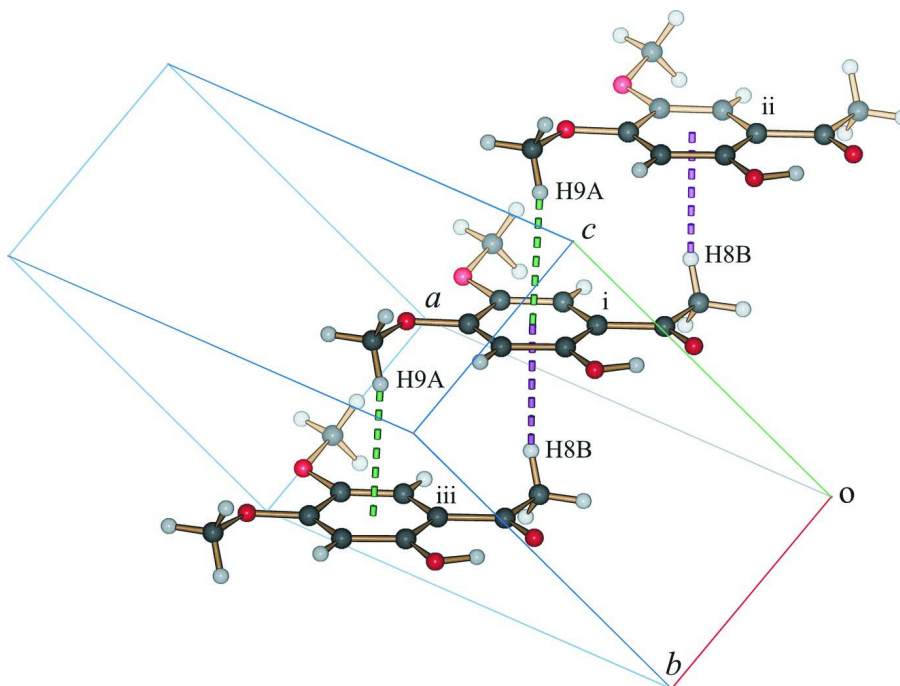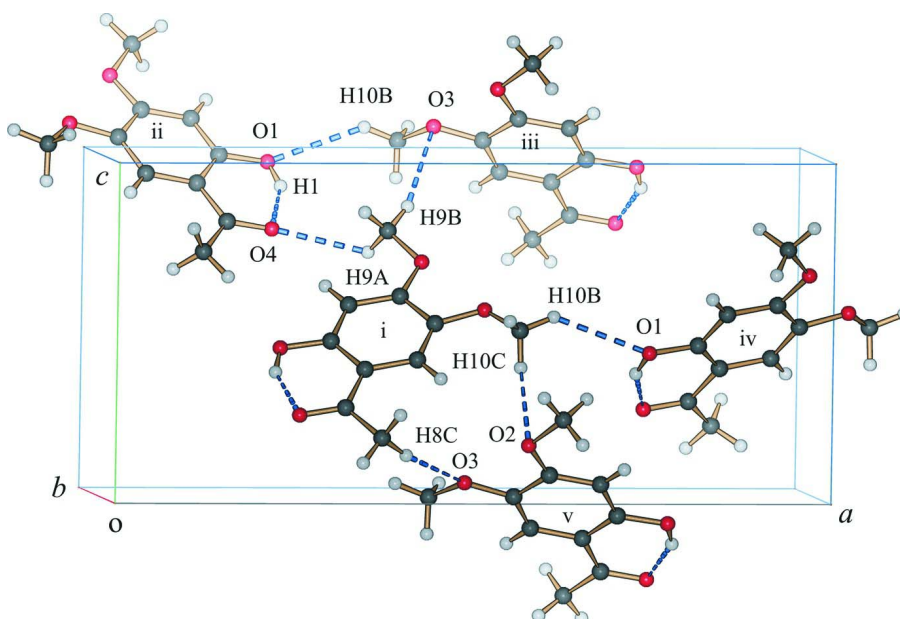|	
$C_{10}H_{12}O_4$	$F(000) = 416$
$M_r = 196.20$	$D_x = 1.373$ Mg m^{-3}
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2c -2ac	Cell parameters from 2177 reflections
$a = 19.1740$ (12) Å	$\theta = 3.1$–27.7°
$b = 5.5026$ (3) Å	$\mu = 0.11$ mm^{-1}
$c = 8.9956$ (5) Å	$T = 173$ K
$V = 949.10$ (9) Å^3	Block, colourless
$Z = 4$	$0.41 \times 0.32 \times 0.20$ mm

Data collection

Bruker APEXII CCD diffractometer	1106 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.032$
Graphite monochromator	$\theta_{max} = 28.0°$, $\theta_{min} = 2.1°$
φ and ω scans	$h = -25 \rightarrow 24$
4718 measured reflections	$k = -7 \rightarrow 7$
1214 independent reflections	$l = -11 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.032$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.085$	$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.0546P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	
1214 reflections	
134 parameters	$(\Delta/\sigma)_{max} < 0.001$
1 restraint	$\Delta\rho_{max} = 0.20$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.18$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.34395 (9)	−0.0487 (3)	0.3973 (2)	0.0287 (4)
C2	0.30480 (9)	0.1288 (3)	0.4721 (2)	0.0322 (4)
C3	0.33683 (9)	0.2885 (3)	0.5713 (2)	0.0307 (4)
H3	0.3100	0.4093	0.6205	0.037*
C4	0.40755 (9)	0.2705 (3)	0.59765 (19)	0.0262 (4)

C5	0.44769 (8)	0.0884 (3)	0.5258 (2)	0.0248 (4)
C6	0.41609 (9)	−0.0644 (3)	0.4263 (2)	0.0271 (4)
H6	0.4432	−0.1829	0.3758	0.033*
C7	0.30942 (10)	−0.2140 (4)	0.2923 (2)	0.0346 (4)
C8	0.35122 (11)	−0.4047 (4)	0.2122 (3)	0.0395 (5)
H8A	0.3210	−0.4921	0.1425	0.059*
H8B	0.3706	−0.5194	0.2845	0.059*
H8C	0.3893	−0.3269	0.1573	0.059*
C9	0.40535 (10)	0.5915 (3)	0.7748 (3)	0.0357 (4)
H9A	0.3838	0.7080	0.7064	0.053*
H9B	0.4368	0.6778	0.8426	0.053*
H9C	0.3690	0.5091	0.8323	0.053*
C10	0.55610 (10)	−0.1202 (3)	0.5150 (3)	0.0364 (5)
H10A	0.5342	−0.2712	0.5491	0.055*
H10B	0.6036	−0.1097	0.5548	0.055*
H10C	0.5578	−0.1188	0.4061	0.055*
O1	0.23555 (7)	0.1547 (3)	0.4504 (2)	0.0469 (4)
O2	0.44429 (7)	0.4153 (2)	0.69134 (15)	0.0308 (3)
O3	0.51633 (6)	0.0824 (3)	0.56605 (17)	0.0321 (3)
O4	0.24611 (9)	−0.2002 (3)	0.2697 (2)	0.0501 (4)
H1	0.2231 (13)	0.032 (5)	0.385 (4)	0.061 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0269 (9)	0.0322 (9)	0.0270 (9)	−0.0045 (7)	−0.0010 (7)	0.0009 (8)
C2	0.0227 (8)	0.0382 (10)	0.0357 (10)	−0.0005 (8)	0.0018 (8)	0.0028 (9)
C3	0.0280 (8)	0.0334 (9)	0.0308 (10)	0.0027 (7)	0.0050 (8)	0.0000 (8)
C4	0.0297 (9)	0.0267 (8)	0.0222 (8)	−0.0035 (7)	0.0024 (7)	0.0010 (7)
C5	0.0214 (8)	0.0284 (8)	0.0247 (8)	−0.0017 (7)	0.0017 (7)	0.0017 (7)
C6	0.0278 (8)	0.0279 (8)	0.0257 (9)	−0.0015 (7)	0.0036 (7)	−0.0002 (7)
C7	0.0331 (10)	0.0384 (10)	0.0322 (10)	−0.0113 (8)	−0.0023 (8)	0.0015 (9)
C8	0.0439 (12)	0.0401 (11)	0.0345 (10)	−0.0141 (9)	0.0022 (9)	−0.0072 (9)
C9	0.0424 (11)	0.0304 (9)	0.0342 (9)	0.0044 (7)	0.0023 (9)	−0.0072 (8)
C10	0.0279 (8)	0.0346 (9)	0.0468 (12)	0.0064 (8)	−0.0022 (9)	−0.0067 (9)
O1	0.0229 (7)	0.0571 (9)	0.0608 (11)	0.0031 (7)	−0.0054 (7)	−0.0103 (9)
O2	0.0298 (7)	0.0323 (6)	0.0304 (7)	0.0003 (5)	−0.0003 (5)	−0.0072 (6)
O3	0.0235 (6)	0.0356 (6)	0.0371 (7)	0.0029 (5)	−0.0026 (5)	−0.0097 (6)
O4	0.0327 (7)	0.0585 (9)	0.0589 (10)	−0.0089 (7)	−0.0106 (8)	−0.0106 (9)

Geometric parameters (Å, º)

C1—C2	1.403 (3)	C7—C8	1.504 (3)
C1—C6	1.410 (2)	C8—H8A	0.9800
C1—C7	1.469 (3)	C8—H8B	0.9800
C2—O1	1.349 (2)	C8—H8C	0.9800
C2—C3	1.395 (3)	C9—O2	1.436 (2)
C3—C4	1.380 (2)	C9—H9A	0.9800

C3—H3	0.9500	C9—H9B	0.9800
C4—O2	1.357 (2)	C9—H9C	0.9800
C4—C5	1.419 (2)	C10—O3	1.426 (2)
C5—O3	1.365 (2)	C10—H10A	0.9800
C5—C6	1.370 (2)	C10—H10B	0.9800
C6—H6	0.9500	C10—H10C	0.9800
C7—O4	1.233 (2)	O1—H1	0.93 (3)
C2—C1—C6	118.60 (16)	C7—C8—H8A	109.5
C2—C1—C7	119.87 (16)	C7—C8—H8B	109.5
C6—C1—C7	121.53 (16)	H8A—C8—H8B	109.5
O1—C2—C3	117.31 (18)	C7—C8—H8C	109.5
O1—C2—C1	122.06 (18)	H8A—C8—H8C	109.5
C3—C2—C1	120.63 (15)	H8B—C8—H8C	109.5
C4—C3—C2	119.84 (16)	O2—C9—H9A	109.5
C4—C3—H3	120.1	O2—C9—H9B	109.5
C2—C3—H3	120.1	H9A—C9—H9B	109.5
O2—C4—C3	125.10 (16)	O2—C9—H9C	109.5
O2—C4—C5	114.56 (15)	H9A—C9—H9C	109.5
C3—C4—C5	120.33 (16)	H9B—C9—H9C	109.5
O3—C5—C6	125.79 (15)	O3—C10—H10A	109.5
O3—C5—C4	114.79 (15)	O3—C10—H10B	109.5
C6—C5—C4	119.42 (15)	H10A—C10—H10B	109.5
C5—C6—C1	121.15 (15)	O3—C10—H10C	109.5
C5—C6—H6	119.4	H10A—C10—H10C	109.5
C1—C6—H6	119.4	H10B—C10—H10C	109.5
O4—C7—C1	120.76 (19)	C2—O1—H1	105.6 (16)
O4—C7—C8	119.24 (18)	C4—O2—C9	116.82 (14)
C1—C7—C8	120.00 (17)	C5—O3—C10	116.68 (14)
C6—C1—C2—O1	−179.90 (19)	O3—C5—C6—C1	177.32 (16)
C7—C1—C2—O1	−0.3 (3)	C4—C5—C6—C1	−2.0 (2)
C6—C1—C2—C3	0.9 (3)	C2—C1—C6—C5	0.5 (2)
C7—C1—C2—C3	−179.47 (17)	C7—C1—C6—C5	−179.13 (17)
O1—C2—C3—C4	−179.95 (18)	C2—C1—C7—O4	−0.6 (3)
C1—C2—C3—C4	−0.7 (3)	C6—C1—C7—O4	178.99 (19)
C2—C3—C4—O2	179.97 (17)	C2—C1—C7—C8	−179.90 (17)
C2—C3—C4—C5	−0.8 (3)	C6—C1—C7—C8	−0.3 (3)
O2—C4—C5—O3	2.1 (2)	C3—C4—O2—C9	3.5 (3)
C3—C4—C5—O3	−177.21 (16)	C5—C4—O2—C9	−175.75 (15)
O2—C4—C5—C6	−178.53 (15)	C6—C5—O3—C10	−8.9 (3)
C3—C4—C5—C6	2.2 (2)	C4—C5—O3—C10	170.47 (16)

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C1–C6 ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O4	0.93 (3)	1.71 (3)	2.549 (2)	150 (2)

C8—H8*C*···O3ⁱ	0.98	2.40	3.365 (2)	168
C9—H9*B*···O3ⁱⁱ	0.98	2.57	3.513 (3)	162
C10—H10*C*···O2ⁱ	0.98	2.53	3.334 (3)	139
C8—H8*B*···*Cg*1ⁱⁱⁱ	0.98	2.80	3.738 (3)	160
C9—H9*A*···*Cg*1ⁱᵛ	0.98	2.90	3.828 (3)	158

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