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3-Carboxy-5-(pyridinium-4-yl)benzoate: a redetermination

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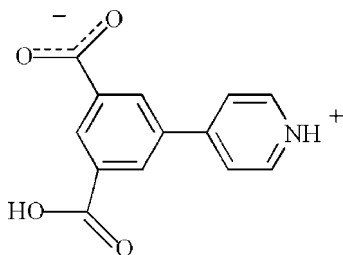
Received 28 April 2011; accepted 30 April 2011

 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.050; wR factor = 0.142; data-to-parameter ratio = 6.2.

The title compound, $\text{C}_{13}\text{H}_9\text{NO}_4$, crystallizes in a zwitterionic form with the pyridine N atom protonated and the carboxyl OH group deprotonated. The benzene and pyridinium rings are inclined with a dihedral angle of $31.42(14)^\circ$ between them. A previous report of this structure claims, we believe incorrectly, that neither of the carboxylate groups is deprotonated [Zhang *et al.* (2010). *Acta Cryst.* E66, o2928–o2928]. In the crystal, intermolecular $\text{O}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{O}$ and weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions link adjacent molecules into a three-dimensional supramolecular network.

Related literature

For coordination polymers based on pyridinecarboxylate ligands, see: Lu & Luck (2003); Ma *et al.* (2009). For a previous report of the structure of this molecule, which claims that neither of the carboxylate groups is deprotonated, see: Zhang *et al.* (2010).



Experimental

Crystal data

 $\text{C}_{13}\text{H}_9\text{NO}_4$
 $M_r = 243.21$

 Orthorhombic, $Fdd2$
 $a = 15.5702(13)$ Å

 $b = 37.377(3)$ Å

 $c = 7.2016(9)$ Å

 $V = 4191.1(7)$ Å³
 $Z = 16$

 Mo $K\alpha$ radiation

 $\mu = 0.12$ mm⁻¹
 $T = 298$ K

 $0.38 \times 0.15 \times 0.07$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer

 Absorption correction: multi-scan (*SADABS*; Bruker, 2007)

 $T_{\min} = 0.957$, $T_{\max} = 0.992$

5456 measured reflections

1024 independent reflections

 885 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.142$
 $S = 1.09$

1024 reflections

164 parameters

4 restraints

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O4}^{\text{i}}$	0.86	1.70	2.562 (4)	175
$\text{N1}-\text{H1}\cdots\text{O3}^{\text{i}}$	0.86	2.67	3.252 (4)	126
$\text{O1}-\text{H1A}\cdots\text{O4}^{\text{ii}}$	0.82	1.96	2.643 (5)	141
$\text{C8}-\text{H8}\cdots\text{O2}^{\text{iii}}$	0.93	2.71	3.632 (5)	171
$\text{C10}-\text{H10}\cdots\text{O2}^{\text{iii}}$	0.93	2.58	3.225 (6)	127
$\text{C9}-\text{H9}\cdots\text{O1}^{\text{iv}}$	0.93	2.59	3.316 (6)	135

 Symmetry codes: (i) $-x + \frac{1}{4}, y - \frac{1}{4}, z - \frac{1}{4}$; (ii) $x + \frac{1}{2}, y, z - \frac{1}{2}$; (iii) $-x + 1, -y, z$; (iv) $-x + \frac{3}{4}, y - \frac{1}{4}, z + \frac{1}{4}$

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ5133).

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supporting information

Acta Cryst. (2011). E67, o1353 [doi:10.1107/S1600536811016394]

3-Carboxy-5-(pyridinium-4-yl)benzoate: a redetermination

Shi-Jie Li, Dong-Liang Miao, Wen-Dong Song and Shao-Wei Tong

S1. Comment

Rigid pyridinecarboxylate ligands have been used extensively to react with metal ions and generate coordination polymers with fascinating structures and properties (Lu & Luck 2003; Ma *et al.*, 2009). As part of an ongoing investigation into coordination polymers based on pyridinecarboxylate ligands, we report here the crystal structure of the title compound.

As shown in Fig. 1, the title compound, C₁₃H₉NO₄, crystallizes in a zwitterionic form with the pyridine N protonated and one of the carboxyl OH groups deprotonated. The locations of the N and O bound H atoms are clearly shown in a difference Fourier map. A previous report of the same structure in the same space group and with similar unit-cell parameters claims that neither of the carboxylate groups are deprotonated (Zhang *et al.*, 2010). We believe this assignment to be in error. A conformational feature of the molecule is a rigid structure with the benzene and pyridinium rings inclined at an angle of 31.42 (14) ° to one another. In the crystal structure, molecules are interconnected by O—H···O, N—H···O and weak C—H···O hydrogen bonding interactions (Table. 1), generating a three-dimensional supramolecular network (Fig. 2).

S2. Experimental

Commercially available 5-(pyridin-4-yl)isophthalic acid was further purified by repeated recrystallization from anhydrous ethanol. Colorless crystals suitable for X-ray analysis were obtained by slow evaporation of the ethanol solvent at room temperature.

S3. Refinement

All H-atoms were positioned geometrically and refined using a riding model with $d(\text{C—H}) = 0.93 \text{ \AA}$, $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for aromatic hydrogen atoms 0.86 \AA , $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{N})$ for the NH group and 0.82 \AA , $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{O})$ for the OH group. In the absence of significant anomalous dispersion effects, Friedel pairs were merged.

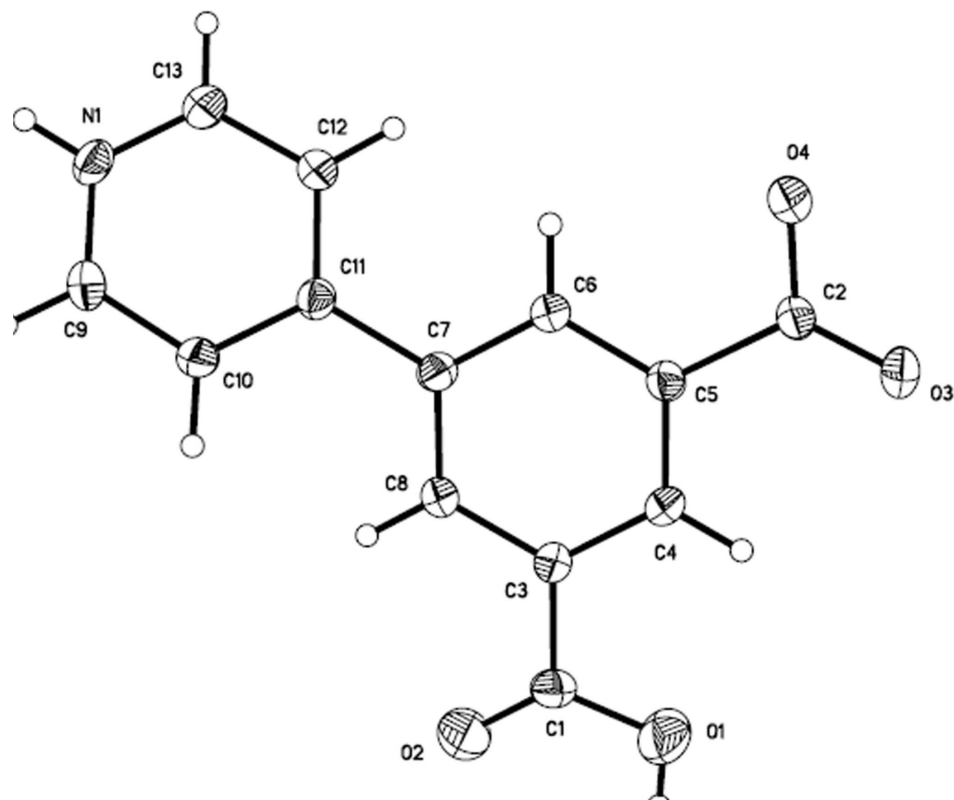
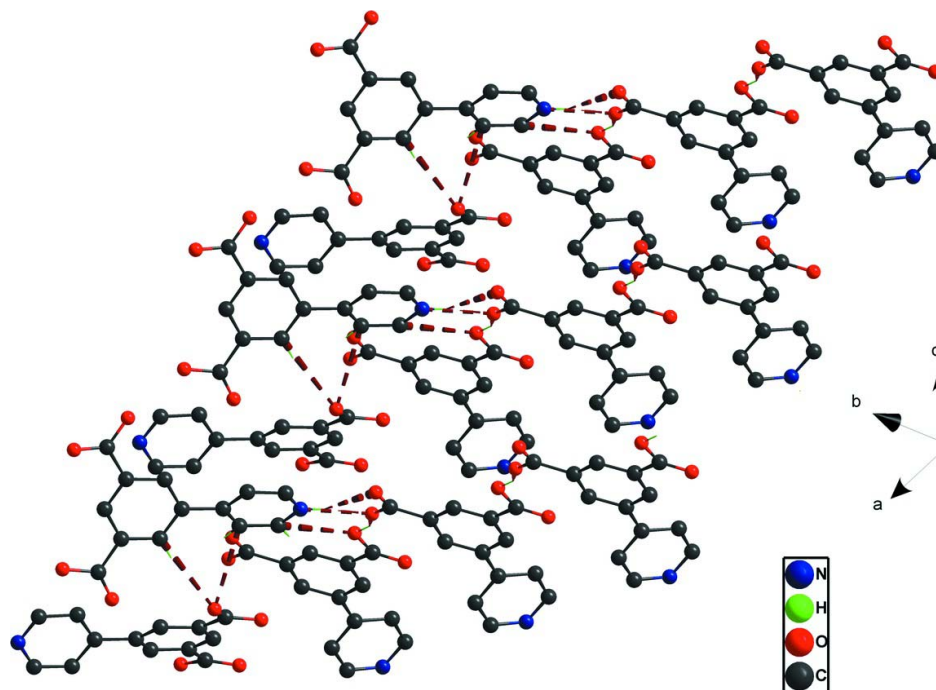


Figure 1

The structure of the title compound, showing the atomic numbering scheme. Non-H atoms are shown with 30% probability displacement ellipsoids.

**Figure 2**

Crystal packing of the title compound (H atoms not involved in forming hydrogen bonds are omitted for clarity).

3-Carboxy-5-(pyridinium-4-yl)benzoate

Crystal data

$C_{13}H_9NO_4$

$M_r = 243.21$

Orthorhombic, *Fdd2*

Hall symbol: *F* 2 -2d

$a = 15.5702$ (13) Å

$b = 37.377$ (3) Å

$c = 7.2016$ (9) Å

$V = 4191.1$ (7) Å³

$Z = 16$

$F(000) = 2016$

$D_x = 1.542$ Mg m⁻³

Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 1702 reflections

$\theta = 2.5$ – 25.9°

$\mu = 0.12$ mm⁻¹

$T = 298$ K

Block, colorless

$0.38 \times 0.15 \times 0.07$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2007)

$T_{\min} = 0.957$, $T_{\max} = 0.992$

5456 measured reflections

1024 independent reflections

885 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.048$

$\theta_{\max} = 25.2^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -15 \rightarrow 18$

$k = -42 \rightarrow 44$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.142$

$S = 1.09$

1024 reflections

164 parameters

4 restraints

Primary atom site location: structure-invariant
direct methods
Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0985P)^2 + 0.9031P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.21 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e } \text{Å}^{-3}$

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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.1480 (2)	-0.05751 (9)	0.2133 (5)	0.0409 (9)
H1	0.1190	-0.0771	0.2101	0.049*
O1	0.5435 (2)	0.10547 (10)	0.0930 (7)	0.0710 (12)
H1A	0.5939	0.1044	0.0606	0.106*
O2	0.5453 (2)	0.04721 (10)	0.0306 (6)	0.0697 (13)
O3	0.29114 (19)	0.16581 (7)	0.3311 (6)	0.0532 (9)
O4	0.18242 (19)	0.13290 (7)	0.4374 (6)	0.0482 (9)
C1	0.5099 (3)	0.07316 (11)	0.0923 (7)	0.0397 (9)
C2	0.2558 (2)	0.13670 (10)	0.3568 (7)	0.0360 (9)
C3	0.4199 (2)	0.07241 (9)	0.1660 (6)	0.0327 (9)
C4	0.3802 (2)	0.10341 (10)	0.2268 (6)	0.0328 (9)
H4A	0.4102	0.1249	0.2255	0.039*
C5	0.2964 (2)	0.10264 (10)	0.2892 (6)	0.0314 (9)
C6	0.2511 (2)	0.07076 (10)	0.2856 (6)	0.0314 (9)
H6	0.1940	0.0704	0.3236	0.038*
C7	0.2898 (2)	0.03945 (10)	0.2260 (6)	0.0315 (9)
C8	0.3750 (2)	0.04014 (10)	0.1687 (6)	0.0325 (9)
H8	0.4020	0.0191	0.1321	0.039*
C9	0.2321 (3)	-0.05851 (11)	0.2449 (7)	0.0422 (10)
H9	0.2589	-0.0804	0.2644	0.051*
C10	0.2804 (3)	-0.02736 (10)	0.2493 (7)	0.0376 (10)
H10	0.3394	-0.0285	0.2688	0.045*
C11	0.2406 (2)	0.00546 (10)	0.2248 (6)	0.0324 (9)
C12	0.1522 (3)	0.00546 (10)	0.1922 (7)	0.0399 (10)
H12	0.1229	0.0269	0.1745	0.048*
C13	0.1090 (3)	-0.02658 (11)	0.1866 (7)	0.0438 (11)
H13	0.0502	-0.0265	0.1632	0.053*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0402 (19)	0.0294 (16)	0.053 (2)	-0.0098 (14)	0.0033 (17)	-0.0067 (17)
O1	0.057 (2)	0.0575 (15)	0.098 (3)	-0.0119 (15)	0.024 (2)	-0.006 (2)
O2	0.052 (2)	0.0601 (15)	0.097 (4)	0.0054 (14)	0.018 (2)	-0.010 (2)
O3	0.0488 (18)	0.0275 (14)	0.083 (3)	-0.0033 (12)	0.0095 (17)	-0.0067 (17)
O4	0.0399 (16)	0.0334 (15)	0.071 (2)	0.0014 (12)	0.0126 (16)	-0.0045 (15)
C1	0.0301 (19)	0.0442 (18)	0.045 (2)	0.0001 (14)	0.0017 (19)	0.0004 (18)
C2	0.0335 (19)	0.028 (2)	0.046 (2)	0.0031 (15)	-0.0038 (18)	-0.0062 (18)
C3	0.0320 (19)	0.0282 (18)	0.038 (2)	-0.0014 (14)	-0.0008 (18)	0.0009 (17)
C4	0.0294 (19)	0.0310 (18)	0.038 (2)	-0.0053 (14)	0.0011 (16)	0.0001 (17)
C5	0.0300 (19)	0.0292 (18)	0.035 (2)	0.0014 (14)	-0.0026 (17)	-0.0039 (16)
C6	0.0274 (18)	0.0298 (19)	0.037 (2)	-0.0010 (14)	0.0009 (16)	-0.0012 (16)
C7	0.0291 (19)	0.0319 (19)	0.033 (2)	-0.0023 (14)	0.0006 (17)	0.0007 (18)
C8	0.032 (2)	0.0280 (18)	0.037 (2)	0.0021 (15)	0.0010 (18)	-0.0013 (16)
C9	0.048 (2)	0.0270 (19)	0.052 (3)	0.0011 (17)	0.000 (2)	-0.0019 (18)
C10	0.030 (2)	0.0340 (19)	0.049 (3)	0.0004 (15)	0.0029 (19)	-0.0046 (19)
C11	0.0336 (19)	0.028 (2)	0.035 (2)	-0.0015 (15)	0.0038 (17)	-0.0027 (17)
C12	0.032 (2)	0.0314 (19)	0.056 (3)	0.0017 (15)	0.0026 (19)	-0.003 (2)
C13	0.036 (2)	0.038 (2)	0.057 (3)	-0.0054 (17)	-0.002 (2)	-0.005 (2)

Geometric parameters (\AA , $^\circ$)

N1—C13	1.320 (5)	C5—C6	1.385 (5)
N1—C9	1.329 (5)	C6—C7	1.385 (5)
N1—H1	0.8600	C6—H6	0.9300
O1—C1	1.316 (5)	C7—C8	1.389 (5)
O1—H1A	0.8200	C7—C11	1.484 (5)
O2—C1	1.201 (5)	C8—H8	0.9300
O3—C2	1.233 (5)	C9—C10	1.386 (5)
O4—C2	1.290 (5)	C9—H9	0.9300
C1—C3	1.498 (5)	C10—C11	1.386 (6)
C2—C5	1.502 (5)	C10—H10	0.9300
C3—C4	1.385 (5)	C11—C12	1.397 (6)
C3—C8	1.394 (5)	C12—C13	1.374 (6)
C4—C5	1.379 (5)	C12—H12	0.9300
C4—H4A	0.9300	C13—H13	0.9300
C13—N1—C9	120.2 (3)	C6—C7—C8	119.5 (3)
C13—N1—H1	119.9	C6—C7—C11	120.0 (3)
C9—N1—H1	119.9	C8—C7—C11	120.5 (3)
C1—O1—H1A	109.5	C7—C8—C3	119.9 (3)
O2—C1—O1	124.0 (4)	C7—C8—H8	120.0
O2—C1—C3	123.1 (4)	C3—C8—H8	120.0
O1—C1—C3	112.8 (4)	N1—C9—C10	121.0 (4)
O3—C2—O4	124.0 (3)	N1—C9—H9	119.5
O3—C2—C5	120.8 (4)	C10—C9—H9	119.5

O4—C2—C5	115.2 (3)	C11—C10—C9	119.9 (4)
C4—C3—C8	119.7 (3)	C11—C10—H10	120.1
C4—C3—C1	120.9 (3)	C9—C10—H10	120.1
C8—C3—C1	119.3 (3)	C10—C11—C12	117.5 (4)
C5—C4—C3	120.5 (3)	C10—C11—C7	121.8 (3)
C5—C4—H4A	119.7	C12—C11—C7	120.7 (3)
C3—C4—H4A	119.7	C13—C12—C11	119.2 (4)
C4—C5—C6	119.6 (3)	C13—C12—H12	120.4
C4—C5—C2	119.1 (3)	C11—C12—H12	120.4
C6—C5—C2	121.4 (3)	N1—C13—C12	122.2 (4)
C7—C6—C5	120.7 (3)	N1—C13—H13	118.9
C7—C6—H6	119.6	C12—C13—H13	118.9
C5—C6—H6	119.6		
O2—C1—C3—C4	-176.6 (5)	C6—C7—C8—C3	-2.0 (6)
O1—C1—C3—C4	-0.2 (6)	C11—C7—C8—C3	178.4 (4)
O2—C1—C3—C8	1.7 (7)	C4—C3—C8—C7	2.2 (6)
O1—C1—C3—C8	178.1 (4)	C1—C3—C8—C7	-176.1 (4)
C8—C3—C4—C5	-0.3 (6)	C13—N1—C9—C10	-0.4 (7)
C1—C3—C4—C5	178.0 (4)	N1—C9—C10—C11	1.5 (7)
C3—C4—C5—C6	-1.9 (6)	C9—C10—C11—C12	-1.3 (7)
C3—C4—C5—C2	179.1 (4)	C9—C10—C11—C7	-179.2 (4)
O3—C2—C5—C4	11.1 (6)	C6—C7—C11—C10	-150.4 (4)
O4—C2—C5—C4	-170.3 (4)	C8—C7—C11—C10	29.3 (6)
O3—C2—C5—C6	-167.9 (4)	C6—C7—C11—C12	31.8 (6)
O4—C2—C5—C6	10.7 (6)	C8—C7—C11—C12	-148.5 (4)
C4—C5—C6—C7	2.2 (6)	C10—C11—C12—C13	0.2 (7)
C2—C5—C6—C7	-178.8 (4)	C7—C11—C12—C13	178.1 (4)
C5—C6—C7—C8	-0.2 (7)	C9—N1—C13—C12	-0.7 (8)
C5—C6—C7—C11	179.4 (4)	C11—C12—C13—N1	0.8 (7)

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O4 ⁱ	0.86	1.70	2.562 (4)	175
N1—H1 \cdots O3 ⁱ	0.86	2.67	3.252 (4)	126
O1—H1A \cdots O4 ⁱⁱ	0.82	1.96	2.643 (5)	141
C8—H8 \cdots O2 ⁱⁱⁱ	0.93	2.71	3.632 (5)	171
C10—H10 \cdots O2 ⁱⁱⁱ	0.93	2.58	3.225 (6)	127
C9—H9 \cdots O1 ^{iv}	0.93	2.59	3.316 (6)	135

Symmetry codes: (i) $-x+1/4, y-1/4, z-1/4$; (ii) $x+1/2, y, z-1/2$; (iii) $-x+1, -y, z$; (iv) $-x+3/4, y-1/4, z+1/4$.