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4,4′-Bipyridine–terephthalic acid (1/1)

Vandavasi Koteswara Rao, Matthias Zeller and Sherri R. Lovelace-Cameron*

Department of Chemistry, Youngstown State University, One University Plaza, Youngstown, OH 44555, USA
Correspondence e-mail: srlovelacecameron@ysu.edu

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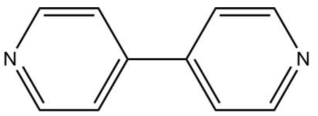
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.049; wR factor = 0.143; data-to-parameter ratio = 20.0.

The asymmetric unit of the title compound, $C_{10}H_8N_2 \cdot C_8H_6O_4$, consists of one half-molecule of each moiety, 4,4′-bipyridine (bpy) and terephthalic acid (bdc), both being located on crystallographic inversion centers. They are linked together *via* strong intermolecular O—H⋯N hydrogen bonds, forming infinite chains propagating along [1$\bar{2}$1]. The chains are further connected through C—H⋯O interactions giving sheets in (012). The sheets are linked *via* π–π interactions between the bpy rings and the bdc–bpy rings [centroid–centroid distances = 3.690 (2) and 3.869 (2) Å], resulting in the formation of a three-dimensional supramolecular layer-like structure.

Related literature

For dissolution of metal salts, see: Karpova *et al.* (2004); Yao *et al.* (2008); Zhao *et al.* (2007).



Experimental

Crystal data

$C_{10}H_8N_2 \cdot C_8H_6O_4$
M_r = 322.31
Triclinic, $P\bar{1}$
a = 6.783 (4) Å
b = 6.895 (4) Å
c = 8.161 (5) Å
α = 98.340 (8)°
β = 95.845 (9)°
γ = 104.623 (8)°
V = 361.5 (4) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 K
0.39 × 0.21 × 0.13 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2011)
T_{min} = 0.659, T_{max} = 0.746
4318 measured reflections
2215 independent reflections
1750 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.143
S = 1.05
2215 reflections
111 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2⋯N1^{i}	1.10	1.49	2.5899 (17)	175
C5—H5⋯O1^{ii}	0.95	2.50	3.231 (3)	134

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

Data collection: *APEX2* (Bruker, 2011); cell refinement: *SAINT* (Bruker, 2011); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXLE* (Hübschle *et al.*, 2011) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2418).

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supplementary materials

Acta Cryst. (2012). E**68**, o1711   [doi:10.1107/S1600536812021113]

4,4′-Bipyridine–terephthalic acid (1/1)

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Comment

The title organic compound was obtained as a side-product during part of our investigations into the solvothermal synthesis of magnesium based metal organic framework compounds. Reaction of magnesium nitrate with terephthalic acid and 4,4′-bipyridine at 373 K did not yield an extended framework, but the high solubility of magnesium nitrate in DMF led to formation of the title organic compound in the form of colorless rod-like crystals. Similar dissolution of metal salts in organic solvents, leaving the organic compound as a side-product, have previously been observed (Karpova *et al.*, 2004; Yao *et al.*, 2008; Zhao *et al.*, 2007).

The asymmetric unit of the title organic compound is composed of one half-molecule of each component, that is 4,4′-bipyridine (bpy) and terephthalic acid (bdc). The inversion symmetry within bpy and bdc generates the full molecules (Fig. 1).

Strong inter-molecular O—H···N hydrogen bonds between the bpy and bdc molecules lead to the formation of infinite one-dimensional chains propagating along [1 -2 1] (Table 1 and Fig. 2). The pyridine rings of the bpy molecule exhibit a planar configuration with a dihedral angle of 0° between the planes of the two pyridyl rings. The dihedral angle between the bpy and bdc molecules within the chains is 7.20 (4)°.

The bpy molecules and the bdc molecules in neighbouring chains are π-stacked above one another [centroid-centroid distance of 3.869 (2) Å; symmetry code: -x+1, -y, -z] in an *ABAB*···fashion resulting in a two-dimensional supramolecular layer-like structure (Fig. 2). The interplanar spacing between the chains, defined as the distance between the planes of neighbouring bpy rings is 3.2512 Å [centroid-centroid distance 3.690 (2) Å; slippage of 1.745 Å]. The layers, formed through π-stacking, are further connected through C-H···O interactions along (012) resulting in a three-dimensional supramolecular-like structure (Fig. 3). Thus the overall structure of the title compound is stabilized by strong hydrogen bonds and π-π interactions.

Experimental

The compound was synthesized under solvothermal conditions. In a typical synthesis, $Mg(NO_3)_2.6H_2O$ (0.129 g, 1.0 mmol) and terepthalic acid (0.169 g, 2.0 mmol) were dissolved in DMF (5.0 ml). Then, 4,4′-bipyridine (0.239 g, 3.0 mmol) was added to the reaction mixture and stirred for one hour before transferring the mixture into a glass vial. The final mixture was heated to 373 K (100 °C) for 24 h. The vial was then slowly cooled to room temperature. Slow cooling of the reaction mixture yielded colorless rod-like crystals of the title compound as a minor product, along with an unidentified white powder.

Refinement

The carboxylic acid H atoms were located in difference electron density maps, but were placed in calculated positions with fixed C—O—H angles, but with the C—C—O—H dihedral angles and the O—H distances freely refined (AFIX

148 command in *SHELXTL*; Sheldrick, 2008). The C-bound H atoms were included in calculated positions: C-H = 0.95 Å; $U_{\mathrm{iso}}(\mathrm{H}) = \mathrm{k} \times U_{\mathrm{eq}}(\mathrm{O,C})$, where k = 1.5 for carboxylic acid H atoms, and = 1.2 for other H atoms.

Computing details

Data collection: *APEX2* (Bruker, 2011); cell refinement: *SAINT* (Bruker, 2011); data reduction: *SAINT* (Bruker, 2011); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXLE* (Hübschle *et al.*, 2011) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

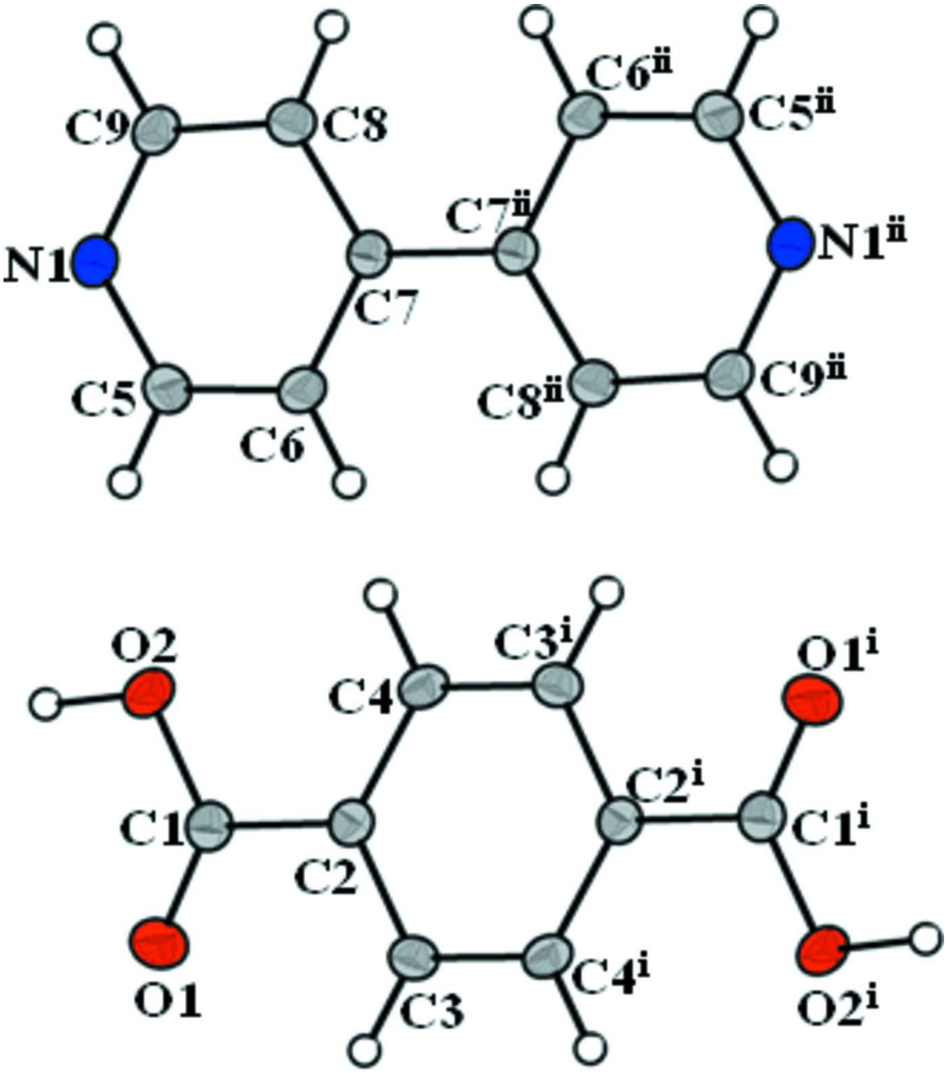

Figure 1

View of the title organic compound with atom numbering. Displacement ellipsoids are drawn at the 50% probability level [symmetry codes: (i) $-x$, $-y + 1$, $-z + 1$; (ii) $-x + 1$, $-y + 1$, $-z$].

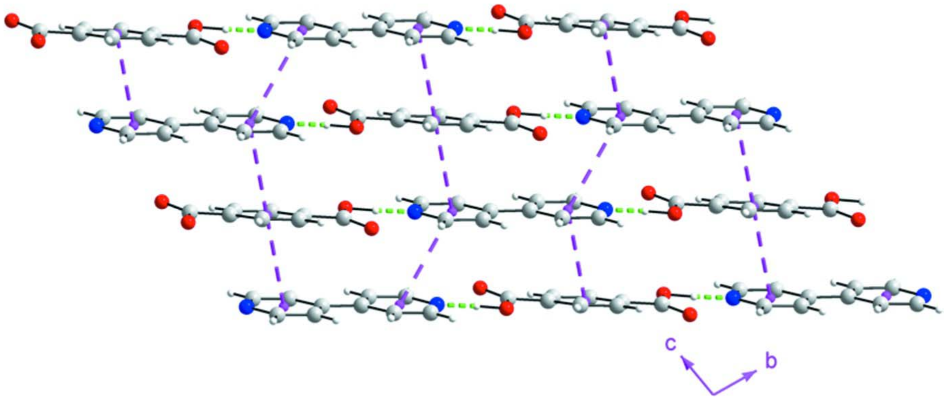

Figure 2

A view along the a axis of the two-dimensional supramolecular layer-like structure of the title compound. Green and purple dots represent the hydrogen bonds within the chains and the $\pi\cdots\pi$ stacking interactions between the chains, respectively [see Table 1 for details].

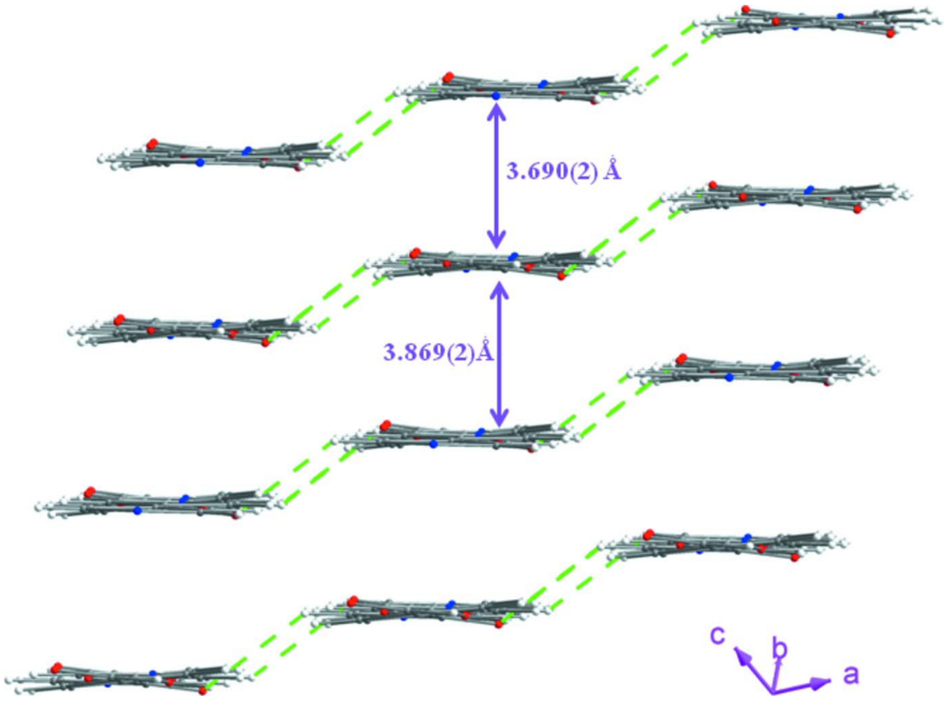

Figure 3

View of the three-dimensional supramolecular-like structure. Green dots represent the C-H···O hydrogen bonds connecting parallel stacks of chains. The purple arrows represent the π-π interactions within the π-stacks [see Table 1 for details].

4,4′-Bipyridine–terephthalic acid (1/1)

Crystal data

$C_{10}H_8N_2 \cdot C_8H_6O_4$	Hall symbol: -P 1
$M_r = 322.31$	$a = 6.783$ (4) Å
Triclinic, $P\overline{1}$	$b = 6.895$ (4) Å

c = 8.161 (5) Å
α = 98.340 (8)°
β = 95.845 (9)°
γ = 104.623 (8)°
V = 361.5 (4) Å^3
Z = 1
$F(000)$ = 168
D_x = 1.480 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 245 reflections
θ = 4.3–31.4°
μ = 0.11 mm^{-1}
T = 100 K
Rod, colorless
0.39 × 0.21 × 0.13 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2011)
$T_{\min}$ = 0.659, $T_{\max}$ = 0.746

4318 measured reflections
2215 independent reflections
1750 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
$\theta_{\max}$ = 31.5°, $\theta_{\min}$ = 2.6°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 9$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.143
S = 1.05
2215 reflections
111 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0819P)^2 + 0.0211P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.43 e Å^{-3}
$\Delta\rho_{\min}$ = −0.33 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	0.11190 (17)	0.19752 (17)	0.67373 (14)	0.0175 (2)
C2	0.05394 (16)	0.35241 (16)	0.58115 (13)	0.0155 (2)
C3	−0.14077 (17)	0.38403 (17)	0.58505 (14)	0.0178 (2)
H3	−0.2370	0.3048	0.6427	0.021*
C4	0.19359 (17)	0.46838 (17)	0.49560 (14)	0.0173 (2)
H4	0.3260	0.4464	0.4924	0.021*
C5	0.44781 (18)	0.16270 (17)	0.21492 (14)	0.0198 (2)
H5	0.3570	0.0943	0.2824	0.024*
C6	0.39356 (17)	0.31190 (17)	0.13785 (14)	0.0187 (2)

H6	0.2664	0.3421	0.1512	0.022*
C7	0.52575 (16)	0.41778 (16)	0.04063 (13)	0.0152 (2)
C8	0.70734 (17)	0.36148 (17)	0.02350 (14)	0.0181 (2)
H8	0.8020	0.4280	−0.0422	0.022*
C9	0.74945 (17)	0.20858 (17)	0.10241 (14)	0.0186 (2)
H9	0.8731	0.1714	0.0881	0.022*
N1	0.62329 (15)	0.11110 (14)	0.19795 (12)	0.0181 (2)
O1	0.00764 (13)	0.12024 (14)	0.77275 (11)	0.0266 (2)
O2	0.28465 (13)	0.15786 (13)	0.63990 (11)	0.0228 (2)
H2	0.3174 (12)	0.044 (2)	0.7131 (16)	0.034*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0174 (5)	0.0182 (5)	0.0173 (5)	0.0061 (4)	0.0004 (4)	0.0040 (4)
C2	0.0166 (5)	0.0167 (5)	0.0140 (5)	0.0060 (4)	0.0013 (4)	0.0032 (4)
C3	0.0165 (5)	0.0207 (5)	0.0181 (5)	0.0056 (4)	0.0042 (4)	0.0067 (4)
C4	0.0146 (5)	0.0214 (5)	0.0182 (5)	0.0079 (4)	0.0030 (4)	0.0047 (4)
C5	0.0202 (5)	0.0197 (5)	0.0214 (5)	0.0060 (4)	0.0046 (4)	0.0074 (4)
C6	0.0169 (5)	0.0207 (5)	0.0216 (5)	0.0086 (4)	0.0043 (4)	0.0065 (4)
C7	0.0152 (5)	0.0153 (5)	0.0149 (5)	0.0048 (4)	0.0002 (4)	0.0025 (4)
C8	0.0162 (5)	0.0205 (5)	0.0195 (5)	0.0063 (4)	0.0030 (4)	0.0064 (4)
C9	0.0159 (5)	0.0200 (5)	0.0214 (5)	0.0080 (4)	0.0010 (4)	0.0042 (4)
N1	0.0187 (5)	0.0179 (5)	0.0184 (5)	0.0069 (4)	−0.0001 (4)	0.0037 (3)
O1	0.0230 (4)	0.0325 (5)	0.0316 (5)	0.0112 (4)	0.0088 (4)	0.0193 (4)
O2	0.0222 (4)	0.0274 (5)	0.0267 (5)	0.0150 (3)	0.0080 (3)	0.0126 (3)

Geometric parameters (Å, º)

C1—O1	1.2198 (14)	C5—H5	0.9500
C1—O2	1.3152 (15)	C6—C7	1.3960 (16)
C1—C2	1.5004 (17)	C6—H6	0.9500
C2—C4	1.3922 (16)	C7—C8	1.3957 (16)
C2—C3	1.3945 (17)	C7—C7^{ii}	1.489 (2)
C3—C4^{i}	1.3883 (16)	C8—C9	1.3853 (16)
C3—H3	0.9500	C8—H8	0.9500
C4—C3^{i}	1.3883 (16)	C9—N1	1.3377 (15)
C4—H4	0.9500	C9—H9	0.9500
C5—N1	1.3399 (16)	O2—H2	1.1019
C5—C6	1.3859 (17)		
O1—C1—O2	124.24 (11)	C5—C6—C7	120.01 (11)
O1—C1—C2	121.98 (11)	C5—C6—H6	120.0
O2—C1—C2	113.77 (10)	C7—C6—H6	120.0
C4—C2—C3	119.74 (10)	C8—C7—C6	116.69 (10)
C4—C2—C1	120.93 (10)	C8—C7—C7^{ii}	121.97 (12)
C3—C2—C1	119.31 (10)	C6—C7—C7^{ii}	121.34 (12)
C4^{i}—C3—C2	119.79 (10)	C9—C8—C7	119.94 (10)
C4^{i}—C3—H3	120.1	C9—C8—H8	120.0
C2—C3—H3	120.1	C7—C8—H8	120.0

C3^{i}—C4—C2	120.48 (11)	N1—C9—C8	122.74 (11)
C3^{i}—C4—H4	119.8	N1—C9—H9	118.6
C2—C4—H4	119.8	C8—C9—H9	118.6
N1—C5—C6	122.57 (11)	C9—N1—C5	118.02 (10)
N1—C5—H5	118.7	C1—O2—H2	109.5
C6—C5—H5	118.7		

O1—C1—C2—C4	166.89 (11)	N1—C5—C6—C7	−1.27 (18)
O2—C1—C2—C4	−11.94 (15)	C5—C6—C7—C8	1.53 (17)
O1—C1—C2—C3	−11.33 (17)	C5—C6—C7—C7^{ii}	−178.58 (12)
O2—C1—C2—C3	169.83 (10)	C6—C7—C8—C9	−0.57 (17)
C4—C2—C3—C4^{i}	−0.35 (18)	C7^{ii}—C7—C8—C9	179.53 (11)
C1—C2—C3—C4^{i}	177.90 (10)	C7—C8—C9—N1	−0.75 (18)
C3—C2—C4—C3^{i}	0.35 (18)	C8—C9—N1—C5	1.07 (17)
C1—C2—C4—C3^{i}	−177.87 (10)	C6—C5—N1—C9	−0.05 (17)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···N1^{iii}	1.10	1.49	2.5899 (17)	175
C5—H5···O1^{iv}	0.95	2.50	3.231 (3)	134

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