

Crystal structures of (5*RS*)-(Z)-4-[5-(furan-2-yl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl]-4-oxobut-2-enoic acid and (5*RS*)-(Z)-4-[5-(furan-2-yl)-3-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrazol-1-yl]-4-oxobut-2-enoic acid

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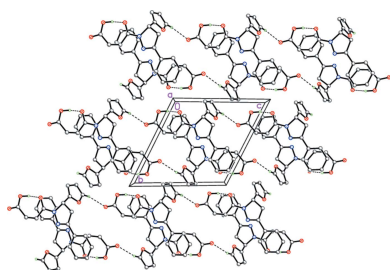
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The title compounds, C₁₇H₁₄N₂O₄ (I) and C₁₅H₁₂N₂O₄S (II), possess very similar molecular geometries. In both molecules, the central 1,3,5-trisubstituted dihydropyrazole ring adopts an envelope conformation. The oxobutenic acid fragment has an almost planar *Z* conformation [r.m.s. deviations of 0.049 and 0.022 Å, respectively, for (I) and (II)] which is determined by the both bond conjugation and the strong intramolecular O—H···O hydrogen bond. The substituents in positions 1 and 3 of the dihydropyrazole ring [oxobutenic acid and phenyl in (I) and oxobutenic acid and thienyl in (II)] are nearly coplanar with its basal plane [the corresponding dihedral angles are 6.14 (9) and 2.22 (11)° in (I) and 6.27 (12) and 3.91 (11)° in (II)]. The furyl ring plane is twisted relative to the basal plane of the dihydropyrazole ring by 85.51 (8) and 88.30 (7)° in (I) and (II), respectively. In the crystal of (I), molecules form zigzag hydrogen-bonded chains along [001] by C—H···O hydrogen bonds, which are further packed in stacks along [100]. Unlike (I), the crystal of (II) contains centrosymmetric hydrogen-bonded dimers formed by pairs of C—H···S hydrogen bonds, which are further linked by weak C—H···O hydrogen bonds into a three-dimensional framework.

1. Chemical context

3-(2-Furyl)pyrazolines and their *N*-acyl derivatives are well known to possess high and diverse biological activity, for example, topoisomerase I and II inhibitory and anti-proliferative activity (Ahmad *et al.*, 2016), 5 α -reductase inhibitory activity (Banday *et al.*, 2014), antibacterial (Joshi *et al.*, 2016; Bhoot *et al.*, 2012), antituberculous (Manna & Agrawal, 2010), anti-inflammatory (Shoman *et al.*, 2009), antifungal activity (Deng *et al.* 2012), and many others. Pyrazolines, fused with other heterocycles, are much less studied. Thus, the main goal of this work was the synthesis of maleic amides (I) and (II) from (*E*)-1-(furan-2-yl)-3-arylprop-2-en-1-ones (Fig. 1) with subsequent their transformation into 3b,6-epoxy-pyrazolo[5,1-*a*]isoindoles by a thermal intramolecular Diels–Alder reaction of furan (the IMDAF reaction). However, we were unable to realize the final stage of the



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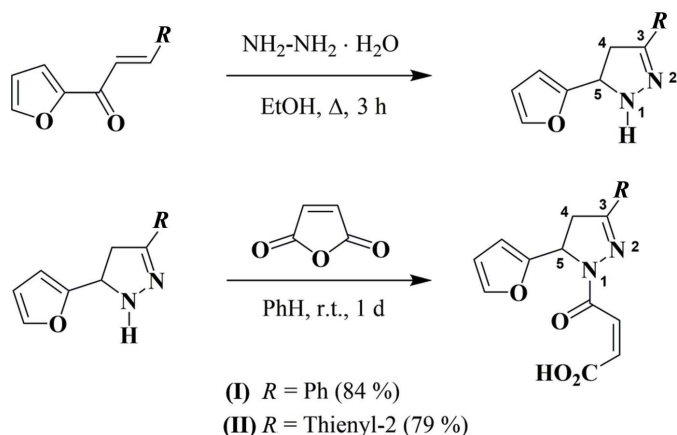
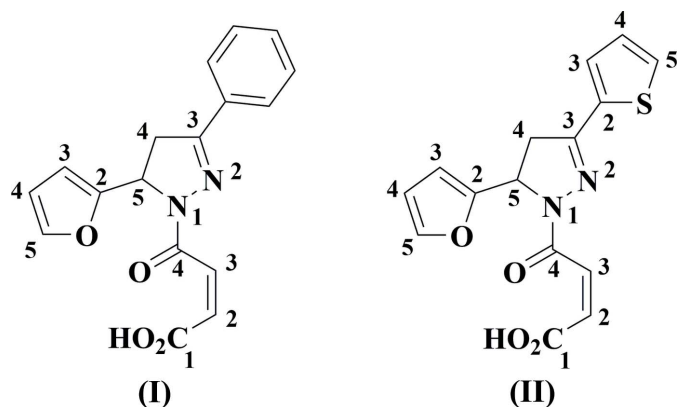


Figure 1
 Synthesis of maleic amides (I) and (II) from (*E*)-1-(furan-2-yl)-3-arylprop-2-en-1-ones.

purposed synthesis – the thermal IMDAF reaction of maleic amides (I) and (II) (Fig. 2). Unexpectedly, these compounds remained unchanged at temperatures up to 413 K. In order to explain this fact by an understanding of their stereochemical features, an X-ray diffraction study of compounds (I) and (II) was undertaken.



2. Structural commentary

Compounds (I), $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_4$, and (II), $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_4\text{S}$, possess very similar molecular geometries (Figs. 3 and 4). In both molecules, the central 1,3,5-trisubstituted dihydropyrazole ring adopts an envelope conformation, with the C5 carbon

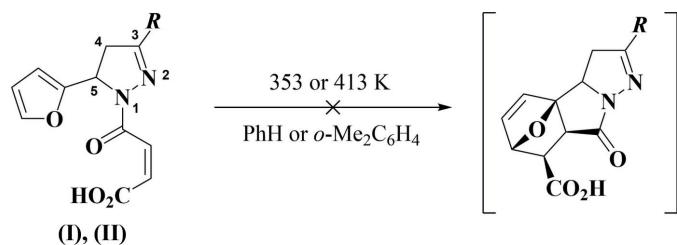


Figure 2
 The purposed thermal IMDAF reaction of maleic amides (I) and (II).

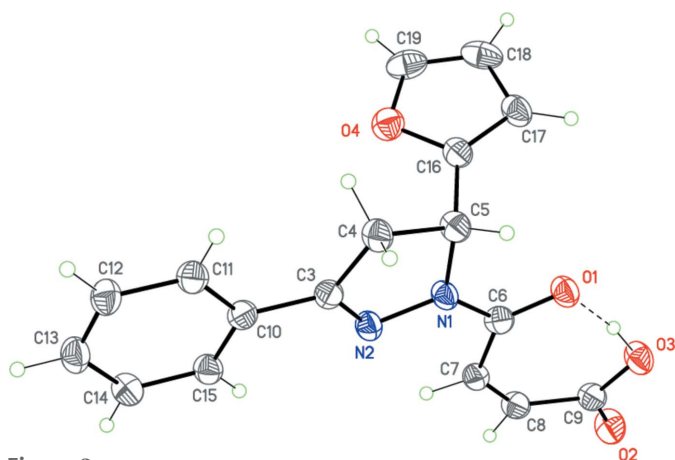


Figure 3
 The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as small spheres of arbitrary radius. The dashed line indicates the intramolecular O—H...O hydrogen bond.

atom deviating from the plane through the other atoms of the ring by 0.251 (3) and 0.178 (3) Å, respectively, in (I) and (II). The oxobutenoic acid fragment has an almost planar *Z* conformation [r.m.s. deviations of 0.049 and 0.022 Å, respectively, for (I) and (II)] which is determined by both the bond conjugation and the strong intramolecular O3—H3...O1 hydrogen bond (Tables 1 and 2, Figs. 3 and 4). The substituents in positions 1 and 3 of the dihydropyrazole ring [oxobutenoic acid and phenyl in (I) and oxobutenoic acid and thienyl in (II)] are practically coplanar with its basal plane [the corresponding dihedral angles are 6.14 (9) and 2.22 (11)° in (I) and 6.27 (12) and 3.91 (11)° in (II)]. Importantly, the furyl ring plane is twisted relative to the basal plane of the dihydropyrazole ring by 85.51 (8) and 88.30 (7)° in (I) and (II), respectively. Apparently, it is such a perpendicular arrangement of the furyl and oxobutenoic acid fragments that inhibits the IMDAF reaction between them.

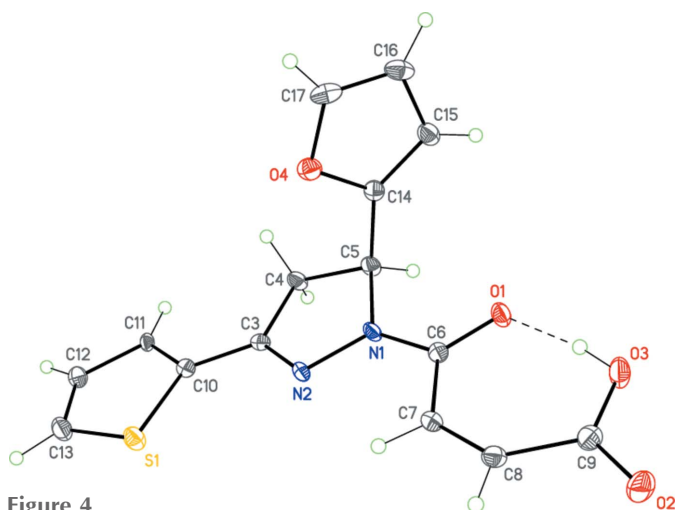


Figure 4
 The molecular structure of (II). Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as small spheres of arbitrary radius. The dashed line indicates the intramolecular O—H...O hydrogen bond.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3 \cdots O1	1.02 (3)	1.50 (3)	2.513 (2)	171 (2)
C19—H19 \cdots O2 ⁱ	0.95	2.40	3.266 (3)	152

Symmetry code: (i) $x, y, z - 1$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3 \cdots O1	0.88 (3)	1.64 (3)	2.5146 (19)	171 (2)
C4—H4B \cdots S1 ⁱ	0.99	2.85	3.820 (2)	165
C17—H17 \cdots O1 ⁱⁱ	0.95	2.51	3.426 (2)	161

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

The nitrogen atom N1 has a planar-trigonal geometry, the sum of the bond angles being 359.9° for (I) and 360.0° for (II). The bond lengths and angles in (I) and (II) are in good agreement with those observed in related structures (Suponitsky *et al.*, 2002; Guo, 2007; Vinutha *et al.*, 2013). The molecules possess an asymmetric center at the C5 carbon atom. The crystals of (I) and (II) are racemic and consist of (5*RS*)-enantiomeric pairs.

3. Supramolecular features

Although the similarity of the molecular geometries and intramolecular interactions might lead to similar packing motifs, this is not found in the case for (I) and (II). The intermolecular interactions, namely C—H \cdots O and C—H \cdots S hydrogen bonding, combined in a different way, give rise to different packing networks.

In the crystal of (I), molecules form zigzag hydrogen-bonded chains along [001] by the C19—H19 \cdots O2($x, y, z - 1$) hydrogen bonds (Table 1 and Fig. 5), which are further packed in stacks along [100] (Fig. 5).

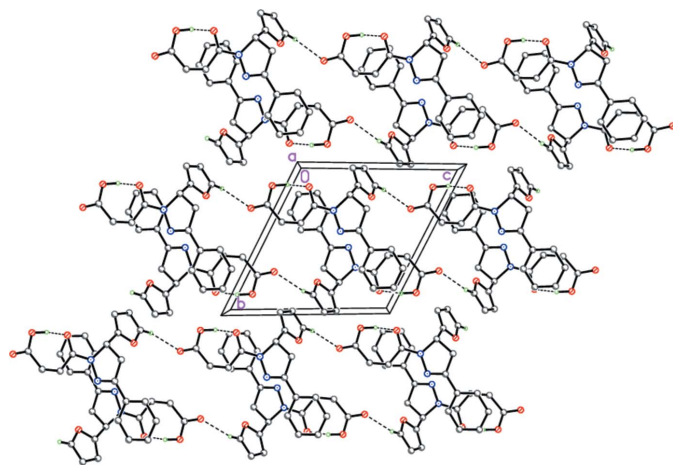


Figure 5
The crystal structure of (I) showing the hydrogen-bonded chains along [001]. Dashed lines indicate the intramolecular O—H \cdots O and intermolecular C—H \cdots O hydrogen bonds.

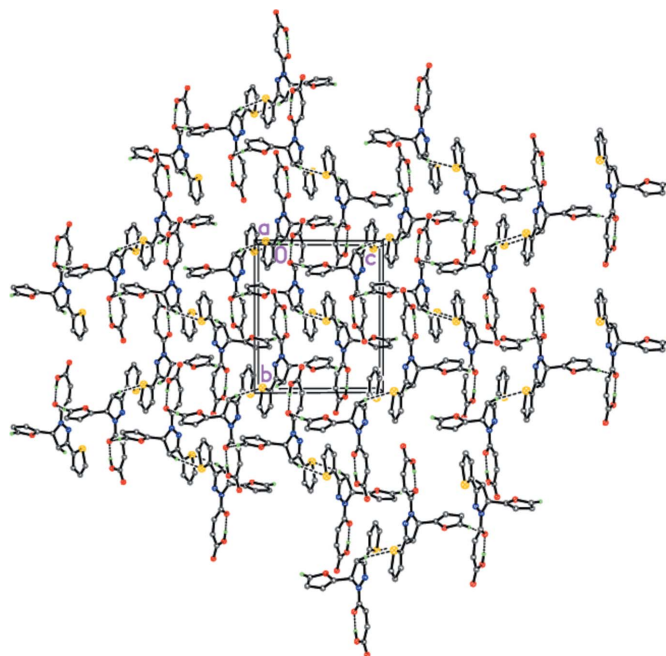


Figure 6
The crystal structure of (II) along the a axis. Dashed lines indicate the intramolecular O—H \cdots O and intermolecular C—H \cdots S and C—H \cdots O hydrogen bonds.

However, unlike in (I), the crystal of (II) contains centrosymmetric hydrogen-bonded dimers formed by the two C4—H4B \cdots S1($-x + 1, -y, -z + 2$) hydrogen bonds (Table 2 and Fig. 6), which are further linked by weak C17—H17 \cdots O1($x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$) hydrogen bonds into a three-dimensional framework (Table 3 and Fig. 6).

4. Synthesis and crystallization

The initial 5-(furan-2-yl)-3-aryl-4,5-dihydro-1*H*-pyrazoles were synthesized from (*E*)-1-(furan-2-yl)-3-arylprop-2-en-1-ones according to the procedure described previously (Grandberg *et al.* 1960; Kriven'ko *et al.* 2000; Cetin *et al.* 2003; Ozdemir *et al.* 2007).

General procedure. A solution of the corresponding (*E*)-1-(furan-2-yl)-3-arylprop-2-en-1-one (0.025 mol) in alcohol (15 mL) was added to a solution of hydrazine hydrate (2.5 mL, 0.05 mol) in alcohol (15 mL). The mixture was heated at reflux for 3–5 h (TLC monitoring), then the solvent and the excess of hydrazine hydrate were removed under reduced pressure. The residue, viscous brown oil, was dissolved in benzene (15 mL) and acylated (stirring at room temperature for 1 day) with a solution of maleic anhydride (2.45 g, 0.025 mol) in benzene (25 mL). The precipitated crystals were filtered off and recrystallized from an EtOH–DMF mixture to give the analytically pure maleic amides (I) and (II).

(5*RS*)-(Z)-4-[5-(Furan-2-yl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl]-4-oxobut-2-enoic acid (I). Colourless rhombic prisms. Yield is 4.88 g (63%). M.p. = 453.7–455.6 K with decomp. (EtOH–DMF). ¹H NMR (DMSO, 600 MHz, 303 K): δ = 3.40 (*dd*, 1H, H4A, $J_{4,4} = 17.7, J_{4A,5} = 5.0$), 3.76 (*dd*, 1H,

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C ₁₇ H ₁₄ N ₂ O ₄	C ₁₅ H ₁₂ N ₂ O ₄ S
<i>M_r</i>	310.30	316.33
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.2940 (15), 10.738 (2), 10.845 (2)	9.6702 (19), 13.150 (3), 11.240 (2)
α , β , γ (°)	114.10 (3), 102.46 (3), 97.57 (3)	90, 98.29 (3), 90
<i>V</i> (Å ³)	733.8 (3)	1414.4 (5)
<i>Z</i>	2	4
Radiation type	Synchrotron, $\lambda = 0.96990$ Å	Synchrotron, $\lambda = 0.96990$ Å
μ (mm ⁻¹)	0.22	0.58
Crystal size (mm)	0.20 × 0.07 × 0.07	0.40 × 0.30 × 0.20
Data collection		
Diffractometer	MAR CCD	MAR CCD
Absorption correction	Multi-scan (<i>SCALA</i> ; Evans, 2006)	Multi-scan (<i>SCALA</i> ; Evans, 2006)
<i>T</i> _{min} , <i>T</i> _{max}	0.950, 0.980	0.789, 0.876
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	10451, 2947, 2189	17279, 2961, 2685
<i>R</i> _{int}	0.103	0.087
(sin θ / λ) _{max} (Å ⁻¹)	0.641	0.642
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.075, 0.199, 1.04	0.045, 0.119, 1.05
No. of reflections	2947	2961
No. of parameters	212	203
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.41, -0.39	0.43, -0.52

Computer programs: *Automar* (MarXperts, 2015), *iMOSFLM* (Battye *et al.*, 2011), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

H4B, *J*_{4,4} = 17.7, *J*_{4B,5} = 11.8), 5.70 (*dd*, 1H, H5, *J*_{5,4A} = 5.0, *J*_{4B,5} = 11.8), 6.29 (*d*, 1H, -CH=CH-CO₂H, *J* = 12.1), 6.39–6.41 [*m*, 2H, H3 and H4 (furyl)], 6.91 (*d*, 1H, -CH=CH-CO₂H, *J* = 12.1), 7.44–7.49 [*m*, 3H, H3, H4 and H5 (Ph)], 7.57 [*m*, 1H, H5 (furyl)], 7.77–7.79 [*m*, 2H, H2 and H6 (Ph)], 12.29 (*br s*, 1H, CO₂H). ¹³C NMR (DMSO-*d*₆, 150.9 MHz, 303 K): δ = 38.8 (C4), 54.0 (C5), 107.9 and 111.0 [C3 and C4 (furyl)], 127.3 [2C, C3 and C5 (Ph)], 129.4 [2C, C2 and C6 (Ph)], 130.1, 131.0, 131.17 [C1 (Ph)], 131.20, 143.0 [C5 (Furyl)], 152.6, 156.2, 163.0, 167.4.

(5*RS*)-(Z)-4-[5-(Furan-2-yl)-3-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrazol-1-yl]-4-oxobut-2-enoic acid (II). Light-yellow rhombic prisms. Yield is 4.03 g (51%). M.p. = 449.8–450.9 K with decomp. (EtOH–DMF). ¹H NMR (DMSO, 600 MHz, 301 K): δ = 3.41 (*dd*, 1H, H4A, *J*_{4,4} = 17.5, *J*_{4A,5} = 4.4), 3.76 (*dd*, 1H, H4B, *J*_{4,4} = 17.5, *J*_{4B,5} = 11.8), 5.69 (*dd*, 1H, H5, *J*_{5,4A} = 4.4, *J*_{4B,5} = 11.8), 6.30 (*d*, 1H, -CH=CH-CO₂H, *J* = 12.1), 6.39–6.41 [*m*, 2H, H3 and H4 (furyl)], 6.81 (*d*, 1H, -CH=CH-CO₂H, *J* = 12.1), 7.16 [*dd*, 1H, H4 (thienyl), *J*_{3,4} = 3.5, *J*_{4,5} = 4.9], 7.52 [*dd*, 1H, H3 (thienyl), *J*_{3,4} = 3.5, *J*_{3,5} = 1.3], 7.57 [*m*, 1H, H5 (furyl)], 7.75 [*dd*, 1H, H5 (thienyl), *J*_{3,5} = 1.3, *J*_{4,5} = 4.9], 12.8 (*br s*, 1H, CO₂H). ¹³C NMR (DMSO, 150.9 MHz, 301 K): δ = 39.5 (C4), 54.1 (C5), 108.0, 111.1, 128.7, 130.3, 130.6, 130.8, 131.4, 134.2 [C1 (Ph)], 143.1 [C5 (furyl)], 152.1, 152.4, 162.7, 167.3.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. X-ray diffraction studies were carried out on the ‘Belok’ beamline ($\lambda = 0.96990$ Å) of the National Research Center “Kurchatov Institute” (Moscow, Russian Federation) using a MAR CCD detector. For each compound a total of 360 images were collected using an oscillation range of 1.0° (φ scan mode, two different crystal orientations) and corrected for absorption using the *SCALA* program (Evans, 2006). The data were indexed, integrated and scaled using the utility *iMOSFLM* in *CCP4* (Battye *et al.*, 2011).

The hydrogen atoms of the hydroxyl groups were localized in difference-Fourier maps and refined in an isotropic approximation with fixed displacement parameters [*U*_{iso}(H) = 1.5*U*_{eq}(O)]. The other hydrogen atoms were placed in calculated positions with C–H = 0.95–1.00 Å and refined using a riding model with fixed isotropic displacement parameters [*U*_{iso}(H) = 1.2*U*_{eq}(C)].

The insufficient data completeness of 96.7% in the case of (I) is determined by the low (triclinic) crystal symmetry. It is very difficult to get good data completeness at this symmetry using the φ scan mode only (‘Belok’ beamline limitation), even though we have run two different crystal orientations.

Acknowledgements

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supporting information

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Crystal structures of (5*RS*)-(Z)-4-[5-(furan-2-yl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl]-4-oxobut-2-enoic acid and (5*RS*)-(Z)-4-[5-(furan-2-yl)-3-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrazol-1-yl]-4-oxobut-2-enoic acid

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Computing details

For both compounds, data collection: *Automar* (MarXperts, 2015); cell refinement: *iMOSFLM* (Battye *et al.*, 2011); data reduction: *iMOSFLM* (Battye *et al.*, 2011); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(I) (5*RS*)-(Z)-4-[5-(Furan-2-yl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl]-4-oxobut-2-enoic acid

Crystal data

$C_{17}H_{14}N_2O_4$	$Z = 2$
$M_r = 310.30$	$F(000) = 324$
Triclinic, $P\bar{1}$	$D_x = 1.404 \text{ Mg m}^{-3}$
$a = 7.2940 (15) \text{ \AA}$	Synchrotron radiation, $\lambda = 0.96990 \text{ \AA}$
$b = 10.738 (2) \text{ \AA}$	Cell parameters from 500 reflections
$c = 10.845 (2) \text{ \AA}$	$\theta = 4.0\text{--}36.0^\circ$
$\alpha = 114.10 (3)^\circ$	$\mu = 0.22 \text{ mm}^{-1}$
$\beta = 102.46 (3)^\circ$	$T = 100 \text{ K}$
$\gamma = 97.57 (3)^\circ$	Needle, colourless
$V = 733.8 (3) \text{ \AA}^3$	$0.20 \times 0.07 \times 0.07 \text{ mm}$

Data collection

MAR CCD	2947 independent reflections
diffractometer	2189 reflections with $I > 2\sigma(I)$
θ scan	$R_{\text{int}} = 0.103$
Absorption correction: multi-scan	$\theta_{\text{max}} = 38.4^\circ$, $\theta_{\text{min}} = 4.0^\circ$
(SCALA; Evans, 2006)	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.950$, $T_{\text{max}} = 0.980$	$k = -13 \rightarrow 12$
10451 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	212 parameters
Least-squares matrix: full	0 restraints
$R[F^2 > 2\sigma(F^2)] = 0.075$	Primary atom site location: difference Fourier map
$wR(F^2) = 0.199$	Secondary atom site location: difference Fourier map
$S = 1.04$	
2947 reflections	

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.088P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.41 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL2014

(Sheldrick, 2015),

$$F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.112 (13)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.53546 (18)	0.85698 (13)	0.87765 (13)	0.0294 (4)
O2	0.8189 (2)	0.71553 (16)	1.17671 (15)	0.0402 (5)
O3	0.7068 (2)	0.86788 (15)	1.11054 (15)	0.0351 (5)
H3	0.644 (3)	0.874 (2)	1.020 (3)	0.053*
O4	0.55732 (19)	0.79397 (15)	0.46578 (14)	0.0329 (5)
N1	0.3716 (2)	0.69540 (16)	0.65583 (16)	0.0249 (5)
N2	0.2966 (2)	0.55549 (16)	0.54965 (17)	0.0256 (5)
C3	0.1865 (2)	0.5590 (2)	0.4406 (2)	0.0242 (5)
C4	0.1695 (3)	0.7049 (2)	0.4619 (2)	0.0275 (5)
H4A	0.0397	0.7182	0.4690	0.033*
H4B	0.1943	0.7229	0.3837	0.033*
C5	0.3284 (3)	0.8010 (2)	0.6030 (2)	0.0269 (5)
H5	0.2761	0.8733	0.6688	0.032*
C6	0.4790 (2)	0.7294 (2)	0.7886 (2)	0.0259 (5)
C7	0.5227 (3)	0.6115 (2)	0.8181 (2)	0.0266 (5)
H7	0.4700	0.5198	0.7415	0.032*
C8	0.6277 (3)	0.6188 (2)	0.9400 (2)	0.0286 (5)
H8	0.6429	0.5301	0.9337	0.034*
C9	0.7259 (3)	0.7393 (2)	1.0843 (2)	0.0293 (6)
C10	0.0858 (2)	0.4281 (2)	0.30984 (19)	0.0254 (5)
C11	-0.0296 (3)	0.4332 (2)	0.1915 (2)	0.0278 (5)
H11	-0.0446	0.5212	0.1955	0.033*
C12	-0.1226 (3)	0.3089 (2)	0.0676 (2)	0.0304 (6)
H12	-0.1982	0.3128	-0.0133	0.036*
C13	-0.1049 (3)	0.1801 (2)	0.0623 (2)	0.0319 (6)
H13	-0.1711	0.0958	-0.0215	0.038*
C14	0.0096 (3)	0.1735 (2)	0.1793 (2)	0.0307 (6)
H14	0.0216	0.0849	0.1751	0.037*
C15	0.1064 (3)	0.2973 (2)	0.3027 (2)	0.0268 (5)
H15	0.1864	0.2931	0.3819	0.032*
C16	0.5068 (3)	0.8691 (2)	0.5855 (2)	0.0268 (5)
C17	0.6447 (3)	0.9908 (2)	0.6709 (2)	0.0311 (6)

H17	0.6450	1.0607	0.7600	0.037*
C18	0.7893 (3)	0.9938 (2)	0.6013 (2)	0.0374 (6)
H18	0.9041	1.0661	0.6349	0.045*
C19	0.7316 (3)	0.8742 (2)	0.4787 (2)	0.0374 (6)
H19	0.8007	0.8486	0.4109	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0309 (7)	0.0236 (8)	0.0258 (8)	0.0015 (6)	0.0020 (6)	0.0084 (6)
O2	0.0480 (9)	0.0376 (9)	0.0283 (9)	0.0095 (7)	−0.0028 (7)	0.0158 (7)
O3	0.0433 (9)	0.0276 (9)	0.0251 (8)	0.0041 (6)	−0.0018 (7)	0.0105 (7)
O4	0.0305 (8)	0.0355 (9)	0.0305 (9)	0.0058 (6)	0.0069 (6)	0.0146 (7)
N1	0.0260 (8)	0.0210 (9)	0.0214 (9)	0.0011 (7)	0.0002 (7)	0.0085 (7)
N2	0.0249 (8)	0.0232 (9)	0.0228 (9)	0.0021 (7)	0.0034 (7)	0.0078 (7)
C3	0.0211 (9)	0.0262 (11)	0.0237 (11)	0.0041 (8)	0.0065 (8)	0.0105 (9)
C4	0.0229 (9)	0.0286 (11)	0.0248 (11)	0.0021 (8)	0.0008 (8)	0.0106 (9)
C5	0.0260 (9)	0.0263 (11)	0.0246 (10)	0.0043 (8)	0.0004 (8)	0.0122 (9)
C6	0.0216 (9)	0.0295 (11)	0.0244 (11)	0.0027 (8)	0.0030 (8)	0.0132 (9)
C7	0.0274 (9)	0.0248 (11)	0.0240 (10)	0.0020 (8)	0.0053 (8)	0.0099 (9)
C8	0.0280 (10)	0.0287 (11)	0.0276 (11)	0.0035 (8)	0.0039 (8)	0.0145 (9)
C9	0.0302 (10)	0.0293 (12)	0.0266 (11)	0.0043 (8)	0.0039 (8)	0.0140 (9)
C10	0.0218 (9)	0.0295 (12)	0.0234 (11)	0.0032 (8)	0.0051 (8)	0.0122 (9)
C11	0.0255 (9)	0.0293 (11)	0.0259 (11)	0.0041 (8)	0.0037 (8)	0.0128 (9)
C12	0.0283 (10)	0.0326 (12)	0.0237 (11)	0.0043 (9)	0.0019 (8)	0.0105 (9)
C13	0.0288 (10)	0.0315 (12)	0.0254 (11)	0.0025 (8)	0.0022 (8)	0.0079 (9)
C14	0.0293 (10)	0.0275 (11)	0.0325 (12)	0.0052 (8)	0.0064 (9)	0.0127 (9)
C15	0.0243 (9)	0.0275 (11)	0.0260 (11)	0.0040 (8)	0.0043 (8)	0.0119 (9)
C16	0.0279 (10)	0.0242 (11)	0.0246 (10)	0.0040 (8)	0.0005 (8)	0.0118 (9)
C17	0.0300 (10)	0.0250 (11)	0.0283 (11)	−0.0009 (8)	−0.0015 (8)	0.0100 (9)
C18	0.0252 (10)	0.0400 (13)	0.0512 (14)	0.0009 (9)	0.0019 (9)	0.0314 (12)
C19	0.0283 (10)	0.0525 (15)	0.0437 (14)	0.0105 (10)	0.0103 (9)	0.0334 (12)

Geometric parameters (Å, °)

O1—C6	1.256 (2)	C8—C9	1.501 (3)
O2—C9	1.222 (2)	C8—H8	0.9500
O3—C9	1.324 (3)	C10—C11	1.400 (3)
O3—H3	1.02 (3)	C10—C15	1.405 (3)
O4—C16	1.379 (3)	C11—C12	1.396 (3)
O4—C19	1.384 (2)	C11—H11	0.9500
N1—C6	1.352 (2)	C12—C13	1.386 (3)
N1—N2	1.408 (2)	C12—H12	0.9500
N1—C5	1.504 (2)	C13—C14	1.395 (3)
N2—C3	1.295 (2)	C13—H13	0.9500
C3—C10	1.475 (3)	C14—C15	1.396 (3)
C3—C4	1.515 (3)	C14—H14	0.9500
C4—C5	1.542 (3)	C15—H15	0.9500

C4—H4A	0.9900	C16—C17	1.357 (3)
C4—H4B	0.9900	C17—C18	1.428 (3)
C5—C16	1.494 (3)	C17—H17	0.9500
C5—H5	1.0000	C18—C19	1.348 (3)
C6—C7	1.483 (3)	C18—H18	0.9500
C7—C8	1.343 (3)	C19—H19	0.9500
C7—H7	0.9500		
C9—O3—H3	111.6 (14)	O3—C9—C8	120.10 (18)
C16—O4—C19	106.22 (16)	C11—C10—C15	119.44 (17)
C6—N1—N2	122.90 (16)	C11—C10—C3	120.42 (19)
C6—N1—C5	124.32 (15)	C15—C10—C3	120.14 (17)
N2—N1—C5	112.71 (14)	C12—C11—C10	120.0 (2)
C3—N2—N1	107.28 (16)	C12—C11—H11	120.0
N2—C3—C10	120.85 (18)	C10—C11—H11	120.0
N2—C3—C4	114.48 (16)	C13—C12—C11	120.21 (19)
C10—C3—C4	124.66 (16)	C13—C12—H12	119.9
C3—C4—C5	102.65 (15)	C11—C12—H12	119.9
C3—C4—H4A	111.2	C12—C13—C14	120.36 (18)
C5—C4—H4A	111.2	C12—C13—H13	119.8
C3—C4—H4B	111.2	C14—C13—H13	119.8
C5—C4—H4B	111.2	C13—C14—C15	119.85 (19)
H4A—C4—H4B	109.1	C13—C14—H14	120.1
C16—C5—N1	110.07 (15)	C15—C14—H14	120.1
C16—C5—C4	113.66 (17)	C14—C15—C10	120.09 (18)
N1—C5—C4	100.45 (14)	C14—C15—H15	120.0
C16—C5—H5	110.8	C10—C15—H15	120.0
N1—C5—H5	110.8	C17—C16—O4	109.89 (18)
C4—C5—H5	110.8	C17—C16—C5	132.7 (2)
O1—C6—N1	118.52 (17)	O4—C16—C5	117.25 (16)
O1—C6—C7	124.58 (16)	C16—C17—C18	106.85 (19)
N1—C6—C7	116.90 (17)	C16—C17—H17	126.6
C8—C7—C6	127.84 (18)	C18—C17—H17	126.6
C8—C7—H7	116.1	C19—C18—C17	106.76 (18)
C6—C7—H7	116.1	C19—C18—H18	126.6
C7—C8—C9	132.8 (2)	C17—C18—H18	126.6
C7—C8—H8	113.6	C18—C19—O4	110.3 (2)
C9—C8—H8	113.6	C18—C19—H19	124.9
O2—C9—O3	121.15 (18)	O4—C19—H19	124.9
O2—C9—C8	118.72 (19)		
C6—N1—N2—C3	173.99 (17)	C4—C3—C10—C11	2.7 (3)
C5—N1—N2—C3	-9.2 (2)	N2—C3—C10—C15	0.8 (3)
N1—N2—C3—C10	179.71 (16)	C4—C3—C10—C15	-177.85 (17)
N1—N2—C3—C4	-1.5 (2)	C15—C10—C11—C12	-0.2 (3)
N2—C3—C4—C5	10.8 (2)	C3—C10—C11—C12	179.26 (18)
C10—C3—C4—C5	-170.49 (19)	C10—C11—C12—C13	1.5 (3)
C6—N1—C5—C16	71.7 (2)	C11—C12—C13—C14	-1.5 (3)

N2—N1—C5—C16	-105.08 (17)	C12—C13—C14—C15	0.2 (3)
C6—N1—C5—C4	-168.17 (19)	C13—C14—C15—C10	1.2 (3)
N2—N1—C5—C4	15.0 (2)	C11—C10—C15—C14	-1.2 (3)
C3—C4—C5—C16	103.36 (18)	C3—C10—C15—C14	179.38 (18)
C3—C4—C5—N1	-14.14 (18)	C19—O4—C16—C17	-0.7 (2)
N2—N1—C6—O1	-178.08 (16)	C19—O4—C16—C5	-176.11 (16)
C5—N1—C6—O1	5.4 (3)	N1—C5—C16—C17	-95.2 (3)
N2—N1—C6—C7	2.3 (3)	C4—C5—C16—C17	153.0 (2)
C5—N1—C6—C7	-174.19 (17)	N1—C5—C16—O4	78.9 (2)
O1—C6—C7—C8	-0.6 (3)	C4—C5—C16—O4	-32.8 (2)
N1—C6—C7—C8	179.0 (2)	O4—C16—C17—C18	0.6 (2)
C6—C7—C8—C9	3.2 (4)	C5—C16—C17—C18	175.1 (2)
C7—C8—C9—O2	-177.6 (2)	C16—C17—C18—C19	-0.3 (2)
C7—C8—C9—O3	4.1 (4)	C17—C18—C19—O4	-0.2 (2)
N2—C3—C10—C11	-178.62 (16)	C16—O4—C19—C18	0.5 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3...O1	1.02 (3)	1.50 (3)	2.513 (2)	171 (2)
C19—H19...O2 ⁱ	0.95	2.40	3.266 (3)	152

Symmetry code: (i) *x*, *y*, *z*-1.**(II) (5*RS*)-(Z)-4-[5-(Furan-2-yl)-3-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrazol-1-yl]-4-oxobut-2-enoic acid***Crystal data*C₁₅H₁₂N₂O₄S*M_r* = 316.33Monoclinic, *P*2₁/*n**a* = 9.6702 (19) Å*b* = 13.150 (3) Å*c* = 11.240 (2) Å

β = 98.29 (3)°

V = 1414.4 (5) Å³*Z* = 4*F*(000) = 656*D_x* = 1.485 Mg m⁻³

Synchrotron radiation, λ = 0.96990 Å

Cell parameters from 600 reflections

θ = 3.6–36.0°

μ = 0.58 mm⁻¹*T* = 100 K

Prism, colourless

0.40 × 0.30 × 0.20 mm

Data collection

MAR CCD

diffractometer

/θ scan

Absorption correction: multi-scan

(SCALA; Evans, 2006)

T_{min} = 0.789, *T_{max}* = 0.876

17279 measured reflections

2961 independent reflections

2685 reflections with *I* > 2σ(*I*)*R_{int}* = 0.087θ_{max} = 38.5°, θ_{min} = 3.6°*h* = -12→12*k* = -16→14*l* = -13→14*Refinement*Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.045*wR*(*F*²) = 0.119*S* = 1.05

2961 reflections

203 parameters

0 restraints

Primary atom site location: difference Fourier map

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

$$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 1.1417P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL2014

(Sheldrick, 2015),

$$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.029 (2)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.18979 (4)	0.02971 (3)	0.94264 (4)	0.01637 (17)
O1	0.62416 (12)	0.37278 (9)	0.76273 (11)	0.0158 (3)
O2	0.46922 (14)	0.66885 (9)	0.86341 (12)	0.0226 (3)
O3	0.60922 (13)	0.56265 (10)	0.78427 (12)	0.0206 (3)
H3	0.621 (3)	0.497 (2)	0.772 (2)	0.031*
O4	0.44618 (12)	0.14434 (10)	0.54975 (11)	0.0165 (3)
N1	0.50566 (14)	0.23234 (10)	0.79925 (12)	0.0118 (3)
N2	0.40101 (14)	0.17978 (11)	0.84886 (12)	0.0120 (3)
C3	0.42845 (16)	0.08325 (12)	0.84155 (14)	0.0114 (3)
C4	0.55685 (17)	0.05821 (13)	0.78427 (15)	0.0133 (3)
H4A	0.5342	0.0104	0.7162	0.016*
H4B	0.6316	0.0285	0.8436	0.016*
C5	0.59983 (16)	0.16366 (12)	0.74062 (15)	0.0124 (3)
H5	0.6999	0.1781	0.7723	0.015*
C6	0.52109 (17)	0.33450 (12)	0.80326 (15)	0.0117 (3)
C7	0.41319 (17)	0.39413 (13)	0.85407 (15)	0.0134 (3)
H7	0.3409	0.3558	0.8819	0.016*
C8	0.40489 (18)	0.49611 (13)	0.86571 (15)	0.0147 (4)
H8	0.3246	0.5181	0.8984	0.018*
C9	0.49805 (18)	0.58175 (13)	0.83701 (15)	0.0158 (4)
C10	0.34310 (17)	0.00445 (13)	0.88510 (14)	0.0123 (3)
C11	0.37250 (16)	-0.10024 (12)	0.88526 (14)	0.0107 (3)
H11	0.4522	-0.1292	0.8579	0.013*
C12	0.26597 (18)	-0.15765 (13)	0.93240 (16)	0.0154 (4)
H12	0.2672	-0.2296	0.9397	0.019*
C13	0.16253 (18)	-0.09732 (14)	0.96569 (16)	0.0178 (4)
H13	0.0841	-0.1231	0.9981	0.021*
C14	0.57458 (17)	0.17614 (12)	0.60747 (15)	0.0125 (3)
C15	0.65215 (18)	0.21555 (13)	0.52703 (16)	0.0162 (4)
H15	0.7443	0.2419	0.5440	0.019*
C16	0.56731 (19)	0.20951 (14)	0.41102 (16)	0.0189 (4)

H16	0.5922	0.2313	0.3364	0.023*
C17	0.44516 (19)	0.16660 (14)	0.42938 (16)	0.0188 (4)
H17	0.3690	0.1535	0.3680	0.023*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0148 (3)	0.0149 (3)	0.0206 (3)	0.00060 (15)	0.00654 (18)	0.00097 (15)
O1	0.0136 (6)	0.0140 (6)	0.0213 (7)	-0.0020 (4)	0.0077 (5)	0.0004 (5)
O2	0.0310 (8)	0.0120 (6)	0.0251 (7)	0.0012 (5)	0.0054 (6)	-0.0003 (5)
O3	0.0192 (6)	0.0131 (6)	0.0311 (8)	-0.0036 (5)	0.0087 (5)	-0.0009 (5)
O4	0.0129 (6)	0.0211 (6)	0.0155 (6)	0.0007 (5)	0.0024 (5)	-0.0019 (5)
N1	0.0115 (7)	0.0111 (7)	0.0144 (7)	-0.0004 (5)	0.0072 (5)	0.0005 (5)
N2	0.0119 (7)	0.0123 (7)	0.0128 (7)	-0.0027 (5)	0.0052 (5)	0.0007 (5)
C3	0.0124 (7)	0.0129 (8)	0.0091 (8)	0.0004 (6)	0.0023 (6)	-0.0005 (6)
C4	0.0136 (8)	0.0132 (8)	0.0143 (8)	0.0014 (6)	0.0062 (6)	0.0007 (6)
C5	0.0105 (7)	0.0118 (8)	0.0160 (8)	0.0022 (6)	0.0061 (6)	-0.0007 (6)
C6	0.0115 (8)	0.0120 (8)	0.0115 (8)	-0.0002 (6)	0.0014 (6)	0.0004 (6)
C7	0.0131 (8)	0.0145 (8)	0.0136 (8)	-0.0008 (6)	0.0049 (6)	-0.0008 (6)
C8	0.0154 (8)	0.0157 (8)	0.0137 (8)	0.0009 (7)	0.0042 (6)	-0.0009 (7)
C9	0.0194 (8)	0.0141 (8)	0.0134 (8)	0.0002 (7)	0.0007 (6)	0.0009 (6)
C10	0.0131 (8)	0.0123 (8)	0.0118 (8)	-0.0009 (6)	0.0025 (6)	-0.0004 (6)
C11	0.0118 (7)	0.0109 (7)	0.0093 (7)	-0.0043 (6)	0.0006 (6)	0.0017 (6)
C12	0.0180 (8)	0.0130 (8)	0.0158 (8)	-0.0030 (6)	0.0041 (6)	0.0012 (6)
C13	0.0159 (8)	0.0183 (9)	0.0203 (9)	-0.0028 (7)	0.0062 (7)	0.0011 (7)
C14	0.0110 (7)	0.0119 (8)	0.0152 (8)	0.0016 (6)	0.0035 (6)	-0.0011 (6)
C15	0.0178 (8)	0.0140 (8)	0.0181 (9)	0.0003 (6)	0.0073 (7)	0.0004 (6)
C16	0.0278 (9)	0.0163 (8)	0.0138 (9)	0.0059 (7)	0.0072 (7)	0.0007 (7)
C17	0.0228 (9)	0.0204 (9)	0.0125 (9)	0.0072 (7)	0.0004 (7)	-0.0033 (7)

Geometric parameters (Å, °)

S1—C13	1.7166 (19)	C5—H5	1.0000
S1—C10	1.7330 (17)	C6—C7	1.484 (2)
O1—C6	1.2592 (19)	C7—C8	1.351 (2)
O2—C9	1.225 (2)	C7—H7	0.9500
O3—C9	1.324 (2)	C8—C9	1.506 (2)
O3—H3	0.88 (3)	C8—H8	0.9500
O4—C14	1.380 (2)	C10—C11	1.406 (2)
O4—C17	1.383 (2)	C11—C12	1.439 (2)
N1—C6	1.352 (2)	C11—H11	0.9500
N1—N2	1.4056 (17)	C12—C13	1.370 (2)
N1—C5	1.5007 (19)	C12—H12	0.9500
N2—C3	1.302 (2)	C13—H13	0.9500
C3—C10	1.453 (2)	C14—C15	1.358 (2)
C3—C4	1.515 (2)	C15—C16	1.439 (3)
C4—C5	1.548 (2)	C15—H15	0.9500
C4—H4A	0.9900	C16—C17	1.351 (3)

C4—H4B	0.9900	C16—H16	0.9500
C5—C14	1.490 (2)	C17—H17	0.9500
C13—S1—C10	91.61 (8)	C7—C8—H8	113.7
C9—O3—H3	113.0 (16)	C9—C8—H8	113.7
C14—O4—C17	105.94 (13)	O2—C9—O3	120.88 (16)
C6—N1—N2	123.90 (13)	O2—C9—C8	118.89 (16)
C6—N1—C5	122.81 (13)	O3—C9—C8	120.23 (15)
N2—N1—C5	113.29 (12)	C11—C10—C3	125.05 (15)
C3—N2—N1	106.83 (12)	C11—C10—S1	111.78 (12)
N2—C3—C10	122.91 (14)	C3—C10—S1	123.17 (13)
N2—C3—C4	115.19 (14)	C10—C11—C12	111.03 (14)
C10—C3—C4	121.90 (14)	C10—C11—H11	124.5
C3—C4—C5	102.36 (13)	C12—C11—H11	124.5
C3—C4—H4A	111.3	C13—C12—C11	112.74 (15)
C5—C4—H4A	111.3	C13—C12—H12	123.6
C3—C4—H4B	111.3	C11—C12—H12	123.6
C5—C4—H4B	111.3	C12—C13—S1	112.84 (13)
H4A—C4—H4B	109.2	C12—C13—H13	123.6
C14—C5—N1	110.66 (13)	S1—C13—H13	123.6
C14—C5—C4	113.85 (14)	C15—C14—O4	110.40 (15)
N1—C5—C4	101.09 (12)	C15—C14—C5	133.19 (16)
C14—C5—H5	110.3	O4—C14—C5	116.40 (14)
N1—C5—H5	110.3	C14—C15—C16	106.54 (15)
C4—C5—H5	110.3	C14—C15—H15	126.7
O1—C6—N1	118.33 (14)	C16—C15—H15	126.7
O1—C6—C7	124.42 (15)	C17—C16—C15	106.33 (16)
N1—C6—C7	117.24 (14)	C17—C16—H16	126.8
C8—C7—C6	128.08 (15)	C15—C16—H16	126.8
C8—C7—H7	116.0	C16—C17—O4	110.78 (16)
C6—C7—H7	116.0	C16—C17—H17	124.6
C7—C8—C9	132.52 (16)	O4—C17—H17	124.6
C6—N1—N2—C3	-172.26 (15)	C4—C3—C10—C11	3.5 (2)
C5—N1—N2—C3	7.76 (17)	N2—C3—C10—S1	4.2 (2)
N1—N2—C3—C10	179.46 (14)	C4—C3—C10—S1	-175.93 (12)
N1—N2—C3—C4	-0.40 (18)	C13—S1—C10—C11	-0.62 (13)
N2—C3—C4—C5	-6.46 (19)	C13—S1—C10—C3	178.89 (14)
C10—C3—C4—C5	173.68 (14)	C3—C10—C11—C12	-178.98 (15)
C6—N1—C5—C14	-70.26 (19)	S1—C10—C11—C12	0.51 (17)
N2—N1—C5—C14	109.72 (15)	C10—C11—C12—C13	-0.1 (2)
C6—N1—C5—C4	168.79 (14)	C11—C12—C13—S1	-0.4 (2)
N2—N1—C5—C4	-11.23 (17)	C10—S1—C13—C12	0.57 (15)
C3—C4—C5—C14	-108.98 (15)	C17—O4—C14—C15	-0.77 (18)
C3—C4—C5—N1	9.68 (16)	C17—O4—C14—C5	177.90 (13)
N2—N1—C6—O1	175.44 (14)	N1—C5—C14—C15	111.5 (2)
C5—N1—C6—O1	-4.6 (2)	C4—C5—C14—C15	-135.49 (19)
N2—N1—C6—C7	-5.4 (2)	N1—C5—C14—O4	-66.83 (17)

C5—N1—C6—C7	174.58 (14)	C4—C5—C14—O4	46.22 (19)
O1—C6—C7—C8	0.2 (3)	O4—C14—C15—C16	0.66 (18)
N1—C6—C7—C8	-178.88 (17)	C5—C14—C15—C16	-177.71 (17)
C6—C7—C8—C9	-2.1 (3)	C14—C15—C16—C17	-0.28 (19)
C7—C8—C9—O2	-175.82 (18)	C15—C16—C17—O4	-0.2 (2)
C7—C8—C9—O3	4.1 (3)	C14—O4—C17—C16	0.59 (19)
N2—C3—C10—C11	-176.34 (15)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3...O1	0.88 (3)	1.64 (3)	2.5146 (19)	171 (2)
C4—H4B...S1 ⁱ	0.99	2.85	3.820 (2)	165
C17—H17...O1 ⁱⁱ	0.95	2.51	3.426 (2)	161

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