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Allyl 6-amino-4-(4-chlorophenyl)-5-cyano-2-methyl-4*H*-pyran-3-carboxylate

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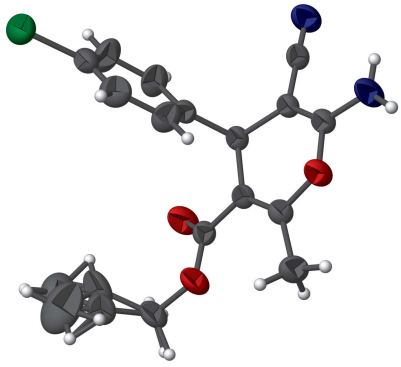
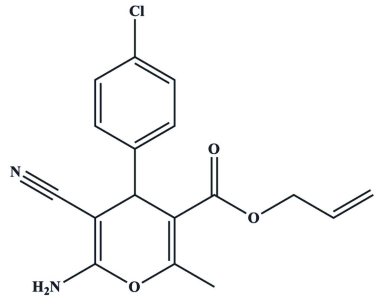
In the title compound, $C_{17}H_{15}ClN_2O_3$, the 4*H*-pyran ring exhibits a shallow-boat conformation and the chlorobenzene ring occupies an axial position. The *O*-allyl side chain is disordered over two orientations in a 0.585 (14):0.415 (14) ratio. In the crystal, inversion dimers linked by pairs of weak N—H···N hydrogen bonds generate $R_2^2(12)$ loops and N—H···O hydrogen bonds link the dimers into [001] chains.

3D view



Chemical scheme



Structure description

Pyran derivatives possess various biological properties such as antimicrobial (Aytemir *et al.*, 2003) and anti-mycobacterial (Kumar *et al.*, 2007) activities. As part of our studies in this area, we now describe the synthesis and structure of the title compound (Fig. 1).

The 4*H*-pyran ring exhibits a shallow boat conformation with puckering parameters Q = 0.2185 (3) Å, θ = 77.49 (7)° and φ = 170.4 (8)°: atoms O1 and C7 deviate by 0.108 (2) and 0.135 (2) Å, respectively, from the mean plane of the other atoms. The dihedral angle between the phenyl ring and the 4*H*-pyran ring (all atoms) is 82.43 (14)°.

In the crystal, inversion dimers linked by pairs of weak N2—H2*A*···N1 hydrogen bonds generate $R_2^2(12)$ loops and N2—H2*B*···O2 hydrogen bonds link the dimers into [001] chains (Table 1, Fig. 2).

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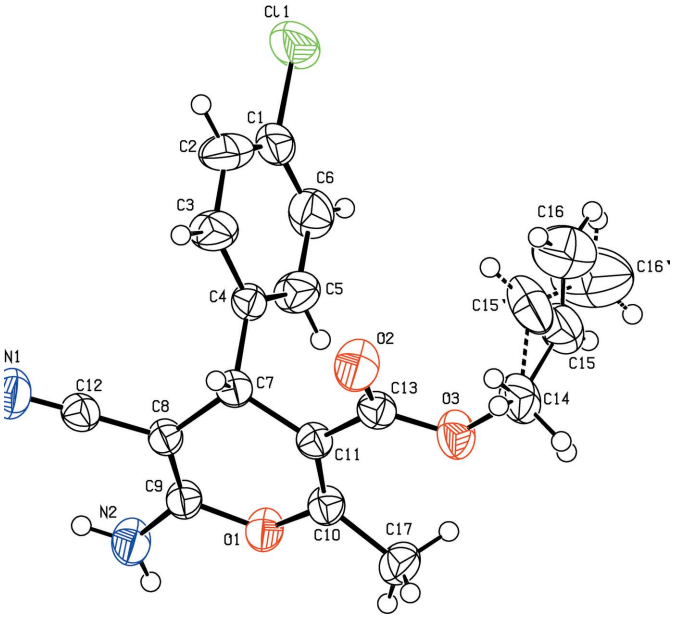

Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

Synthesis and crystallization

A mixture of 4-chlorobenzaldehyde (1.0 mmol), malononitrile (1.0 mmol), allyl 3-oxobutanoate (1.0 mmol) and a few drops of piperidine was stirred magnetically in 30 ml of absolute ethanol at 80°C for 90 min. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was allowed to cool to room temperature and the solvent was evaporated. The solid thus appeared was collected and washed with cold water and recrystallized from ethanol solution to result in colourless blocks of the title compound (yield 84%).

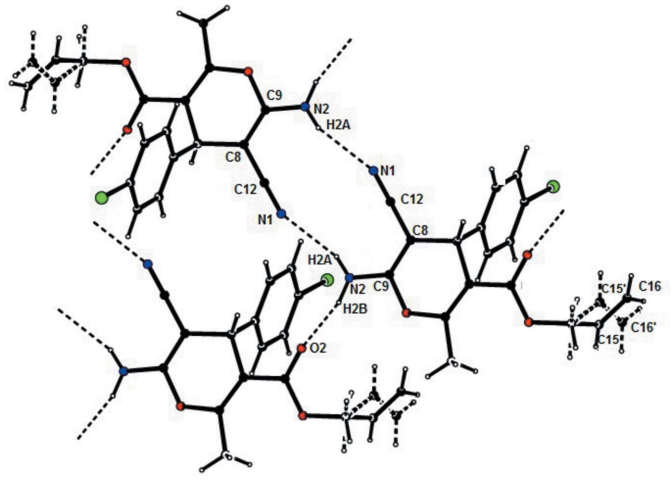

Figure 2
Partial packing diagram for the title compound showing the N—H···N and N—H···O interactions as dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···N1^{i}	0.83 (3)	2.33 (3)	3.126 (4)	160 (2)
N2—H2B···O2^{ii}	0.88 (4)	2.05 (3)	2.894 (3)	161 (3)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{15}ClN_2O_3$
M_r	330.73
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	9.3609 (6), 20.3984 (16), 8.5280 (7)
β (°)	95.691 (2)
V (Å^3)	1620.4 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.25
Crystal size (mm)	0.15 × 0.15 × 0.10
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.963, 0.975
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17502, 2850, 2011
R_{int}	0.036
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.139, 1.05
No. of reflections	2850
No. of parameters	241
No. of restraints	38
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.32

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *ORTEP-3 for Windows* (Farrugia, 2012).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The atoms of the allyl group (C15 and C16 and attached H atoms) are disordered over two sets of sites in a 0.585 (14):0.415 (14) ratio.

Acknowledgements

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full crystallographic data

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Crystal data

$C_{17}H_{15}ClN_2O_3$
M_r = 330.73
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 9.3609 (6) Å
b = 20.3984 (16) Å
c = 8.5280 (7) Å
β = 95.691 (2)°
V = 1620.4 (2) Å^3
Z = 4
$F(000)$ = 688
D_x = 1.356 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5292 reflections
θ = 2.6–24.2°
μ = 0.25 mm^{-1}
T = 296 K
BLOCK, colourless
0.15 × 0.15 × 0.10 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 2008)
T_{min} = 0.963, T_{max} = 0.975
17502 measured reflections
2850 independent reflections
2011 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 25.0°, θ_{min} = 2.4°
h = −11→10
k = −24→24
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.139
S = 1.05
2850 reflections
241 parameters
38 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 not defined?
$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 1.3356P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All esds are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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 $F^2 > 2\text{sigma}(F^2)$ 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. The hydrogen atoms bound to the C atoms are treated as riding atoms. The H atoms bonded to N were freely refined.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	−0.00313 (10)	0.32803 (5)	0.07877 (13)	0.0874 (4)	
O1	0.46275 (18)	0.07969 (10)	−0.32817 (19)	0.0440 (6)	
O2	0.4430 (2)	0.07085 (12)	0.2207 (2)	0.0600 (8)	
O3	0.6401 (2)	0.11435 (10)	0.1389 (2)	0.0516 (7)	
N1	−0.0094 (3)	0.00114 (14)	−0.2957 (3)	0.0595 (10)	
N2	0.2910 (3)	0.04447 (15)	−0.5067 (3)	0.0551 (10)	
C1	0.0785 (3)	0.25483 (16)	0.0326 (4)	0.0542 (11)	
C2	0.0284 (4)	0.19701 (19)	0.0833 (4)	0.0700 (16)	
C3	0.0968 (3)	0.13891 (16)	0.0521 (4)	0.0563 (11)	
C4	0.2143 (3)	0.13860 (13)	−0.0331 (3)	0.0357 (8)	
C5	0.2604 (3)	0.19807 (15)	−0.0864 (4)	0.0528 (11)	
C6	0.1941 (3)	0.25649 (15)	−0.0529 (4)	0.0609 (11)	
C7	0.2883 (3)	0.07482 (12)	−0.0704 (3)	0.0344 (8)	
C8	0.2411 (3)	0.05042 (12)	−0.2353 (3)	0.0341 (8)	
C9	0.3244 (3)	0.05766 (13)	−0.3537 (3)	0.0373 (8)	
C10	0.5275 (3)	0.08513 (13)	−0.1753 (3)	0.0381 (8)	
C11	0.4502 (3)	0.08235 (12)	−0.0517 (3)	0.0341 (8)	
C12	0.1022 (3)	0.02369 (13)	−0.2684 (3)	0.0392 (9)	
C13	0.5096 (3)	0.08802 (13)	0.1148 (3)	0.0385 (8)	
C14	0.6952 (4)	0.12629 (18)	0.3027 (4)	0.0575 (11)	
C15	0.6737 (10)	0.1954 (4)	0.3396 (10)	0.063 (3)	0.585 (14)
C16	0.6009 (11)	0.2171 (7)	0.4480 (10)	0.088 (4)	0.585 (14)
C17	0.6848 (3)	0.09330 (16)	−0.1840 (3)	0.0519 (10)	
C15′	0.6098 (16)	0.1800 (5)	0.3735 (17)	0.075 (4)	0.415 (14)
C16′	0.660 (2)	0.2373 (7)	0.391 (3)	0.127 (8)	0.415 (14)
H2B	0.355 (4)	0.0512 (16)	−0.574 (4)	0.062 (10)*	
H3	0.06296	0.09957	0.08928	0.0675*	
H5	0.33816	0.19901	−0.14630	0.0633*	
H6	0.22786	0.29618	−0.08817	0.0728*	
H7	0.26255	0.04150	0.00459	0.0413*	
H14A	0.79655	0.11562	0.31821	0.0690*	0.585 (14)
H14B	0.64492	0.09880	0.37213	0.0690*	0.585 (14)
H15	0.71649	0.22621	0.27898	0.0751*	0.585 (14)
H16A	0.55631	0.18794	0.51141	0.1052*	0.585 (14)
H16B	0.59278	0.26201	0.46347	0.1052*	0.585 (14)
H17A	0.70457	0.09322	−0.29230	0.0778*	
H17B	0.73535	0.05782	−0.12929	0.0778*	
H17C	0.71572	0.13413	−0.13593	0.0778*	
H2	−0.05207	0.19634	0.13904	0.0840*	

H2A	0.207 (3)	0.0344 (14)	−0.538 (3)	0.045 (9)*	
H14C	0.812 (9)	0.126 (4)	0.277 (9)	0.0690*	0.415 (14)
H14D	0.681 (8)	0.084 (4)	0.364 (9)	0.0690*	0.415 (14)
H15′	0.51942	0.17057	0.40428	0.0903*	0.415 (14)
H16C	0.75006	0.24702	0.36055	0.1522*	0.415 (14)
H16D	0.60634	0.26982	0.43468	0.1522*	0.415 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0708 (6)	0.0727 (7)	0.1122 (8)	0.0276 (5)	−0.0227 (5)	−0.0415 (6)
O1	0.0404 (10)	0.0636 (13)	0.0290 (10)	−0.0127 (9)	0.0085 (8)	−0.0011 (9)
O2	0.0564 (13)	0.0928 (17)	0.0314 (11)	−0.0153 (11)	0.0075 (9)	0.0024 (10)
O3	0.0510 (12)	0.0656 (14)	0.0369 (11)	−0.0125 (10)	−0.0025 (9)	−0.0035 (9)
N1	0.0499 (15)	0.0711 (19)	0.0576 (17)	−0.0178 (14)	0.0059 (12)	−0.0069 (14)
N2	0.0469 (16)	0.089 (2)	0.0302 (13)	−0.0183 (15)	0.0084 (12)	−0.0110 (13)
C1	0.0465 (18)	0.055 (2)	0.058 (2)	0.0072 (15)	−0.0106 (15)	−0.0197 (16)
C2	0.060 (2)	0.076 (3)	0.079 (3)	0.0079 (19)	0.0318 (19)	−0.016 (2)
C3	0.0572 (19)	0.057 (2)	0.059 (2)	−0.0054 (15)	0.0276 (15)	−0.0046 (15)
C4	0.0351 (14)	0.0424 (15)	0.0298 (13)	−0.0040 (12)	0.0044 (10)	−0.0037 (11)
C5	0.0490 (17)	0.0488 (19)	0.063 (2)	−0.0017 (14)	0.0174 (15)	0.0013 (15)
C6	0.061 (2)	0.0420 (18)	0.078 (2)	−0.0004 (15)	−0.0014 (18)	−0.0006 (16)
C7	0.0378 (14)	0.0384 (15)	0.0277 (13)	−0.0049 (11)	0.0071 (10)	0.0009 (11)
C8	0.0348 (14)	0.0364 (14)	0.0314 (13)	−0.0050 (11)	0.0055 (10)	−0.0017 (11)
C9	0.0365 (14)	0.0428 (16)	0.0328 (14)	−0.0062 (11)	0.0050 (11)	−0.0018 (11)
C10	0.0384 (14)	0.0404 (15)	0.0356 (14)	−0.0042 (12)	0.0045 (11)	0.0006 (12)
C11	0.0374 (14)	0.0347 (14)	0.0305 (13)	−0.0029 (11)	0.0054 (10)	−0.0001 (11)
C12	0.0431 (16)	0.0411 (16)	0.0344 (14)	−0.0042 (12)	0.0085 (12)	−0.0025 (12)
C13	0.0414 (15)	0.0395 (15)	0.0345 (14)	0.0013 (12)	0.0036 (12)	−0.0008 (12)
C14	0.061 (2)	0.066 (2)	0.0419 (17)	−0.0012 (17)	−0.0130 (15)	−0.0092 (15)
C15	0.068 (6)	0.047 (5)	0.071 (5)	−0.002 (4)	−0.006 (4)	−0.009 (4)
C16	0.101 (7)	0.090 (8)	0.072 (5)	0.023 (6)	0.006 (5)	0.001 (5)
C17	0.0387 (16)	0.069 (2)	0.0493 (17)	−0.0069 (14)	0.0110 (13)	−0.0054 (15)
C15′	0.099 (9)	0.063 (7)	0.063 (7)	−0.027 (6)	0.004 (7)	−0.018 (6)
C16′	0.154 (14)	0.074 (10)	0.159 (15)	0.028 (9)	0.049 (11)	0.019 (10)

Geometric parameters (Å, º)

Cl1—C1	1.740 (3)	C11—C13	1.477 (4)
O1—C9	1.368 (3)	C14—C15	1.463 (9)
O1—C10	1.387 (3)	C14—C15′	1.516 (13)
O2—C13	1.199 (3)	C15—C16	1.281 (13)
O3—C13	1.332 (3)	C15′—C16′	1.263 (19)
O3—C14	1.461 (4)	C2—H2	0.9298
N1—C12	1.144 (4)	C3—H3	0.9299
N2—C9	1.339 (4)	C5—H5	0.9300
N2—H2A	0.83 (3)	C6—H6	0.9299
N2—H2B	0.88 (4)	C7—H7	0.9796

C1—C2	1.356 (5)	C14—H14A	0.9696
C1—C6	1.364 (4)	C14—H14B	0.9705
C2—C3	1.385 (5)	C14—H14C	1.14 (8)
C3—C4	1.377 (4)	C14—H14D	1.02 (8)
C4—C5	1.380 (4)	C15—H15	0.9294
C4—C7	1.522 (4)	C15′—H15′	0.9304
C5—C6	1.386 (4)	C16—H16A	0.9302
C7—C8	1.516 (4)	C16—H16B	0.9297
C7—C11	1.516 (4)	C16′—H16C	0.9278
C8—C12	1.412 (4)	C16′—H16D	0.9318
C8—C9	1.344 (4)	C17—H17A	0.9598
C10—C17	1.491 (4)	C17—H17B	0.9600
C10—C11	1.338 (4)	C17—H17C	0.9602
C9—O1—C10	119.7 (2)	C1—C2—H2	119.95
C13—O3—C14	116.5 (2)	C3—C2—H2	119.93
C9—N2—H2B	120 (2)	C2—C3—H3	119.55
H2A—N2—H2B	121 (3)	C4—C3—H3	119.53
C9—N2—H2A	119.0 (18)	C4—C5—H5	119.11
Cl1—C1—C2	120.0 (3)	C6—C5—H5	119.09
Cl1—C1—C6	119.3 (2)	C1—C6—H6	120.51
C2—C1—C6	120.7 (3)	C5—C6—H6	120.55
C1—C2—C3	120.1 (3)	C4—C7—H7	108.06
C2—C3—C4	120.9 (3)	C8—C7—H7	108.05
C5—C4—C7	121.3 (2)	C11—C7—H7	108.05
C3—C4—C7	121.2 (2)	O3—C14—H14A	109.94
C3—C4—C5	117.5 (3)	O3—C14—H14B	109.91
C4—C5—C6	121.8 (3)	O3—C14—H14C	94 (4)
C1—C6—C5	118.9 (3)	O3—C14—H14D	107 (4)
C4—C7—C8	112.2 (2)	C15—C14—H14A	109.92
C4—C7—C11	111.2 (2)	C15—C14—H14B	109.89
C8—C7—C11	109.1 (2)	H14A—C14—H14B	108.32
C7—C8—C12	119.3 (2)	C15′—C14—H14C	129 (4)
C7—C8—C9	121.6 (2)	C15′—C14—H14D	108 (4)
C9—C8—C12	118.9 (2)	H14C—C14—H14D	106 (6)
O1—C9—N2	110.3 (2)	C14—C15—H15	117.13
O1—C9—C8	121.8 (2)	C16—C15—H15	117.22
N2—C9—C8	127.8 (3)	C16′—C15′—H15′	119.74
C11—C10—C17	131.2 (2)	C14—C15′—H15′	119.53
O1—C10—C17	107.7 (2)	C15—C16—H16B	119.99
O1—C10—C11	121.2 (2)	C15—C16—H16A	120.02
C7—C11—C10	122.3 (2)	H16A—C16—H16B	119.99
C7—C11—C13	112.7 (2)	C15′—C16′—H16C	120.16
C10—C11—C13	124.9 (3)	C15′—C16′—H16D	119.80
N1—C12—C8	179.0 (3)	H16C—C16′—H16D	120.04
O3—C13—C11	115.6 (2)	H17A—C17—H17C	109.49
O2—C13—O3	122.6 (2)	H17B—C17—H17C	109.47
O2—C13—C11	121.8 (3)	C10—C17—H17A	109.47

O3—C14—C15	108.9 (4)	C10—C17—H17B	109.46
O3—C14—C15′	110.6 (6)	C10—C17—H17C	109.46
C14—C15—C16	125.7 (9)	H17A—C17—H17B	109.49
C14—C15′—C16′	120.7 (14)		
C9—O1—C10—C17	165.8 (2)	C4—C7—C8—C12	−72.5 (3)
C10—O1—C9—N2	−168.6 (2)	C4—C7—C8—C9	102.8 (3)
C10—O1—C9—C8	10.3 (4)	C11—C7—C8—C12	163.7 (2)
C9—O1—C10—C11	−13.8 (4)	C4—C7—C11—C10	−106.8 (3)
C14—O3—C13—C11	174.3 (2)	C11—C7—C8—C9	−20.9 (3)
C13—O3—C14—C15	−99.1 (5)	C8—C7—C11—C13	−164.1 (2)
C14—O3—C13—O2	−4.6 (4)	C8—C7—C11—C10	17.5 (3)
Cl1—C1—C6—C5	178.7 (3)	C4—C7—C11—C13	71.6 (3)
C2—C1—C6—C5	−0.4 (5)	C12—C8—C9—O1	−176.2 (2)
C6—C1—C2—C3	1.7 (5)	C12—C8—C9—N2	2.5 (4)
Cl1—C1—C2—C3	−177.4 (3)	C7—C8—C9—O1	8.4 (4)
C1—C2—C3—C4	−1.3 (5)	C7—C8—C9—N2	−172.9 (3)
C2—C3—C4—C7	−178.9 (3)	O1—C10—C11—C7	−1.5 (4)
C2—C3—C4—C5	−0.3 (4)	C17—C10—C11—C13	0.8 (5)
C3—C4—C7—C11	−138.7 (3)	C17—C10—C11—C7	178.9 (3)
C5—C4—C7—C11	42.8 (3)	O1—C10—C11—C13	−179.7 (2)
C7—C4—C5—C6	−179.8 (3)	C10—C11—C13—O3	18.1 (4)
C3—C4—C5—C6	1.6 (5)	C7—C11—C13—O2	18.7 (4)
C3—C4—C7—C8	98.8 (3)	C10—C11—C13—O2	−163.0 (3)
C5—C4—C7—C8	−79.7 (3)	C7—C11—C13—O3	−160.2 (2)
C4—C5—C6—C1	−1.3 (5)	O3—C14—C15—C16	121.1 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···N1^{i}	0.83 (3)	2.33 (3)	3.126 (4)	160 (2)
N2—H2*B*···O2^{ii}	0.88 (4)	2.05 (3)	2.894 (3)	161 (3)

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