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2-Amino-4-(4-methoxyphenyl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile acetic acid monosolvate

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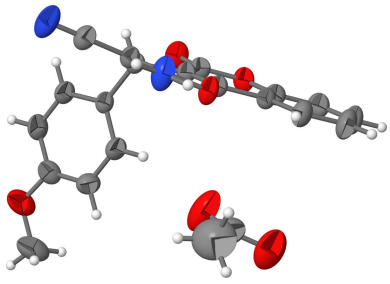
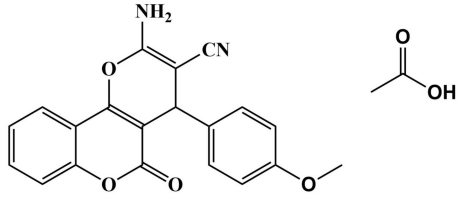
Structural data: full structural data are available from iucrdata.iucr.org

In the title co-crystal, $C_{20}H_{14}N_2O_4\cdot C_2H_4O_2$, the expected proton transfer from acetic acid to amine has not occurred. In the crystal, the chromene molecules are linked by N—H···O and N—H···N hydrogen bonds to generate [100] columns. The acetic acid molecules form inversion dimers linked by pairwise O—H···O hydrogen bonds and occupy voids between the columns.

3D view



Chemical scheme



Structure description

Pyrano[3,2-*c*]chromene derivatives enjoy attention from researchers due to their pharmacological activity (Siziani *et al.*, 2022; Tashrifi *et al.*, 2020), heavy metal chemisensing (Mohajer *et al.*, 2022), semiconductivity (Mal *et al.*, 2022), *etc*. As part of our studies in this area, the crystal structure of the 1:1 co-crystal of 2-amino-4-(4-methoxyphenyl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile and acetic acid is now reported. The compound was crystallized from acetic acid, but the expected proton transfer from the carboxylic acid to the amine group did not occur.

The title compound crystallizes in the triclinic space group $P\overline{1}$ with one pyrano[3,2-*c*]-chromene molecule and one acetic acid molecule in the asymmetric unit (Fig. 1). Unexpectedly, although crystallized from a solvent of glacial acetic acid, the $-NH_2$ group present in the pyranochromene framework was not protonated. The dihedral angle between the planes of the C1–C12/O2/O3 fused ring (r.m.s. deviation = 0.079 Å) and the pendant C14–C19 ring is 89.00 (6)°, and the C atom of the methoxy substituent deviates by 0.132 (2) Å from its attached ring.

In the crystal, the pyrano[3,2-*c*]chromene molecules are linked by N1—H11···N2^{i} hydrogen bonds (Table 1) to generate centrosymmetric $R_2^2(12)$ loops and the dimers are linked into [100] chains by N1—H10···O1^{ii} links to generate [100] columns. The acetic

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11···N2^{i}	0.85 (2)	2.22 (2)	3.062 (2)	172 (2)
N1—H10···O1^{ii}	0.81 (2)	2.31 (2)	3.111 (2)	168 (2)
O6—H15···O5^{iii}	1.00 (4)	1.67 (4)	2.664 (3)	172 (3)
C15—H6···O5	0.93	2.39	3.251 (2)	154

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

acid molecules maintain their hydrogen-bonded dimeric form (*via* pairwise O6—H15···O5^{iii} links) without any directional interactions with the pyrano[3,2-*c*]chromene columns (Fig. 2). The acetic acid dimers occupy the space between pyranochromene columns (about 7.4 Å) and are positioned approximately parallel to the pyranochromene plane of the host molecule; a weak C15—H6···O5 hydrogen bond occurs between host and guest. The significant difference between the lengths of the C21—O5 [1.197 (3) Å] and C21—O6 [1.284 (3) Å] bonds infers that the acetic acid molecule remains in its protonated state.

Synthesis and crystallization

4-Hydroxycoumarin or 4-hydroxy-2*H*-benzo[*h*]chromen-2-one (1.00 mmol), 4-methoxybenzaldehyde (1.00 mmol), malononitrile (1.00 mmol) and catalyst DABCO (10 mol%) were ground with a mortar and pestle for about 10 min. Upon completion of the reaction, the product was washed several times with ethanol to get the pure product, a white solid. The purity of the compound was confirmed by fluorescent HPTLC (Merck) and melting point (observed 238°C, reported 237°C; Shaabani *et al.*, 2007). FT–IR (KBr, cm^{-1}): 3360, 3184, 2980, 1726, 1596, 1462; ^{1}H NMR (400 MHz, DMSO-d_6): 3.73 (*s*, 3H), 4.40 (*s*, 1H), 6.89 (*d*, 2H, J = 8.8 Hz, 7.19 (*d*, 2H, J = 8.4 Hz), 7.35 (*s*, 2H), 7.52–7.40 (*m*, 2H), 7.73 (*dt*, 1H, J = 8.8, 1.6 Hz), 7.92 (*dd*, J = 8.0, 1.6 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): 36.1, 55.0, 58.3, 104.3, 112.9, 113.9, 116.5, 119.2, 122.4, 124.6, 128.7, 132.8, 135.4, 152.1, 153.1, 157.9, 158.3, 159.5. Suitable crystals of the title compound were grown by dissolving the compound in glacial acetic acid. The solution was kept undisturbed for a period of two weeks in an NMR tube (OD 5 mm) and the grown crystals were carefully recovered and washed with hexane and dried.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{14}N_2O_4{\cdot}C_2H_4O_2$
M_r	406.38
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	7.9303 (6), 11.2977 (9), 11.9988 (9)
α, β, γ (°)	82.468 (4), 77.379 (4), 73.419 (4)
V (Å^3)	1002.71 (14)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.36 × 0.36 × 0.30
Data collection	
Diffractometer	Bruker APEXII CCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17101, 4807, 3457
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.662
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.157, 1.06
No. of reflections	4807
No. of parameters	285
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.25

Computer programs: *APEX2* and *SAINT* (Bruker 2015), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009; Bourhis *et al.*, 2015).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

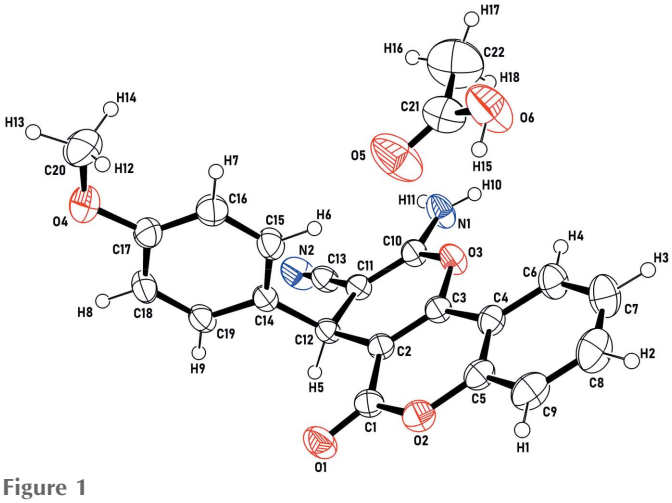


Figure 1
Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

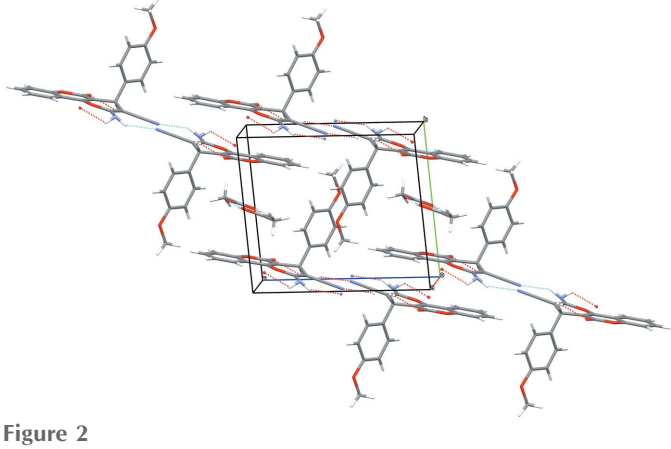


Figure 2
Packing arrangement of the title compound. Hydrogen bonds are shown as dotted lines.

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full crystallographic data

IUCrData (2023). **8**, x230558 [https://doi.org/10.1107/S2414314623005588]

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Crystal data

$C_{20}H_{14}N_2O_4·C_2H_4O_2$
M_r = 406.38
Triclinic, $P\overline{1}$
a = 7.9303 (6) Å
b = 11.2977 (9) Å
c = 11.9988 (9) Å
α = 82.468 (4)°
β = 77.379 (4)°
γ = 73.419 (4)°
V = 1002.71 (14) Å^3
Z = 2
$F(000)$ = 424
D_x = 1.346 Mg m^{-3}
Melting point: 511.15 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5371 reflections
θ = 2.7–27.9°
μ = 0.10 mm^{-1}
T = 296 K
Block, white
0.36 × 0.36 × 0.30 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
φ and ω scans
17101 measured reflections
4807 independent reflections
3457 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 28.1°, θ_{min} = 2.7°
h = −10→10
k = −14→14
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.157
S = 1.06
4807 reflections
285 parameters
0 restraints
Primary atom site location: iterative
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0858P)^2 + 0.1068P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction: SHELXL2018 (Sheldrick, 2015*b*), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.037 (6)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.28503 (19)	0.15224 (13)	0.94770 (12)	0.0398 (3)
C2	0.46268 (18)	0.13992 (12)	0.87929 (11)	0.0343 (3)
C3	0.59600 (18)	0.14624 (12)	0.92882 (11)	0.0351 (3)
C4	0.5684 (2)	0.16975 (12)	1.04776 (11)	0.0388 (3)
C5	0.3950 (2)	0.18548 (13)	1.10966 (11)	0.0416 (3)
C6	0.7039 (2)	0.17741 (15)	1.10147 (13)	0.0506 (4)
H4	0.820649	0.167223	1.060769	0.061*
C7	0.6624 (3)	0.20027 (18)	1.21552 (15)	0.0649 (5)
H3	0.752115	0.204468	1.252281	0.078*
C8	0.4892 (3)	0.21697 (18)	1.27573 (14)	0.0662 (5)
H2	0.463455	0.233314	1.352487	0.079*
C9	0.3539 (3)	0.20992 (16)	1.22439 (13)	0.0566 (4)
H1	0.237323	0.221273	1.265566	0.068*
C10	0.81505 (19)	0.09187 (13)	0.76421 (11)	0.0372 (3)
C11	0.69033 (18)	0.08117 (12)	0.70792 (11)	0.0350 (3)
C12	0.49036 (17)	0.12492 (12)	0.75303 (10)	0.0339 (3)
H5	0.434598	0.060982	0.742969	0.041*
C13	0.74784 (19)	0.03627 (13)	0.59735 (12)	0.0414 (3)
C14	0.40507 (17)	0.24512 (12)	0.68869 (10)	0.0345 (3)
C15	0.4317 (2)	0.35587 (13)	0.70738 (13)	0.0471 (4)
H6	0.499634	0.356797	0.761194	0.056*
C16	0.3594 (2)	0.46567 (14)	0.64780 (14)	0.0506 (4)
H7	0.378473	0.539410	0.661815	0.061*
C17	0.2593 (2)	0.46490 (14)	0.56784 (13)	0.0478 (4)
C18	0.2344 (2)	0.35441 (16)	0.54666 (14)	0.0506 (4)
H8	0.168538	0.353381	0.491619	0.061*
C19	0.3064 (2)	0.24558 (14)	0.60666 (12)	0.0423 (3)
H9	0.288535	0.171768	0.591792	0.051*
C20	0.1897 (3)	0.68441 (18)	0.5279 (2)	0.0792 (6)
H12	0.134892	0.699323	0.606260	0.119*
H13	0.127714	0.747593	0.478338	0.119*
H14	0.312930	0.685832	0.515177	0.119*
N1	0.99246 (18)	0.06727 (16)	0.73010 (13)	0.0548 (4)
H11	1.045 (3)	0.044 (2)	0.664 (2)	0.082*
H10	1.050 (3)	0.0795 (18)	0.7738 (17)	0.063 (6)*
N2	0.7914 (2)	0.00034 (16)	0.50810 (12)	0.0636 (4)
O1	0.15733 (14)	0.14244 (11)	0.91391 (10)	0.0554 (3)
O2	0.25831 (14)	0.17565 (10)	1.06096 (8)	0.0469 (3)
O3	0.76834 (13)	0.13240 (10)	0.87243 (8)	0.0438 (3)

O4	0.18023 (18)	0.56733 (12)	0.50445 (12)	0.0718 (4)
C21	0.7402 (3)	0.47407 (18)	0.9117 (2)	0.0699 (5)
C22	0.9237 (4)	0.4564 (3)	0.8413 (3)	0.1178 (10)
H16	0.917608	0.462359	0.761649	0.177*
H17	0.974923	0.519298	0.855137	0.177*
H18	0.997116	0.376303	0.861655	0.177*
O5	0.6192 (2)	0.4549 (2)	0.87859 (14)	0.1048 (6)
O6	0.7183 (3)	0.51493 (19)	1.01024 (16)	0.0988 (6)
H15	0.594 (5)	0.518 (3)	1.052 (3)	0.139 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0345 (7)	0.0454 (7)	0.0371 (7)	−0.0108 (6)	−0.0012 (6)	−0.0037 (5)
C2	0.0324 (7)	0.0380 (6)	0.0312 (6)	−0.0091 (5)	−0.0030 (5)	−0.0035 (5)
C3	0.0335 (7)	0.0403 (7)	0.0302 (6)	−0.0096 (6)	−0.0023 (5)	−0.0047 (5)
C4	0.0451 (8)	0.0401 (7)	0.0304 (6)	−0.0095 (6)	−0.0066 (6)	−0.0051 (5)
C5	0.0478 (9)	0.0398 (7)	0.0337 (7)	−0.0098 (6)	−0.0024 (6)	−0.0032 (5)
C6	0.0531 (10)	0.0607 (9)	0.0406 (8)	−0.0132 (8)	−0.0120 (7)	−0.0119 (7)
C7	0.0770 (13)	0.0790 (12)	0.0458 (9)	−0.0182 (10)	−0.0217 (9)	−0.0178 (8)
C8	0.0889 (15)	0.0741 (11)	0.0341 (8)	−0.0165 (11)	−0.0079 (9)	−0.0174 (8)
C9	0.0674 (11)	0.0580 (9)	0.0369 (7)	−0.0129 (8)	0.0051 (7)	−0.0104 (7)
C10	0.0343 (7)	0.0459 (7)	0.0304 (6)	−0.0098 (6)	−0.0025 (5)	−0.0073 (5)
C11	0.0342 (7)	0.0404 (7)	0.0303 (6)	−0.0107 (6)	−0.0018 (5)	−0.0072 (5)
C12	0.0321 (7)	0.0398 (6)	0.0321 (6)	−0.0123 (6)	−0.0054 (5)	−0.0060 (5)
C13	0.0351 (8)	0.0517 (8)	0.0395 (7)	−0.0145 (6)	−0.0022 (6)	−0.0121 (6)
C14	0.0307 (7)	0.0434 (7)	0.0301 (6)	−0.0105 (6)	−0.0044 (5)	−0.0058 (5)
C15	0.0541 (9)	0.0471 (8)	0.0470 (8)	−0.0148 (7)	−0.0214 (7)	−0.0051 (6)
C16	0.0561 (10)	0.0423 (7)	0.0578 (9)	−0.0149 (7)	−0.0172 (8)	−0.0039 (6)
C17	0.0379 (8)	0.0505 (8)	0.0515 (8)	−0.0089 (7)	−0.0104 (7)	0.0051 (7)
C18	0.0455 (9)	0.0646 (10)	0.0477 (8)	−0.0164 (8)	−0.0222 (7)	0.0009 (7)
C19	0.0402 (8)	0.0517 (8)	0.0412 (7)	−0.0179 (7)	−0.0113 (6)	−0.0064 (6)
C20	0.0751 (14)	0.0545 (10)	0.1034 (16)	−0.0150 (10)	−0.0250 (12)	0.0192 (10)
N1	0.0308 (7)	0.0912 (11)	0.0429 (7)	−0.0141 (7)	−0.0023 (6)	−0.0193 (7)
N2	0.0572 (9)	0.0925 (11)	0.0472 (8)	−0.0284 (8)	0.0044 (7)	−0.0316 (7)
O1	0.0353 (6)	0.0801 (8)	0.0527 (6)	−0.0193 (6)	−0.0039 (5)	−0.0101 (6)
O2	0.0403 (6)	0.0604 (6)	0.0357 (5)	−0.0130 (5)	0.0036 (4)	−0.0076 (4)
O3	0.0319 (5)	0.0684 (7)	0.0334 (5)	−0.0147 (5)	−0.0026 (4)	−0.0144 (4)
O4	0.0689 (9)	0.0603 (7)	0.0882 (9)	−0.0144 (6)	−0.0377 (7)	0.0201 (6)
C21	0.0617 (13)	0.0648 (11)	0.0844 (14)	−0.0198 (10)	−0.0065 (11)	−0.0153 (10)
C22	0.0723 (17)	0.126 (2)	0.137 (3)	−0.0156 (16)	0.0149 (16)	−0.0281 (19)
O5	0.0846 (12)	0.1625 (17)	0.0870 (11)	−0.0550 (12)	0.0017 (9)	−0.0599 (11)
O6	0.0784 (12)	0.1447 (16)	0.0913 (12)	−0.0462 (11)	−0.0156 (10)	−0.0361 (11)

Geometric parameters (Å, º)

C2—C1	1.4459 (19)	C18—H8	0.9300
C2—C3	1.3435 (19)	C18—C19	1.380 (2)

C3—C4	1.4439 (18)	C19—C14	1.3834 (19)
C4—C6	1.396 (2)	C19—H9	0.9300
C5—C4	1.387 (2)	C20—H12	0.9600
C5—C9	1.389 (2)	C20—H13	0.9600
C6—H4	0.9300	C20—H14	0.9600
C7—C6	1.377 (2)	N1—C10	1.3339 (19)
C7—H3	0.9300	N1—H11	0.85 (2)
C8—C7	1.378 (3)	N1—H10	0.81 (2)
C8—H2	0.9300	N2—C13	1.1416 (18)
C9—C8	1.374 (3)	O1—C1	1.2072 (17)
C9—H1	0.9300	O2—C1	1.3776 (17)
C11—C10	1.3529 (19)	O2—C5	1.3753 (18)
C11—C13	1.4161 (18)	O3—C3	1.3608 (16)
C12—C2	1.5075 (17)	O3—C10	1.3718 (15)
C12—C11	1.5165 (18)	O4—C17	1.3691 (18)
C12—H5	0.9800	O4—C20	1.414 (2)
C14—C12	1.5253 (18)	C22—C21	1.488 (3)
C14—C15	1.380 (2)	C22—H16	0.9600
C15—H6	0.9300	C22—H17	0.9600
C15—C16	1.385 (2)	C22—H18	0.9600
C16—H7	0.9300	O5—C21	1.197 (3)
C17—C16	1.375 (2)	O6—C21	1.284 (3)
C17—C18	1.381 (2)	O6—H15	1.00 (4)

O1—C1—C2	125.22 (13)	C15—C14—C12	120.49 (12)
O1—C1—O2	116.85 (13)	C15—C14—C19	118.23 (13)
O2—C1—C2	117.93 (12)	C19—C14—C12	121.21 (12)
C1—C2—C12	118.49 (12)	C14—C15—H6	119.2
C3—C2—C1	119.38 (12)	C14—C15—C16	121.51 (13)
C3—C2—C12	122.09 (12)	C16—C15—H6	119.2
C2—C3—C4	122.65 (13)	C15—C16—H7	120.2
C2—C3—O3	123.72 (11)	C17—C16—C15	119.55 (14)
O3—C3—C4	113.62 (12)	C17—C16—H7	120.2
C5—C4—C3	116.32 (13)	C16—C17—C18	119.60 (14)
C5—C4—C6	119.71 (13)	O4—C17—C16	124.86 (15)
C6—C4—C3	123.98 (14)	O4—C17—C18	115.54 (14)
C4—C5—C9	120.82 (15)	C17—C18—H8	119.8
O2—C5—C4	121.65 (12)	C19—C18—C17	120.42 (13)
O2—C5—C9	117.52 (14)	C19—C18—H8	119.8
C4—C6—H4	120.5	C14—C19—H9	119.7
C7—C6—C4	119.07 (16)	C18—C19—C14	120.67 (13)
C7—C6—H4	120.5	C18—C19—H9	119.7
C6—C7—H3	119.7	H12—C20—H13	109.5
C6—C7—C8	120.64 (17)	H12—C20—H14	109.5
C8—C7—H3	119.7	H13—C20—H14	109.5
C7—C8—H2	119.4	O4—C20—H12	109.5
C9—C8—C7	121.17 (15)	O4—C20—H13	109.5
C9—C8—H2	119.4	O4—C20—H14	109.5

C5—C9—H1	120.7	C10—N1—H11	122.0 (16)
C8—C9—C5	118.59 (17)	C10—N1—H10	117.6 (14)
C8—C9—H1	120.7	H11—N1—H10	120 (2)
C11—C10—O3	121.49 (12)	C5—O2—C1	121.99 (11)
N1—C10—C11	129.17 (13)	C3—O3—C10	118.34 (11)
N1—C10—O3	109.34 (12)	C17—O4—C20	118.28 (15)
C10—C11—C12	123.19 (11)	O5—C21—C22	123.0 (2)
C10—C11—C13	118.66 (12)	O5—C21—O6	121.7 (2)
C13—C11—C12	117.94 (12)	O6—C21—C22	115.3 (2)
C2—C12—C11	107.92 (10)	C21—C22—H16	109.5
C2—C12—H5	108.6	C21—C22—H17	109.5
C2—C12—C14	111.51 (10)	C21—C22—H18	109.5
C11—C12—H5	108.6	H17—C22—H16	109.5
C11—C12—C14	111.56 (10)	H18—C22—H16	109.5
C14—C12—H5	108.6	H18—C22—H17	109.5
N2—C13—C11	178.91 (16)	C21—O6—H15	108.3 (19)

C1—C2—C3—C4	−2.4 (2)	C12—C11—C10—N1	−173.68 (14)
C1—C2—C3—O3	178.15 (12)	C12—C11—C10—O3	6.6 (2)
C1—O2—C5—C4	−1.4 (2)	C12—C14—C15—C16	178.31 (14)
C1—O2—C5—C9	179.66 (13)	C13—C11—C10—N1	1.0 (2)
C2—C3—C4—C5	0.2 (2)	C13—C11—C10—O3	−178.68 (12)
C2—C3—C4—C6	−179.69 (13)	C14—C12—C2—C1	71.60 (15)
C2—C12—C11—C10	−18.04 (17)	C14—C12—C2—C3	−106.15 (14)
C2—C12—C11—C13	167.21 (11)	C14—C12—C11—C10	104.78 (14)
C3—C2—C1—O1	−176.40 (14)	C14—C12—C11—C13	−69.97 (15)
C3—C2—C1—O2	2.84 (19)	C14—C15—C16—C17	−0.2 (3)
C3—C4—C6—C7	179.99 (14)	C15—C14—C12—C2	47.04 (17)
C3—O3—C10—C11	8.62 (19)	C15—C14—C12—C11	−73.70 (16)
C3—O3—C10—N1	−171.14 (12)	C16—C17—C18—C19	1.2 (3)
C4—C5—C9—C8	−0.7 (2)	C17—C18—C19—C14	−0.1 (2)
C5—C4—C6—C7	0.2 (2)	C18—C17—C16—C15	−1.0 (3)
C5—C9—C8—C7	0.0 (3)	C18—C19—C14—C12	−178.09 (13)
C5—O2—C1—C2	−0.99 (19)	C18—C19—C14—C15	−1.0 (2)
C5—O2—C1—O1	178.31 (12)	C19—C14—C12—C2	−135.97 (13)
C8—C7—C6—C4	−0.8 (3)	C19—C14—C12—C11	103.28 (14)
C9—C5—C4—C3	−179.26 (12)	C19—C14—C15—C16	1.2 (2)
C9—C5—C4—C6	0.6 (2)	C20—O4—C17—C16	−5.0 (3)
C9—C8—C7—C6	0.8 (3)	C20—O4—C17—C18	175.46 (17)
C10—O3—C3—C2	−10.0 (2)	O2—C5—C4—C3	1.79 (19)
C10—O3—C3—C4	170.56 (11)	O2—C5—C4—C6	−178.36 (13)
C11—C12—C2—C1	−165.55 (11)	O2—C5—C9—C8	178.34 (14)
C11—C12—C2—C3	16.70 (17)	O3—C3—C4—C5	179.61 (12)
C12—C2—C1—O1	5.8 (2)	O3—C3—C4—C6	−0.2 (2)
C12—C2—C1—O2	−174.98 (11)	O4—C17—C16—C15	179.48 (15)
C12—C2—C3—C4	175.29 (11)	O4—C17—C18—C19	−179.25 (14)
C12—C2—C3—O3	−4.1 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···N2^{i}	0.85 (2)	2.22 (2)	3.062 (2)	172 (2)
N1—H10···O1^{ii}	0.81 (2)	2.31 (2)	3.111 (2)	168 (2)
O6—H15···O5^{iii}	1.00 (4)	1.67 (4)	2.664 (3)	172 (3)
C15—H6···O5	0.93	2.39	3.251 (2)	154

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