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Synthesis and structure of 2,4-bis(2,6-dimethyl-4*H*-pyran-4-ylidene)-3-oxopentanedinitrile, an unexpected product of a Knoevenagel condensation reaction

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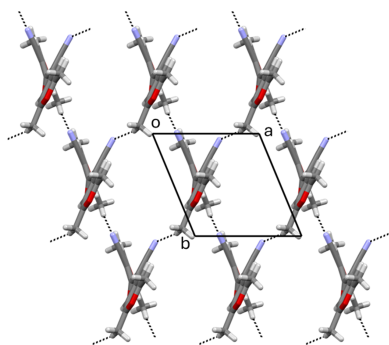
Edited by W. T. A. Harrison, University of Aberdeen, United Kingdom

Keywords: crystal structure; molecular structure; Knoevenagel condensation.**CCDC reference:** 2524654**Supporting information:** this article has supporting information at journals.iucr.org/e^aDipartimento di Scienze Chimiche, Università degli Studi di Napoli 'Federico II', Complesso di Monte S. Angelo, Via Cinthia, 80126 Napoli, Italy, and ^bDepartment of Applied Sciences and Technology, Polytechnic of Turin, Corso Duca degli Abruzzi 24, I-10129 Turin, Italy. *Correspondence e-mail: roberto.centore@unina.it

The title compound, C₁₉H₁₆N₂O₃, was the unexpected product of the Knoevenagel condensation between 2,6-dimethyl- γ -pyrone and cyanoacetic acid in the presence of acetic anhydride and piperidine as catalyst. The molecule is formed by two almost planar 2,6-dimethyl-4*H*-pyran-4-cyanoylidene halves connected by the central carbonyl group. The two halves are not coplanar, the dihedral angle between their planes being 47.51 (3)°. The packing shows the formation of (001) sheets of molecules held together by weak C—H...N and C—H...O hydrogen bonds. A mechanism for the reaction is proposed.

1. Chemical context

The Knoevenagel condensation is a classic organic reaction where an aldehyde or ketone reacts with a compound containing an activated methylene group, *i.e.* a CH₂ group linked to electron-withdrawing groups in the presence of a weak base as the catalyst or in a dehydrating environment (for reviews, see Jones, 1967; Heravi *et al.*, 2020). A new carbon–carbon bond is formed, resulting in an α,β -unsaturated compound after dehydration. This reaction is widely used in the synthesis of *n*-type organic semiconductors to introduce terminal electron-acceptor groups into the molecular backbone (Fusco *et al.*, 2021; Fusco *et al.*, 2022; Yao *et al.*, 2023) and in the synthesis of organic sensitizers for Dye Sensitized Solar Cells (DSSC) (Yahya *et al.*, 2021; D'Amico *et al.*, 2023). In the latter case, typically, an aldehydic precursor is condensed with cyanoacetic acid to introduce a cyanoacrylic functionality essential to anchor the dye on a TiO₂ mesoporous layer through the carboxylic acid group. Some of us reported on pyran-based organic sensitizers for DSSC, whose structure was based on a pyran electron-acceptor core symmetrically linked to two carbazole donor moieties and end capped with cyanoacrylic acid groups (Bonomo *et al.*, 2020). The studied dyes differ with respect to the electron-acceptor groups functionalizing the pyran core: by reacting commercial 2,6-dimethyl- γ -pyrone with four different molecules containing activated methylene groups in a Knoevenagel condensation, four different electron-acceptor groups were linked to the pyran core. Following the same synthetic strategy, we tried to react the commercial pyranone derivative with cyanoacetic acid to introduce a cyanoacrylic acid functionality directly on the pyran core. To our surprise, the main obtained product was not that expected, but 2,4-bis(2,6-dimethyl-4*H*-pyran-4-ylidene)-3-oxopentanedinitrile, CC (Scheme 1), resulting from a



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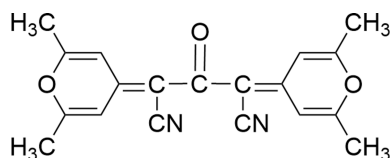
Table 1

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>
C4—H4...O2	0.93	2.26	2.876 (2)	123
C17—H17...O2	0.93	2.33	2.908 (2)	120
C6—H6A...N1 ⁱ	0.96	2.62	3.557 (3)	166
C18—H18A...N2 ⁱⁱ	0.96	2.48	3.425 (3)	169
C19—H19A...O2 ⁱⁱⁱ	0.96	2.55	3.446 (3)	155

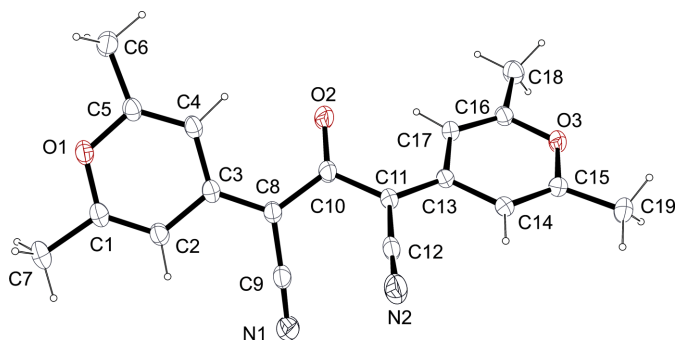
Symmetry codes: (i) $x - 1, y + 1, z$; (ii) $x, y + 1, z$; (iii) $-x, -y + 1, -z + 2$.

more complex reaction involving two molecules of 2,6-dimethyl- γ -pyrone and two of cyanoacetic acid. In this article, we report a full mechanistic and structural analysis of this new compound.

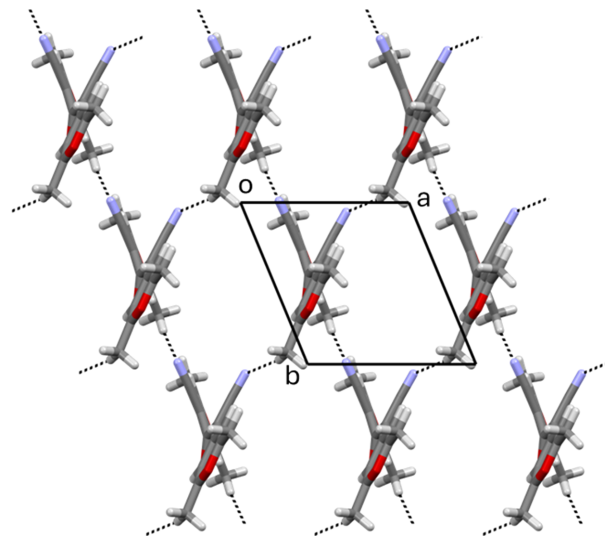


2. Structural commentary

The molecular structure of **CC**, which crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit, is shown in Fig. 1. The molecule is formed from two 2,6-dimethyl-4*H*-pyran-4-cyanoylidene ($C_9H_8N_2O_2$) halves connected to the central C10=O2 carbonyl group. The two halves (H atoms excluded) are close to being planar [within 0.070 (2) Å] and the pattern of bond lengths clearly evidences π -conjugation, for example, C11—C10 = 1.486 (2) Å, C11—C13 = 1.385 (2) Å and C11—C12 = 1.426 (2) Å. However, the two halves are not coplanar, their least-squares planes making a dihedral angle of 47.51 (3)°. This dihedral angle is basically the result of twists around the C8—C10 and C10—C11 bonds [C3—C8—C10—O2 = −23.9 (3)° and O2—C10—C11—C13 = −26.7 (3)°]. These twists seem mainly due to the need to relax the close contact between the C atoms of the two cyano groups [C9...C12 = 2.830 (2) Å]. Two short intramolecular C—H...O contacts (Table 1) to the central ketone O atom occur.

**Figure 1**

The molecular structure of **CC**, with displacement ellipsoids drawn at the 30% probability level.

**Figure 2**

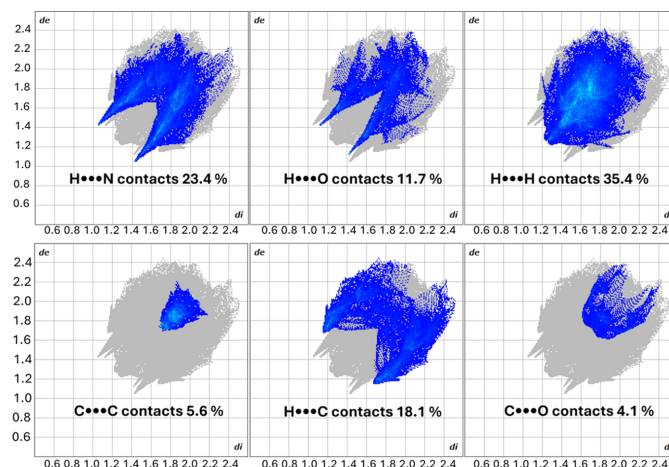
The crystal packing of **CC**, viewed down *c*.

3. Supramolecular features

Each molecule of **CC** is involved in the formation of two chains, through weak C—H...N hydrogen bonds (Table 1 and Fig. 2). One chain is parallel to the $[\bar{1}10]$ direction (C6—H6A...N1) and the other is parallel to $[010]$ (C18—H18A...N2). In this way, an (001) bidimensional network of weakly hydrogen-bonded molecules is formed. The crystal packing is further consolidated by a weak C—H...O hydrogen bond involving the carbonyl O atom as the acceptor (C19—H19A...O2).

4. Hirshfeld surface analysis

Hirshfeld surfaces were generated using the standard promolecule electron density based on spherical atomic electron densities, following the original definition of Hirshfeld parti-

**Figure 3**

Fingerprint plots for the intermolecular H...N, H...O, H...H, C...C, H...C and C...O contacts in the crystal structure of **CC**. All other interactions contribute less than 1%.

tioning of the crystal electron density (Spackman *et al.*, 2021). The d_{norm} surfaces were mapped over the range typically used for organic molecular crystals (-0.5 to $+1.5$ Å). Distances d_i (internal, from the surface to the nearest atom inside the surface) and d_e (external, to the nearest atom outside the surface) were computed for each surface point, and used to generate the corresponding two-dimensional fingerprint plots (d_e versus d_i), shown in Fig. 3, that summarize all intermolecular contacts around the reference molecule.

A distinctive feature is represented by the two spikes at $d_i + d_e = 2.5$ Å, pointing to the lower left of the plots and symmetrically disposed with respect to the diagonal. They correspond to the $\text{C}-\text{H}\cdots\text{N}\equiv\text{C}$ weak hydrogen-bonding interactions. The two more internal symmetrical spikes at $d_i + d_e = 2.54$ Å correspond instead to weak $\text{C}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bonding. The most abundant contacts are $\text{H}\cdots\text{H}$, as expected. The green area centred at about $(d_i, d_e) = (1.8, 1.8)$, corresponds to π - π stacking contacts.

5. Database survey

We searched the Cambridge Structural Database (CSD, Version 2025.6.0; Groom *et al.*, 2016) for structures similar to the title compound. In particular, we searched for structures containing the fragment composed of a central carbonyl group bonded to two C—CN groups. In the search, we applied the filters ‘no ions’ and ‘only organics’. Three hits were found [CSD refcodes AXOQOU and AXOQUA (Shiraki *et al.*, 2011), and CIFFAY (Medici *et al.*, 1984)], but none is really analogous to the title compound. In fact, in the three hits, the C atoms adjacent to the carbonyl group and bearing the cyano groups are sp^3 -hybridized. By releasing the filters, three additional hits were found [CSD refcodes PTCYPO (Klewe, 1971), VELPAE (de Oliveira *et al.*, 2006) and VODLIK (Atmani *et al.*, 2008)]. In PTCYPO and VELPAE, which are ionic, one C atom adjacent to the carbonyl group is sp^3 -

Table 2

Experimental details.

Crystal data	
Chemical formula	$\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_3$
M_r	320.34
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	294
a, b, c (Å)	7.7530 (7), 8.0810 (14), 14.869 (2)
α, β, γ (°)	74.275 (13), 75.185 (12), 64.741 (13)
V (Å ³)	800.4 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.09
Crystal size (mm)	0.40 × 0.40 × 0.10
Data collection	
Diffractionmeter	Bruker–Nonius KappaCCD
Absorption correction	Multi-scan (SADABS; Bruker, 2000)
$T_{\text{min}}, T_{\text{max}}$	0.950, 0.980
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8620, 3584, 2683
R_{int}	0.037
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.051, 0.140, 1.04
No. of reflections	3584
No. of parameters	221
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.21, -0.23

Computer programs: COLLECT (Nonius, 1999), DIRAX/LSQ (Duisenberg *et al.*, 2000), EVALCCD (Duisenberg *et al.*, 2003), SIR97 (Altomare *et al.*, 1999), SHELXL2019 (Sheldrick, 2015), ORTEP-3 for Windows (Farrugia, 2012) and Mercury (Macrae *et al.*, 2020).

hybridized and bears one CN group, while the other bears two CN groups and is anionic. In VODLIK, each C atom adjacent to the carbonyl bears two cyano groups and is anionic, with the CN groups coordinated to Cu^{II} ions in a coordination polymer.

6. Synthesis and crystallization

6.1. Synthesis

2,6-Dimethyl- γ -pyrone (11.0 g, 88.6 mmol) and cyanoacetic acid (9.0 g, 106 mmol) were dissolved in 30 ml of acetic anhydride, and a few drops of piperidine were added. The solution was refluxed, under nitrogen flux, overnight. A brown solid formed during the reaction that, after the system was cooled to room temperature, was recovered by filtration. The recovered solid was washed in 100 ml of methanol and filtered again. Pure compound **CC** was obtained (yield 35%). Recrystallization from hot dimethylformamide (DMF) solution afforded orange plates suitable for single-crystal X-ray analysis. ¹H NMR (CDCl_3 , 400 MHz): δ (ppm) 7.63 (s, 1H), 6.67 (s, 1H), 2.32 (s, 3H), 2.29 (s, 3H). ¹³C NMR (CDCl_3 , 100 MHz): δ (ppm) 184.0, 162.8, 162.1, 153.8, 119.0, 90.1, 19.9.

6.2. Mechanism of reaction

The central bis-cyanoacetone portion of **CC** can be traced back to two cyanoacetic acid molecules with the $-\text{COOH}$ group of one cyanoacetic acid becoming the carbonyl group of

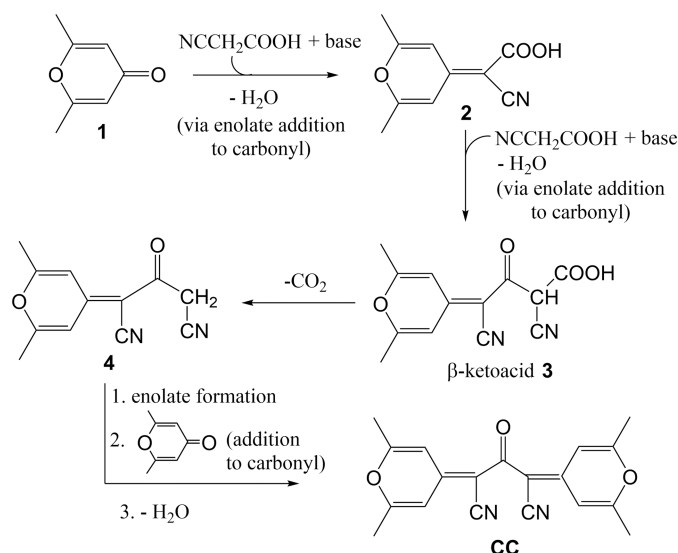


Figure 4
Possible reaction mechanism leading to **CC**.

CC, and the other one is lost, possibly as CO₂, during the process.

Based on this, a plausible mechanistic hypothesis is shown in Fig. 4. In particular, attack of the enolate derived from cyanoacetic acid on the carbonyl group of 2,6-dimethyl- γ -pyrone (**1**), followed by loss of water gives cyanoacid **2**, which was the expected product. Attack of the enolate formed from a second cyanoacetic acid on the carbonyl group of the carboxylic acid function of **2**, and water loss, then follows giving β -ketoacid **3**. It is well known that β -ketoacids are prone to decarboxylation. Thus, decarboxylation of **3** gives β -ketonitrile **4**, the enolate form of which attacks the carbonyl group of a second molecule of **1**, eventually giving the final product CC, after water elimination. It is likely that the process is driven to completion by the extended conjugation of the final product CC and by its precipitation from the reaction medium.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were placed in calculated positions and refined using the riding model, with C—H distances of 0.93 Å for Csp² and 0.96 Å for Csp³ atoms. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$ was applied in all cases.

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Synthesis and structure of 2,4-bis(2,6-dimethyl-4*H*-pyran-4-ylidene)-3-oxopentanedinitrile, an unexpected product of a Knoevenagel condensation reaction

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Computing details

2,4-Bis(2,6-dimethyl-4*H*-pyran-4-ylidene)-3-oxopentanedinitrile

Crystal data

$C_{19}H_{16}N_2O_3$

$M_r = 320.34$

Triclinic, $P\bar{1}$

$a = 7.7530$ (7) Å

$b = 8.0810$ (14) Å

$c = 14.869$ (2) Å

$\alpha = 74.275$ (13)°

$\beta = 75.185$ (12)°

$\gamma = 64.741$ (13)°

$V = 800.4$ (2) Å³

$Z = 2$

$F(000) = 336$

$D_x = 1.329$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 140 reflections

$\theta = 3.1$ – 23.8°

$\mu = 0.09$ mm⁻¹

$T = 294$ K

Plate, orange

$0.40 \times 0.40 \times 0.10$ mm

Data collection

Bruker–Nonius KappaCCD
diffractometer

Radiation source: normal-focus sealed tube

Graphite monochromator

Detector resolution: 9 pixels mm⁻¹

CCD rotation images, thick slices scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2000)

$T_{\min} = 0.950$, $T_{\max} = 0.980$

8620 measured reflections

3584 independent reflections

2683 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.1^\circ$

$h = -10 \rightarrow 9$

$k = -10 \rightarrow 10$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.051$

$wR(F^2) = 0.140$

$S = 1.04$

3584 reflections

221 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-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2 + 0.2356P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.21$ e Å⁻³

$\Delta\rho_{\min} = -0.23$ e Å⁻³

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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2922 (3)	0.4830 (3)	0.37307 (11)	0.0388 (4)
C2	0.3497 (2)	0.3930 (2)	0.45670 (11)	0.0367 (4)
H2	0.450561	0.276722	0.460459	0.044*
C3	0.2594 (2)	0.4718 (2)	0.54069 (10)	0.0318 (4)
C4	0.1080 (2)	0.6506 (2)	0.52650 (11)	0.0344 (4)
H4	0.041867	0.709707	0.577950	0.041*
C5	0.0581 (2)	0.7362 (2)	0.44048 (11)	0.0352 (4)
C6	−0.0906 (3)	0.9234 (3)	0.41601 (14)	0.0490 (5)
H6A	−0.159310	0.971978	0.472773	0.073*
H6B	−0.179447	0.915454	0.384245	0.073*
H6C	−0.029885	1.004411	0.375101	0.073*
C7	0.3683 (3)	0.4138 (3)	0.28208 (13)	0.0591 (6)
H7A	0.472739	0.294551	0.290938	0.089*
H7B	0.414138	0.500210	0.235151	0.089*
H7C	0.267133	0.402004	0.261421	0.089*
C8	0.3153 (2)	0.3736 (2)	0.62836 (11)	0.0336 (4)
C9	0.4731 (3)	0.1983 (3)	0.63024 (11)	0.0400 (4)
C10	0.2283 (3)	0.4439 (2)	0.71759 (11)	0.0368 (4)
C11	0.2435 (2)	0.3048 (2)	0.80721 (11)	0.0337 (4)
C12	0.2411 (3)	0.1301 (3)	0.80563 (11)	0.0394 (4)
C13	0.2435 (2)	0.3373 (2)	0.89399 (11)	0.0311 (3)
C14	0.2535 (2)	0.1961 (2)	0.97809 (11)	0.0350 (4)
H14	0.262779	0.080200	0.973095	0.042*
C15	0.2500 (2)	0.2248 (2)	1.06311 (11)	0.0346 (4)
C16	0.2392 (2)	0.5267 (2)	0.99654 (11)	0.0336 (4)
C17	0.2370 (2)	0.5076 (2)	0.90996 (11)	0.0330 (4)
H17	0.231191	0.606318	0.859428	0.040*
C18	0.2362 (3)	0.6932 (3)	1.02192 (13)	0.0455 (4)
H18A	0.224286	0.790773	0.967157	0.068*
H18B	0.354003	0.662126	1.044252	0.068*
H18C	0.128336	0.734558	1.070808	0.068*
C19	0.2482 (3)	0.0926 (3)	1.15466 (12)	0.0511 (5)
H19A	0.127048	0.141621	1.194979	0.077*
H19B	0.351677	0.076023	1.184774	0.077*
H19C	0.264671	−0.025091	1.143354	0.077*
N1	0.6038 (3)	0.0598 (3)	0.62864 (12)	0.0595 (5)
N2	0.2324 (3)	−0.0090 (2)	0.80821 (11)	0.0579 (5)
O1	0.14832 (18)	0.65436 (17)	0.36313 (8)	0.0407 (3)
O2	0.1467 (2)	0.61046 (18)	0.71935 (9)	0.0600 (4)

O3	0.24437 (17)	0.38884 (16)	1.07394 (8)	0.0379 (3)
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Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0468 (10)	0.0461 (10)	0.0275 (8)	−0.0229 (8)	−0.0015 (7)	−0.0089 (7)
C2	0.0410 (9)	0.0405 (9)	0.0280 (8)	−0.0168 (7)	−0.0013 (7)	−0.0076 (7)
C3	0.0400 (9)	0.0373 (9)	0.0255 (8)	−0.0233 (7)	−0.0028 (6)	−0.0056 (6)
C4	0.0483 (9)	0.0356 (9)	0.0256 (8)	−0.0218 (8)	−0.0038 (6)	−0.0078 (6)
C5	0.0477 (9)	0.0360 (9)	0.0289 (8)	−0.0218 (7)	−0.0062 (7)	−0.0070 (7)
C6	0.0687 (13)	0.0397 (11)	0.0392 (10)	−0.0174 (9)	−0.0189 (9)	−0.0045 (8)
C7	0.0714 (14)	0.0700 (14)	0.0280 (9)	−0.0185 (11)	−0.0017 (9)	−0.0171 (9)
C8	0.0413 (9)	0.0355 (9)	0.0262 (8)	−0.0174 (7)	−0.0048 (6)	−0.0052 (6)
C9	0.0452 (10)	0.0479 (11)	0.0250 (8)	−0.0186 (9)	−0.0028 (7)	−0.0050 (7)
C10	0.0489 (10)	0.0365 (10)	0.0268 (8)	−0.0158 (8)	−0.0094 (7)	−0.0066 (7)
C11	0.0411 (9)	0.0338 (9)	0.0250 (8)	−0.0124 (7)	−0.0047 (6)	−0.0073 (6)
C12	0.0548 (10)	0.0419 (10)	0.0214 (8)	−0.0196 (8)	−0.0036 (7)	−0.0063 (7)
C13	0.0303 (8)	0.0332 (8)	0.0253 (7)	−0.0077 (6)	−0.0036 (6)	−0.0065 (6)
C14	0.0417 (9)	0.0319 (9)	0.0281 (8)	−0.0100 (7)	−0.0053 (6)	−0.0077 (7)
C15	0.0362 (8)	0.0335 (9)	0.0294 (8)	−0.0081 (7)	−0.0066 (6)	−0.0059 (7)
C16	0.0334 (8)	0.0368 (9)	0.0295 (8)	−0.0117 (7)	−0.0045 (6)	−0.0079 (7)
C17	0.0357 (8)	0.0347 (9)	0.0258 (8)	−0.0118 (7)	−0.0039 (6)	−0.0051 (6)
C18	0.0573 (11)	0.0469 (11)	0.0400 (10)	−0.0242 (9)	−0.0079 (8)	−0.0128 (8)
C19	0.0711 (13)	0.0456 (11)	0.0282 (9)	−0.0160 (10)	−0.0118 (8)	−0.0007 (8)
N1	0.0545 (10)	0.0586 (11)	0.0410 (9)	−0.0029 (9)	−0.0031 (7)	−0.0072 (8)
N2	0.0952 (14)	0.0525 (11)	0.0367 (9)	−0.0405 (10)	−0.0071 (8)	−0.0083 (7)
O1	0.0550 (7)	0.0432 (7)	0.0253 (6)	−0.0199 (6)	−0.0073 (5)	−0.0063 (5)
O2	0.1017 (12)	0.0355 (8)	0.0332 (7)	−0.0097 (7)	−0.0227 (7)	−0.0082 (5)
O3	0.0483 (7)	0.0410 (7)	0.0248 (6)	−0.0157 (5)	−0.0086 (5)	−0.0068 (5)

Geometric parameters ($\text{\AA}$, $^\circ$)

C1—C2	1.338 (2)	C10—C11	1.486 (2)
C1—O1	1.356 (2)	C11—C13	1.385 (2)
C1—C7	1.487 (2)	C11—C12	1.426 (2)
C2—C3	1.435 (2)	C12—N2	1.144 (2)
C2—H2	0.9300	C13—C17	1.437 (2)
C3—C8	1.397 (2)	C13—C14	1.440 (2)
C3—C4	1.423 (2)	C14—C15	1.337 (2)
C4—C5	1.345 (2)	C14—H14	0.9300
C4—H4	0.9300	C15—O3	1.360 (2)
C5—O1	1.3620 (19)	C15—C19	1.486 (2)
C5—C6	1.476 (3)	C16—C17	1.343 (2)
C6—H6A	0.9600	C16—O3	1.363 (2)
C6—H6B	0.9600	C16—C18	1.482 (2)
C6—H6C	0.9600	C17—H17	0.9300
C7—H7A	0.9600	C18—H18A	0.9600
C7—H7B	0.9600	C18—H18B	0.9600

C7—H7C	0.9600	C18—H18C	0.9600
C8—C9	1.421 (2)	C19—H19A	0.9600
C8—C10	1.470 (2)	C19—H19B	0.9600
C9—N1	1.147 (2)	C19—H19C	0.9600
C10—O2	1.223 (2)		
C2—C1—O1	121.73 (15)	C13—C11—C12	117.26 (14)
C2—C1—C7	126.75 (18)	C13—C11—C10	124.94 (15)
O1—C1—C7	111.51 (15)	C12—C11—C10	117.57 (14)
C1—C2—C3	121.56 (16)	N2—C12—C11	176.67 (19)
C1—C2—H2	119.2	C11—C13—C17	125.09 (14)
C3—C2—H2	119.2	C11—C13—C14	121.37 (15)
C8—C3—C4	124.46 (14)	C17—C13—C14	113.53 (14)
C8—C3—C2	121.12 (15)	C15—C14—C13	122.65 (15)
C4—C3—C2	114.39 (14)	C15—C14—H14	118.7
C5—C4—C3	121.60 (15)	C13—C14—H14	118.7
C5—C4—H4	119.2	C14—C15—O3	121.20 (14)
C3—C4—H4	119.2	C14—C15—C19	126.78 (16)
C4—C5—O1	121.51 (16)	O3—C15—C19	112.01 (14)
C4—C5—C6	126.76 (16)	C17—C16—O3	122.46 (15)
O1—C5—C6	111.71 (14)	C17—C16—C18	126.40 (16)
C5—C6—H6A	109.5	O3—C16—C18	111.14 (14)
C5—C6—H6B	109.5	C16—C17—C13	121.18 (15)
H6A—C6—H6B	109.5	C16—C17—H17	119.4
C5—C6—H6C	109.5	C13—C17—H17	119.4
H6A—C6—H6C	109.5	C16—C18—H18A	109.5
H6B—C6—H6C	109.5	C16—C18—H18B	109.5
C1—C7—H7A	109.5	H18A—C18—H18B	109.5
C1—C7—H7B	109.5	C16—C18—H18C	109.5
H7A—C7—H7B	109.5	H18A—C18—H18C	109.5
C1—C7—H7C	109.5	H18B—C18—H18C	109.5
H7A—C7—H7C	109.5	C15—C19—H19A	109.5
H7B—C7—H7C	109.5	C15—C19—H19B	109.5
C3—C8—C9	117.56 (14)	H19A—C19—H19B	109.5
C3—C8—C10	124.29 (15)	C15—C19—H19C	109.5
C9—C8—C10	118.07 (14)	H19A—C19—H19C	109.5
N1—C9—C8	177.40 (19)	H19B—C19—H19C	109.5
O2—C10—C8	122.05 (15)	C1—O1—C5	119.20 (13)
O2—C10—C11	120.33 (15)	C15—O3—C16	118.93 (12)
C8—C10—C11	117.62 (14)		
O1—C1—C2—C3	1.2 (3)	C12—C11—C13—C17	−177.06 (15)
C7—C1—C2—C3	−177.46 (17)	C10—C11—C13—C17	−2.8 (3)
C1—C2—C3—C8	177.42 (15)	C12—C11—C13—C14	4.0 (2)
C1—C2—C3—C4	−0.5 (2)	C10—C11—C13—C14	178.25 (15)
C8—C3—C4—C5	−178.45 (15)	C11—C13—C14—C15	−178.69 (15)
C2—C3—C4—C5	−0.7 (2)	C17—C13—C14—C15	2.3 (2)
C3—C4—C5—O1	1.0 (2)	C13—C14—C15—O3	−2.7 (2)

C3—C4—C5—C6	−177.63 (16)	C13—C14—C15—C19	176.24 (16)
C4—C3—C8—C9	−178.33 (15)	O3—C16—C17—C13	−1.1 (2)
C2—C3—C8—C9	4.0 (2)	C18—C16—C17—C13	179.01 (15)
C4—C3—C8—C10	−1.6 (2)	C11—C13—C17—C16	−179.40 (15)
C2—C3—C8—C10	−179.27 (15)	C14—C13—C17—C16	−0.4 (2)
C3—C8—C10—O2	−23.9 (3)	C2—C1—O1—C5	−0.9 (2)
C9—C8—C10—O2	152.77 (18)	C7—C1—O1—C5	178.00 (15)
C3—C8—C10—C11	156.50 (15)	C4—C5—O1—C1	−0.3 (2)
C9—C8—C10—C11	−26.8 (2)	C6—C5—O1—C1	178.58 (15)
O2—C10—C11—C13	−26.7 (3)	C14—C15—O3—C16	1.0 (2)
C8—C10—C11—C13	152.82 (16)	C19—C15—O3—C16	−178.02 (14)
O2—C10—C11—C12	147.49 (18)	C17—C16—O3—C15	0.9 (2)
C8—C10—C11—C12	−33.0 (2)	C18—C16—O3—C15	−179.25 (14)

Hydrogen-bond geometry (Å, °)

<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>
C4—H4 $\cdots$ O2	0.93	2.26	2.876 (2)	123
C17—H17 $\cdots$ O2	0.93	2.33	2.908 (2)	120
C6—H6 <i>A</i> $\cdots$ N1 ⁱ	0.96	2.62	3.557 (3)	166
C18—H18 <i>A</i> $\cdots$ N2 ⁱⁱ	0.96	2.48	3.425 (3)	169
C19—H19 <i>A</i> $\cdots$ O2 ⁱⁱⁱ	0.96	2.55	3.446 (3)	155

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