



Absolute structure of the chiral pyrrolidine derivative (2*S*)-methyl (*Z*)-5-(2-*tert*-butoxy-1-cyano-2-oxoethylidene)pyrrolidine-2-carboxylate, a compound with low resonant scattering

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The enantiopure monopyrrolidine derivative (2*S*)-methyl (*Z*)-5-(2-*tert*-butoxy-1-cyano-2-oxoethylidene)pyrrolidine-2-carboxylate, C₁₃H₁₈N₂O₄, (**1**), represents a potential ligand and an attractive intermediate for the synthesis of chiral metal complexes. At the molecular level, the compound features an intramolecular N–H···O hydrogen bond; neighbouring molecules interact *via* N–H···N contacts to form chains along [100]. Due to its elemental composition, resonant scattering of the target compound is entirely insignificant for diffraction experiments with Mo *K*α and small even for Cu *K*α radiation. A preliminary study with the harder radiation type confirmed the chiral space group and the suitability of the single crystal chosen; as expected, the results concerning the absolute structure remained completely inconclusive. A second data collection with the longer wavelength gave satisfactory quality indicators for the correct handedness of the molecule, albeit with high standard uncertainties. The absolute configuration has been assessed independently: CD spectra for both enantiomers of the target molecule were calculated and the spectrum for the *S*-configured stereoisomer was in agreement with the experiment. The Cotton effect of (**1**) may be ascribed to π–π* transitions from HOMO to LUMO and from HOMO to LUMO+1. As both independent techniques agree with respect to the handedness of the target molecule, the absolute structure may be assigned with a high degree of confidence.

1. Introduction

Pyrrolidine derivatives have found applications as potential ligands, as organic intermediates and in medicinal chemistry. They can inhibit the activity of over-expressed protein tyrosine phosphatases (PTPs) of cancer cells and may be employed as anticancer drugs (IC₅₀ value is 3.65 ± 0.08 μM) (Chen *et al.*, 2017). By forming imine or enamine intermediates with aldehydes and ketones, chiral monopyrrolidine derivatives have been widely used in asymmetric catalysis, and alkylation and acylation reactions of aldehydes and ketones have been achieved (Jensen *et al.*, 2012). We report here the absolute configuration of the chiral pyrrolidine derivative (2*S*)-methyl (*Z*)-5-(2-*tert*-butoxy-1-cyano-2-oxoethylidene)pyrrolidine-2-carboxylate, (**1**) (Scheme 1). The compound has been synthesized and spectroscopically characterized by Pfaltz and co-workers (Pfaltz *et al.*, 1977; Fritschi *et al.*, 1988; Pfaltz, 1993); retention of the configuration at C1 may be assumed. No studies in medicinal chemistry have been conducted on (**1**), but a closely related compound was investigated, *i.e.* methyl 5-[1-cyano-2-oxo-2-(2,3,4-trimethoxyphenyl)ethylidene]prolinate was screened by the National Cancer Institution, USA, against

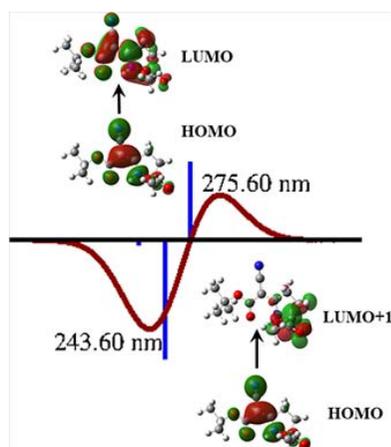


Table 1

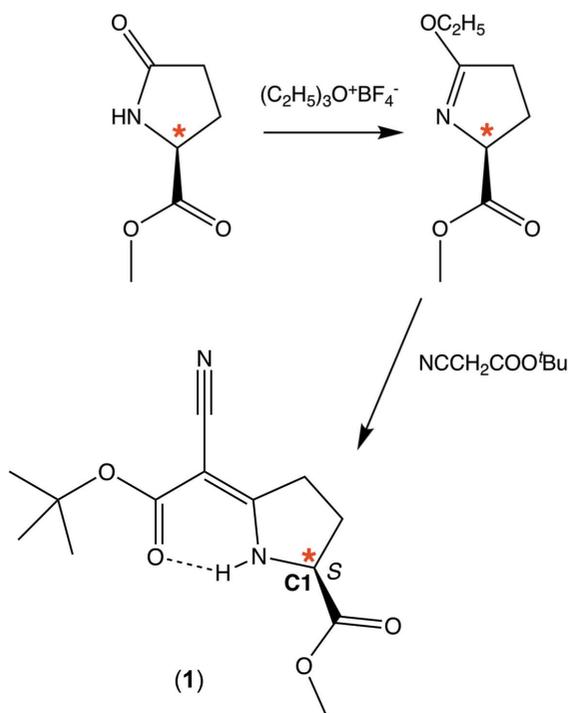
Experimental details.

For both determinations: $C_{13}H_{18}N_2O_4$, $M_r = 266.29$, orthorhombic, $P2_12_12_1$, $Z = 4$. Experiments were carried out at 100 K using a D8 goniometer with an APEX CCD area detector. Absorption was corrected for by multi-scan methods (SADABS; Bruker, 2008). H atoms were treated by a mixture of independent and constrained refinement.

	(1mo)	(1cu)
Crystal data		
a, b, c (Å)	7.347 (4), 10.197 (6), 18.477 (10)	7.3731 (3), 10.1909 (4), 18.4972 (7)
V (Å ³)	1384.1 (13)	1389.85 (9)
Radiation type	Mo $K\alpha$	Cu $K\alpha$
μ (mm ⁻¹)	0.10	0.79
Crystal size (mm)	0.35 × 0.29 × 0.28	0.35 × 0.29 × 0.28
Data collection		
T_{\min}, T_{\max}	0.473, 0.745	0.579, 0.753
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10626, 2290, 2051	17945, 2408, 2266
R_{int}	0.091	0.083
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.583	0.597
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.051, 0.124, 1.08	0.032, 0.077, 1.10
No. of reflections	2290	2408
No. of parameters	180	181
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.21, -0.18	0.17, -0.15
Absolute structure	Flack x determined using 710 quotients [$(I^+) - (I^-)$]/[$(I^+) + (I^-)$] (Parsons <i>et al.</i> , 2013)	Flack x determined using 879 quotients [$(I^+) - (I^-)$]/[$(I^+) + (I^-)$] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	1.1 (10)	-0.04 (12)

Computer programs: SMART (Bruker, 2001), SAINT-Plus (Bruker, 2009), SHELXS2013 (Sheldrick, 2008), SHELXL2017 (Sheldrick, 2015) and PLATON (Spek, 2009).

60 human tumour cell lines and showed moderate cell-growth inhibition at 10 μM concentration for renal cancer and leukemia



Scheme 1

(Ghinet *et al.*, 2012). To the best of our knowledge, the structure of **1** has never been investigated and its absolute configuration has not been confirmed. Our assignment relies on a combination of diffraction experiments, experimental circular dichroism (CD)

spectroscopy and theoretical calculations of these spectra. We will show that diffraction results, albeit with only a modest contribution of resonant scattering, and CD spectroscopy agree in their assignment of the absolute structure, whereas a diffraction experiment without relevant anomalous dispersion remains inconclusive.

2. Experimental

2.1. Synthesis and crystallization

All reagents were commercially available and were used without further purification. The powder diffraction experiment was recorded at the Institute of Inorganic Chemistry, RWTH Aachen University, using a Stoe imaging-plate detector (IP-PSD). The diffractogram was recorded on a flat sample at ambient temperature in transmission mode using Cu $K\alpha_1$ radiation. The title compound was synthesized following the procedure of Pfaltz (Pfaltz *et al.*, 1977; Fritschi *et al.*, 1988; Pfaltz, 1993). The reaction combines *S*-configured pyroglutamic acid methyl ester and *tert*-butyl 2-cyanoacetate; retention of the configuration at the chiral centre (*) was expected [see Scheme 1 for a summary of the synthesis for **1**] according to Pfaltz *et al.* (1977)] and is confirmed by the results reported in this work.

Crystals were grown by slow partial evaporation of a methanol solvent at ambient temperature over a period of one week. CHN microanalysis was carried out at the Institute of Organic Chemistry, RWTH Aachen University, using a HERAEUS CHNO-Rapid. Analysis calculated (%) for $C_{13}H_{18}N_2O_4$: C 58.74, H 6.81, N 10.52; found: C 58.62, H 6.53, N 10.72. The powder X-ray diffraction (PXRD) pattern (see

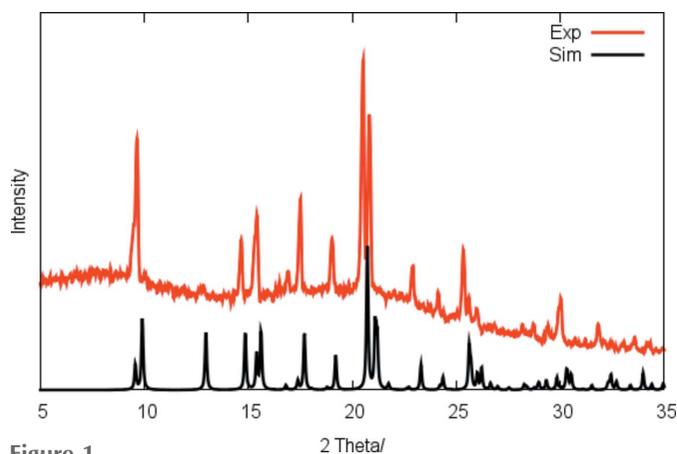


Figure 1
Powder X-ray diffraction pattern of **(1)**.

Fig. 1) confirms that **(1)** is obtained as an essentially phase-pure product; the shift of the calculated lines of two larger angles can be attributed to the different data-collection temperatures for the single-crystal and powder analyses. The IR spectrum shows an absorption associated with the triple bond in the nitrile group at $\nu(\text{C}\equiv\text{N}) = 2205 \text{ cm}^{-1}$, in good agreement with the reported frequency of 2207 cm^{-1} , and the ^1H NMR spectrum matches that available in the literature (Fritschi *et al.*, 1988).

2.2. Refinement

Crystal data, data collection parameters and refinement results for both single-crystal X-ray diffraction experiments with Mo $K\alpha$ (**1mo**) and Cu $K\alpha$ (**1cu**) radiation are summarized in Table 1. H atoms attached to C atoms were introduced in calculated positions and treated as riding, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for CH_3 groups and $1.2U_{\text{eq}}(\text{C})$ otherwise. For the H atom attached to an N atom, the positional coordinates and an isotropic displacement parameter were refined freely. For the diffraction experiment (**1mo**), resonant scattering is insignificant; no information can be deduced from the refined enantiopol parameter and its very high standard uncertainty.

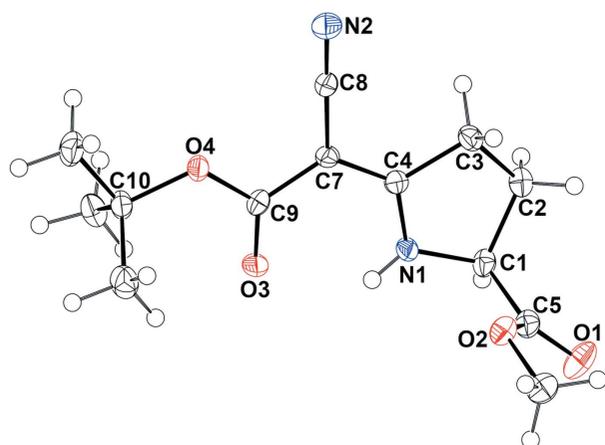


Figure 2
The asymmetric unit of **(1)** based on data set (**1cu**), with displacement ellipsoids enclosing 50% of electron density.

Table 2
Hydrogen-bond geometry (\AA , $^\circ$) for (**1cu**).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1N}\cdots\text{O3}$	0.81 (3)	2.13 (2)	2.714 (2)	129 (2)
$\text{N1}-\text{H1N}\cdots\text{N2}^i$	0.81 (3)	2.33 (2)	2.924 (2)	131 (2)
$\text{C11}-\text{H11B}\cdots\text{O2}^{ii}$	0.98	2.60	3.565 (3)	169

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$.

For a better comparison with the results of (**1cu**) on the same single crystal, the same absolute structure model was chosen in both cases.

2.3. CD spectroscopy

The experimental electronic circular dichroism (CD) spectrum of **(1)** was recorded in methanol on a Chirascan circular dichroism chiroptical spectrometer at the Institutes of Biomedical Sciences of Shanxi University; it shows a positive Cotton effect at 278.40 nm and a negative Cotton effect at 245.60 nm.

3. Results and discussion

3.1. Molecular structure

The chiral compound **(1)** was obtained as an essentially monophasic crystalline product. In view of its elemental composition, the determination of the absolute structure was expected to be challenging. With respect to resonant scattering, we calculated values of 6 and 33 for *Friedif* (Flack & Shmueli, 2007) for diffraction experiments with Mo and Cu $K\alpha$ radiation, respectively. Even the higher second value is dangerously low if the diffraction experiments are hampered by additional complications, such as disorder or twinning. An initial data collection with our standard set-up (**1mo**) was performed to ensure sufficient quality for the selected crystal and to confirm the chiral space group: even for high enantiomeric excesses, a small amount of racemic solid might precipitate (Böhme & Fels, 2013).

The second data set collected with Cu $K\alpha$ radiation resulted in slightly smaller standard uncertainties; all numerical values reported below therefore refer to (**1cu**) (see §3.3). As expected, the enantiopure compound **(1)** crystallized in a chiral space group. The asymmetric unit consists of a single molecule in the space group $P2_12_12_1$; Fig. 2 shows a displacement ellipsoid plot.

Atoms N1, N2, O3, O4, C3, C4 and C7–C10 define an almost planar core of the molecule shown in Fig. 3. The maximum deviation from that least-squares plane is 0.045 (2) \AA for atom C3. Within the core plane, the pyrrolidine N–H group acts as a hydrogen-bond donor towards carbonyl atom O3; the hydrogen-bond geometry is summarized in Table 2.

The pyrrolidine ring is nonplanar and its C2 atom is significantly displaced from the above-defined plane by 0.364 (2) \AA .

In contrast to the carboxylate group (C9/O3/O4), the C5/O1/O2 group is not coplanar with the core of the molecule but

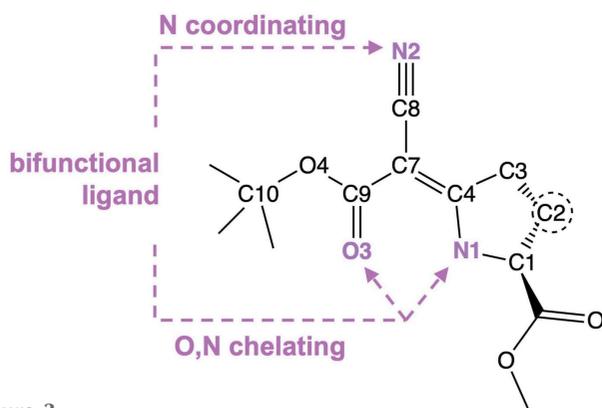


Figure 3
The planar core of (**1**).

subtends an angle of $86.1(2)^\circ$ with the least-squares plane defined by atoms N1, N2, O3, O4, C3, C4 and C7–C10 (Fig. 2). Table 3 contains selected torsion angles.

The overall conformation of the molecule suggests its use as a ditopic ligand, similar to substituted acetylacetonates (Kremer & Englert, 2018). The potential coordination sites have been indicated in Fig. 3.

3.2. Intermolecular contacts

The H atom of the pyrrolidine N–H group represents the only potential donor for classical hydrogen bonds. In addition to the intramolecular N–H \cdots O contact described above, it is involved in an intermolecular N–H \cdots N hydrogen bond to the nitrile group of a neighbouring molecule. The resulting chain runs along [100] (Fig. 4). The closest contacts perpendicular to this chain are due to nonclassical C–H \cdots O interactions. Numerical values and symmetry operators for the short contacts have been compiled in Table 2.

3.3. Absolute structure

3.3.1. Resonant scattering. Our first intensity data collection, *i.e.* the (**1mo**) data, had provided a consistent structure model without disorder and confirmed the quality of the chosen sample. As expected, however, the commonly applied methods for assigning the absolute structure gave inconclusive

Table 3
Selected torsion angles ($^\circ$) for (**1cu**).

C4–N1–C1–C5	109.61 (19)	N1–C1–C5–O2	–26.3 (2)
C4–N1–C1–C2	–12.9 (2)	C2–C1–C5–O2	90.1 (2)
C1–N1–C4–C7	–179.84 (18)	C3–C4–C7–C8	–2.4 (3)
C1–N1–C4–C3	–0.6 (2)	N1–C4–C7–C9	–2.1 (3)
C2–C3–C4–N1	14.0 (2)	C10–O4–C9–O3	–2.1 (3)
C6–O2–C5–O1	–2.2 (3)	C4–C7–C9–O3	–1.4 (3)
C6–O2–C5–C1	179.93 (16)	C8–C7–C9–O4	0.4 (3)
N1–C1–C5–O1	155.73 (19)	C9–O4–C10–C13	61.8 (2)

results for (**1mo**) with its negligible resonant scattering. The Flack (1983, 2003), Parsons (Parsons *et al.*, 2013) and Hooft (Hooft *et al.*, 2010) parameters refined to values of *ca* 1, with standard uncertainties equally large; no conclusions could be drawn from these numbers. Therefore, a second diffraction experiment with Cu $K\alpha$ radiation, *i.e.* the (**1cu**) data, was performed on the same single crystal. Fractional coordinates and derived geometry parameters agreed with the results of (**1mo**) within error, but resonant scattering was more pronounced and led to information about the absolute structure, *i.e.* the Flack (1983) parameter refined to $-0.04(12)$; very similar values and standard uncertainties were obtained for Parsons' quotient method [$-0.01(13)$, Parsons *et al.*, 2013] and Hooft's Bayesian procedure [$0.01(10)$, Hooft *et al.*, 2010].

3.3.2. CD spectra. An independent assessment of the absolute structure of (**1**) relies on a comparison of the experimentally observed and theoretically calculated electronic circular dichroism (ECD) spectra; they are shown in Fig. 5.

The calculations were based initially on the molecular geometry obtained from (**1cu**). Ground-state geometry optimization and subsequent frequency calculations were performed *via* the density functional theory (DFT) method as implemented in *GAUSSIAN09* (Frisch *et al.*, 2009) using the B3LYP hybrid functional (Becke, 1993) and the 6-311++G(2d,p) basis set. The excitation energies, oscillator and rotational strengths of the excited singlet states for the optimized geometry were calculated according to the time-dependent DFT (TDDFT) method with the same functional and basis set. The effects of the solvent (methanol) were included using the polarizable continuum model (PCM)

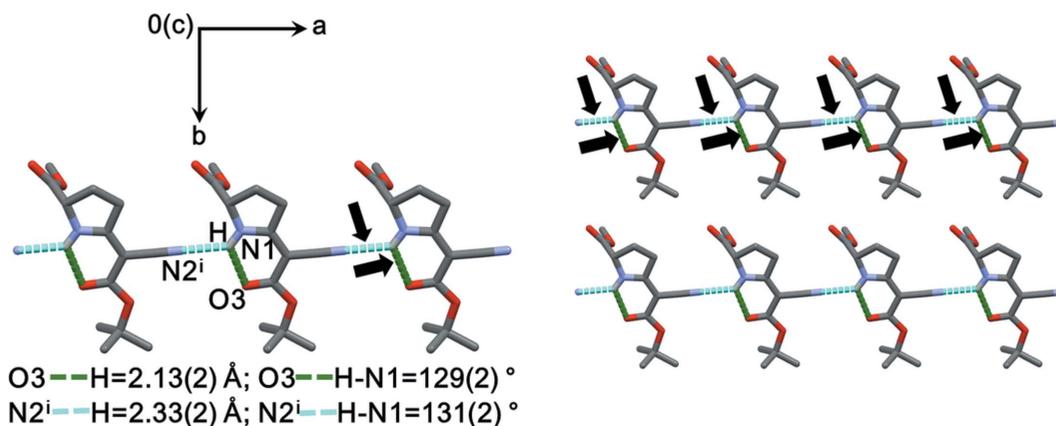


Figure 4
Intra- and intermolecular hydrogen bonds in the crystal of (**1**). H atoms not involved in hydrogen bonds have been omitted for clarity.

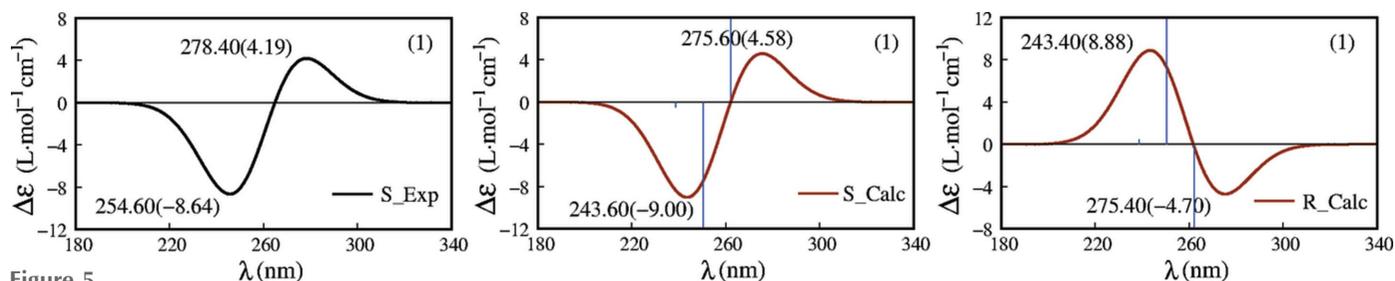


Figure 5 Experimental (left) and calculated CD spectra for **(1)** in methanol. The spectrum in the centre corresponds to the (correct) *S* enantiomer and that on the right to the alternative *R* enantiomer.

Table 4

Excitation wavelengths (λ , nm), oscillator (f) and rotational (R , DBM) strengths and transition assignments from occupied (Occ) to virtual (Virt) orbitals.

λ	f	R	Occ-Virt	Assignments
262	0.2670	0.4600	HOMO→LUMO HOMO→LUMO+1	$\pi(\text{coplanar})\rightarrow\pi^*(\text{coplanar})$ (77%) $\pi(\text{coplanar})\rightarrow\pi^*(\text{COO in COOCH}_3)$ (19%)
250	0.1642	−0.6047	HOMO→LUMO+1 HOMO→LUMO	$\pi(\text{coplanar})\rightarrow\pi^*(\text{COO in COOCH}_3)$ (77%) $\pi(\text{coplanar})\rightarrow\pi^*(\text{coplanar})$ (20%)
239	0.0028	−0.0173	HOMO-1→LUMO	$\sigma+n_N+n_O\rightarrow\pi^*(\text{coplanar})$ (89%)

(Tomasi *et al.*, 2005) in the integral equation formalism (IEF). With the PCM, a ground-state energy of -916.95 a.u. for **(1)** was obtained.

3.3.3. DFT energy levels and Kohn–Sham orbitals. The DFT energy levels show a HOMO–LUMO gap of 5.25 eV. A detailed analysis of the Kohn–Sham orbitals has been graphically summarized in Fig. 6. The two lowest unoccupied orbitals are dominated by a π^* region in the planar core and in the carboxylate group of the methyl ester (C5/O1/O2). The absolute value of the energy difference between these LUMO and LUMO+1 orbitals is 0.72 eV. Both of them may well act as electron-acceptor orbitals when electrons from the HOMO and HOMO-1 orbitals are excited. The HOMO is dominated by the π region of the planar core of **(1)**. The HOMO-1 essentially corresponds to a combination of $\sigma + n_N + n_O$ orbitals; the energy difference of the HOMO and HOMO-1 amounts to 1.28 eV.

3.3.4. Rotational strengths and transition assignments. The contribution of different transition probabilities to the chiroptical properties of **(1)** were analyzed. The calculated excitation energies and oscillator and rotational strengths (in velocity form), as well as the transition assignments, have been compiled in Table 4. Results for the three excitations of the

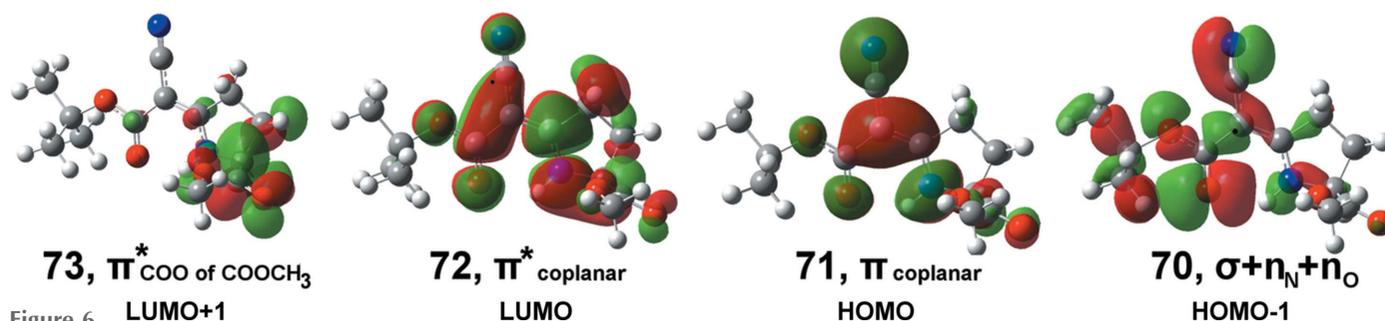


Figure 6 Selected Kohn–Sham orbitals for **(1)**.

lowest energy conformer are given; they cover the spectral range $180 < \lambda < 350$ nm.

Using the excitation energies and rotational strengths calculated by TDDFT, theoretical CD spectra for both stereoisomers of **(1)** were generated as the sum of Gaussians, centred at the calculated wavelengths λ_{calc} with integral intensities proportional to the rotational strengths R of the corresponding transitions.

The half bandwidths Γ at the $\Delta\epsilon_{\text{max}}/e$ of Gaussians were assumed as $\Gamma = k\lambda_{\text{calc}}^{3/2}$ (Brown *et al.*, 1971) with $k = 0.00385$ to best reproduce the experiment. The experimental spectrum and calculated spectra for both enantiomers have been compiled in Fig. 5. Ideally, experimental CD spectra of opposite enantiomers are mirror images of each other (Flack & Bernardinelli, 2003).

It is obvious that the CD curve calculated for *S*-configured **(1)** is in excellent agreement with the observed curve, with only a small blue shift in the calculated maximum. The agreement confirms that our spectroscopic interpretation of the DFT results is correct.

The observed CD curve consists of two absorption bands, *i.e.* a positive band around 278 nm arising from the first π – π^* transition in which electrons are transferred from the HOMO to the LUMO (77%) and from the HOMO to the LUMO+1 (19%), and a negative band around 243 nm, which can also be ascribed to the second π – π^* transition and a minor contribution of a σ – π^* transition. The main contribution to this significant negative π – π^* transition, however, is associated with the transition from HOMO to LUMO+1 (77%) and from HOMO to LUMO (20%). The σ – π^* transition can be assigned to electronic excitation from HOMO-1 to LUMO. Thus, the optical properties of chiral compound **(1)** are mainly domi-

nated by a combination of π - π^* transitions from HOMO to LUMO and HOMO to LUMO+1.

4. Conclusion and outlook

The absolute structure of (**1**) could reliably be assigned as *S*, despite the limited contribution of resonant scattering; a low-temperature diffraction experiment with Cu $K\alpha$ radiation resulted in consistent values for the commonly applied enantiopol parameters. Their final standard uncertainties are still rather high, but our assignment is in agreement with the expected retention at the stereocentre of the starting material and could be further corroborated by the match between experimentally observed and theoretically calculated CD spectra. The associated Cotton effect was well reproduced by our TDDFT calculations, thus confirming that our methodology was suitable. We hope to use enantiopure (**1**) in future experiments as a ditopic ligand with the additional possibility to transfer central chirality from the ligand to its coordination complexes (Wang *et al.*, 2015).

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supporting information

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Absolute structure of the chiral pyrrolidine derivative (2*S*)-methyl (Z)-5-(2-*tert*-butoxy-1-cyano-2-oxoethylidene)pyrrolidine-2-carboxylate, a compound with low resonant scattering

Ai Wang and Ulli Englert

Computing details

For both structures, data collection: *SMART* (Bruker, 2001); cell refinement: *SMART* (Bruker, 2001); data reduction: *SAINTE-Plus* (Bruker, 2009); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015); software used to prepare material for publication: *SHELXL2017* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

(2*S*)-Methyl (Z)-5-(2-*tert*-butoxy-1-cyano-2-oxoethylidene)pyrrolidine-2-carboxylate (1mo)

Crystal data

C₁₃H₁₈N₂O₄

M_r = 266.29

Orthorhombic, *P*2₁2₁2₁

a = 7.347 (4) Å

b = 10.197 (6) Å

c = 18.477 (10) Å

V = 1384.1 (13) Å³

Z = 4

F(000) = 568

D_x = 1.278 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 1389 reflections

θ = 2.3–20.4°

μ = 0.10 mm⁻¹

T = 100 K

Block, colourless

0.35 × 0.29 × 0.28 mm

Data collection

D8 goniometer with APEX CCD area detector diffractometer

Radiation source: Incoatec microsource

Multilayer optics monochromator

ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2008)

T_{min} = 0.473, *T_{max}* = 0.745

10626 measured reflections

2290 independent reflections

2051 reflections with *I* > 2σ(*I*)

R_{int} = 0.091

θ_{max} = 24.5°, θ_{min} = 2.2°

h = -8→8

k = -11→11

l = -21→21

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.051

wR(*F*²) = 0.124

S = 1.08

2290 reflections

180 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0228*P*)² + 0.6063*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

$$\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack x determined using
710 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 1.1 (10)

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	0.4701 (4)	0.3508 (3)	0.57875 (17)	0.0391 (9)
O2	0.6551 (4)	0.4427 (3)	0.66052 (15)	0.0254 (7)
O3	0.7806 (4)	0.8818 (3)	0.62664 (16)	0.0255 (7)
O4	1.0663 (4)	0.9541 (2)	0.64917 (14)	0.0209 (7)
N1	0.7498 (4)	0.6385 (3)	0.56925 (18)	0.0209 (8)
H1N	0.678 (6)	0.706 (4)	0.587 (2)	0.022 (11)*
N2	1.3786 (5)	0.7260 (3)	0.5969 (2)	0.0288 (9)
C1	0.6749 (6)	0.5183 (3)	0.5387 (2)	0.0222 (9)
H1	0.582280	0.541944	0.501289	0.027*
C2	0.8415 (6)	0.4571 (4)	0.5008 (2)	0.0261 (10)
H2A	0.843025	0.360684	0.507255	0.031*
H2B	0.840489	0.477085	0.448324	0.031*
C3	1.0056 (6)	0.5202 (4)	0.5376 (2)	0.0225 (9)
H3A	1.055995	0.462237	0.575657	0.027*
H3B	1.102471	0.540554	0.502126	0.027*
C4	0.9278 (5)	0.6441 (4)	0.5701 (2)	0.0188 (9)
C5	0.5863 (6)	0.4285 (4)	0.5946 (2)	0.0250 (10)
C6	0.5754 (7)	0.3593 (5)	0.7167 (2)	0.0337 (11)
H6A	0.447561	0.383309	0.723879	0.051*
H6B	0.642325	0.371383	0.762109	0.051*
H6C	0.583167	0.267216	0.701744	0.051*
C7	1.0311 (5)	0.7484 (4)	0.5966 (2)	0.0191 (9)
C8	1.2223 (6)	0.7373 (4)	0.5960 (2)	0.0213 (9)
C9	0.9428 (6)	0.8655 (4)	0.6249 (2)	0.0195 (9)
C10	1.0040 (6)	1.0830 (3)	0.6775 (2)	0.0244 (10)
C11	1.1794 (7)	1.1500 (4)	0.6988 (3)	0.0343 (11)
H11A	1.260278	1.154912	0.656748	0.051*
H11B	1.238827	1.099748	0.737386	0.051*
H11C	1.152872	1.238765	0.716218	0.051*
C12	0.9109 (7)	1.1592 (4)	0.6177 (2)	0.0321 (11)
H12A	0.985600	1.155885	0.573823	0.048*
H12B	0.895526	1.250717	0.632817	0.048*
H12C	0.791425	1.120475	0.607869	0.048*
C13	0.8851 (7)	1.0623 (4)	0.7430 (2)	0.0339 (11)
H13A	0.861422	1.146855	0.766397	0.051*

H13B	0.947119	1.003897	0.777191	0.051*
H13C	0.769592	1.022628	0.728074	0.051*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.043 (2)	0.0376 (18)	0.0362 (19)	-0.0213 (16)	-0.0071 (16)	0.0021 (15)
O2	0.0312 (16)	0.0225 (13)	0.0224 (15)	-0.0040 (13)	-0.0023 (13)	0.0021 (12)
O3	0.0196 (15)	0.0217 (14)	0.0351 (17)	0.0004 (12)	0.0010 (13)	-0.0057 (13)
O4	0.0229 (14)	0.0140 (13)	0.0259 (16)	-0.0008 (11)	-0.0018 (12)	-0.0007 (12)
N1	0.0199 (19)	0.0180 (17)	0.0247 (19)	0.0009 (15)	-0.0011 (14)	-0.0002 (15)
N2	0.026 (2)	0.030 (2)	0.030 (2)	0.0012 (15)	-0.0002 (16)	-0.0005 (16)
C1	0.027 (2)	0.0156 (18)	0.024 (2)	-0.0012 (16)	-0.0083 (18)	-0.0005 (16)
C2	0.035 (2)	0.019 (2)	0.023 (2)	-0.001 (2)	-0.0034 (19)	-0.0032 (17)
C3	0.027 (2)	0.0164 (19)	0.024 (2)	0.0032 (17)	0.0009 (18)	-0.0004 (17)
C4	0.025 (2)	0.017 (2)	0.015 (2)	0.0015 (17)	-0.0002 (17)	0.0040 (16)
C5	0.027 (2)	0.020 (2)	0.027 (3)	-0.0005 (18)	-0.0028 (19)	0.0000 (18)
C6	0.039 (3)	0.032 (2)	0.030 (3)	-0.004 (2)	0.005 (2)	0.008 (2)
C7	0.022 (2)	0.0164 (18)	0.019 (2)	0.0017 (17)	-0.0016 (17)	0.0003 (16)
C8	0.030 (2)	0.0147 (19)	0.020 (2)	0.0002 (17)	0.0030 (18)	0.0011 (16)
C9	0.023 (2)	0.0178 (19)	0.017 (2)	-0.0015 (17)	0.0005 (17)	0.0023 (17)
C10	0.034 (2)	0.0133 (18)	0.026 (2)	0.0014 (17)	0.000 (2)	-0.0048 (16)
C11	0.043 (3)	0.022 (2)	0.038 (3)	-0.006 (2)	-0.004 (2)	-0.006 (2)
C12	0.047 (3)	0.020 (2)	0.030 (3)	0.009 (2)	0.000 (2)	0.0000 (19)
C13	0.049 (3)	0.027 (2)	0.025 (2)	-0.004 (2)	0.009 (2)	-0.005 (2)

Geometric parameters (Å, °)

O1—C5	1.201 (5)	C4—C7	1.395 (5)
O2—C5	1.327 (5)	C6—H6A	0.9800
O2—C6	1.464 (5)	C6—H6B	0.9800
O3—C9	1.204 (5)	C6—H6C	0.9800
O4—C9	1.357 (5)	C7—C8	1.409 (6)
O4—C10	1.487 (5)	C7—C9	1.456 (5)
N1—C4	1.309 (5)	C10—C13	1.507 (6)
N1—C1	1.457 (5)	C10—C11	1.511 (6)
N1—H1N	0.93 (4)	C10—C12	1.514 (6)
N2—C8	1.154 (5)	C11—H11A	0.9800
C1—C5	1.525 (6)	C11—H11B	0.9800
C1—C2	1.543 (6)	C11—H11C	0.9800
C1—H1	1.0000	C12—H12A	0.9800
C2—C3	1.527 (6)	C12—H12B	0.9800
C2—H2A	0.9900	C12—H12C	0.9800
C2—H2B	0.9900	C13—H13A	0.9800
C3—C4	1.510 (5)	C13—H13B	0.9800
C3—H3A	0.9900	C13—H13C	0.9800
C3—H3B	0.9900		

C5—O2—C6	115.8 (3)	H6A—C6—H6C	109.5
C9—O4—C10	119.9 (3)	H6B—C6—H6C	109.5
C4—N1—C1	114.7 (4)	C4—C7—C8	118.6 (4)
C4—N1—H1N	122 (3)	C4—C7—C9	120.6 (3)
C1—N1—H1N	123 (3)	C8—C7—C9	120.8 (4)
N1—C1—C5	113.9 (3)	N2—C8—C7	178.3 (5)
N1—C1—C2	102.5 (3)	O3—C9—O4	124.1 (4)
C5—C1—C2	113.8 (3)	O3—C9—C7	124.3 (4)
N1—C1—H1	108.8	O4—C9—C7	111.5 (3)
C5—C1—H1	108.8	O4—C10—C13	109.7 (3)
C2—C1—H1	108.8	O4—C10—C11	103.2 (3)
C3—C2—C1	104.6 (3)	C13—C10—C11	110.4 (4)
C3—C2—H2A	110.8	O4—C10—C12	109.6 (3)
C1—C2—H2A	110.8	C13—C10—C12	113.3 (4)
C3—C2—H2B	110.8	C11—C10—C12	110.1 (4)
C1—C2—H2B	110.8	C10—C11—H11A	109.5
H2A—C2—H2B	108.9	C10—C11—H11B	109.5
C4—C3—C2	103.4 (3)	H11A—C11—H11B	109.5
C4—C3—H3A	111.1	C10—C11—H11C	109.5
C2—C3—H3A	111.1	H11A—C11—H11C	109.5
C4—C3—H3B	111.1	H11B—C11—H11C	109.5
C2—C3—H3B	111.1	C10—C12—H12A	109.5
H3A—C3—H3B	109.1	C10—C12—H12B	109.5
N1—C4—C7	125.5 (4)	H12A—C12—H12B	109.5
N1—C4—C3	109.7 (4)	C10—C12—H12C	109.5
C7—C4—C3	124.8 (3)	H12A—C12—H12C	109.5
O1—C5—O2	124.5 (4)	H12B—C12—H12C	109.5
O1—C5—C1	122.3 (4)	C10—C13—H13A	109.5
O2—C5—C1	113.2 (3)	C10—C13—H13B	109.5
O2—C6—H6A	109.5	H13A—C13—H13B	109.5
O2—C6—H6B	109.5	C10—C13—H13C	109.5
H6A—C6—H6B	109.5	H13A—C13—H13C	109.5
O2—C6—H6C	109.5	H13B—C13—H13C	109.5

(1cu)

*Crystal data*C₁₃H₁₈N₂O₄ $M_r = 266.29$ Orthorhombic, $P2_12_12_1$ $a = 7.3731 (3) \text{ \AA}$ $b = 10.1909 (4) \text{ \AA}$ $c = 18.4972 (7) \text{ \AA}$ $V = 1389.85 (9) \text{ \AA}^3$ $Z = 4$ $F(000) = 568$ $D_x = 1.273 \text{ Mg m}^{-3}$ Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$

Cell parameters from 6101 reflections

 $\theta = 7.4\text{--}66.3^\circ$ $\mu = 0.79 \text{ mm}^{-1}$ $T = 100 \text{ K}$

Block, colourless

 $0.35 \times 0.29 \times 0.28 \text{ mm}$

Data collection

D8 goniometer with APEX CCD area detector
diffractometer
Radiation source: microsource
Multilayer optics monochromator
 ω scans
Absorption correction: multi-scan
(SADABS; Bruker, 2008)
 $T_{\min} = 0.579$, $T_{\max} = 0.753$

17945 measured reflections
2408 independent reflections
2266 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.083$
 $\theta_{\text{max}} = 67.0^\circ$, $\theta_{\text{min}} = 4.8^\circ$
 $h = -6 \rightarrow 8$
 $k = -11 \rightarrow 12$
 $l = -21 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.077$
 $S = 1.10$
2408 reflections
181 parameters
0 restraints
Primary atom site location: other
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.044P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.17 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.15 \text{ e } \text{\AA}^{-3}$
Extinction correction: SHELXL2017
(Sheldrick, 2015),
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0076 (11)
Absolute structure: Flack x determined using
879 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: -0.04 (12)

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.4715 (2)	0.35039 (16)	0.57878 (9)	0.0376 (4)
O2	0.65579 (19)	0.44278 (13)	0.66057 (7)	0.0237 (3)
O3	0.78055 (18)	0.88187 (13)	0.62654 (8)	0.0237 (3)
O4	1.06691 (18)	0.95433 (13)	0.64909 (7)	0.0202 (3)
N1	0.7503 (2)	0.63780 (17)	0.56914 (9)	0.0187 (4)
H1N	0.692 (3)	0.697 (2)	0.5869 (12)	0.018 (6)*
N2	1.3791 (2)	0.72560 (18)	0.59679 (10)	0.0267 (4)
C1	0.6751 (3)	0.51862 (18)	0.53858 (11)	0.0203 (4)
H1	0.582817	0.542374	0.501179	0.024*
C2	0.8411 (3)	0.4564 (2)	0.50098 (11)	0.0234 (5)
H2A	0.842350	0.360143	0.508020	0.028*
H2B	0.840037	0.475475	0.448498	0.028*
C3	1.0061 (3)	0.52038 (19)	0.53757 (11)	0.0213 (5)
H3A	1.056634	0.462757	0.575653	0.026*
H3B	1.102239	0.540275	0.501863	0.026*
C4	0.9292 (3)	0.64441 (19)	0.56957 (10)	0.0174 (4)
C5	0.5877 (3)	0.4288 (2)	0.59448 (12)	0.0231 (5)
C6	0.5765 (3)	0.3592 (2)	0.71600 (12)	0.0313 (5)

H6A	0.450624	0.385732	0.724633	0.047*
H6B	0.646158	0.367859	0.760875	0.047*
H6C	0.579413	0.267623	0.699820	0.047*
C7	1.0309 (3)	0.74868 (19)	0.59624 (10)	0.0177 (4)
C8	1.2227 (3)	0.73732 (18)	0.59618 (10)	0.0189 (4)
C9	0.9449 (3)	0.86551 (18)	0.62494 (10)	0.0184 (4)
C10	1.0050 (3)	1.08275 (18)	0.67754 (11)	0.0223 (5)
C11	1.1811 (3)	1.1505 (2)	0.69862 (13)	0.0316 (5)
H11A	1.259369	1.158332	0.656003	0.047*
H11B	1.243147	1.098650	0.735767	0.047*
H11C	1.154341	1.238116	0.717651	0.047*
C12	0.9115 (3)	1.1594 (2)	0.61785 (12)	0.0285 (5)
H12A	0.987690	1.158864	0.574426	0.043*
H12B	0.892301	1.250088	0.633701	0.043*
H12C	0.794285	1.118712	0.606871	0.043*
C13	0.8863 (3)	1.0623 (2)	0.74316 (12)	0.0317 (5)
H13A	0.860354	1.147194	0.765735	0.047*
H13B	0.949275	1.005642	0.777859	0.047*
H13C	0.772320	1.020617	0.728442	0.047*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0368 (9)	0.0376 (9)	0.0386 (9)	-0.0201 (8)	-0.0091 (7)	0.0024 (7)
O2	0.0232 (7)	0.0229 (7)	0.0250 (7)	-0.0035 (6)	-0.0033 (6)	0.0027 (6)
O3	0.0129 (7)	0.0230 (7)	0.0353 (8)	0.0011 (6)	0.0011 (6)	-0.0047 (6)
O4	0.0180 (7)	0.0152 (6)	0.0275 (7)	-0.0006 (6)	-0.0014 (5)	-0.0026 (6)
N1	0.0145 (8)	0.0154 (8)	0.0262 (9)	0.0022 (7)	-0.0009 (6)	-0.0020 (7)
N2	0.0182 (10)	0.0293 (10)	0.0328 (10)	-0.0002 (7)	-0.0007 (7)	-0.0005 (8)
C1	0.0182 (10)	0.0169 (9)	0.0257 (10)	-0.0003 (8)	-0.0065 (8)	-0.0009 (7)
C2	0.0265 (11)	0.0190 (10)	0.0248 (10)	-0.0002 (9)	-0.0017 (8)	-0.0024 (8)
C3	0.0196 (10)	0.0191 (10)	0.0253 (10)	0.0038 (8)	-0.0003 (8)	-0.0015 (8)
C4	0.0168 (9)	0.0170 (10)	0.0184 (9)	0.0017 (8)	-0.0002 (7)	0.0034 (8)
C5	0.0182 (10)	0.0202 (10)	0.0310 (12)	0.0001 (9)	-0.0045 (8)	-0.0021 (8)
C6	0.0332 (12)	0.0291 (11)	0.0315 (12)	-0.0038 (10)	0.0041 (10)	0.0046 (9)
C7	0.0140 (9)	0.0175 (9)	0.0216 (10)	0.0015 (8)	0.0008 (8)	0.0013 (8)
C8	0.0193 (10)	0.0162 (9)	0.0212 (10)	-0.0011 (8)	0.0013 (8)	0.0013 (7)
C9	0.0199 (10)	0.0163 (9)	0.0189 (9)	-0.0026 (8)	-0.0019 (8)	0.0028 (8)
C10	0.0254 (11)	0.0152 (9)	0.0262 (11)	0.0005 (8)	-0.0007 (9)	-0.0029 (7)
C11	0.0337 (12)	0.0220 (10)	0.0391 (12)	-0.0057 (10)	-0.0048 (10)	-0.0058 (9)
C12	0.0367 (12)	0.0213 (10)	0.0276 (11)	0.0054 (10)	-0.0001 (9)	-0.0018 (9)
C13	0.0423 (13)	0.0272 (11)	0.0254 (11)	-0.0010 (11)	0.0044 (10)	-0.0048 (9)

Geometric parameters (Å, °)

O1—C5	1.207 (3)	C4—C7	1.391 (3)
O2—C5	1.329 (3)	C6—H6A	0.9800
O2—C6	1.456 (3)	C6—H6B	0.9800

O3—C9	1.223 (2)	C6—H6C	0.9800
O4—C9	1.352 (2)	C7—C8	1.419 (3)
O4—C10	1.483 (2)	C7—C9	1.450 (3)
N1—C4	1.321 (3)	C10—C13	1.511 (3)
N1—C1	1.450 (3)	C10—C12	1.518 (3)
N1—H1N	0.81 (3)	C10—C11	1.522 (3)
N2—C8	1.159 (3)	C11—H11A	0.9800
C1—C5	1.524 (3)	C11—H11B	0.9800
C1—C2	1.544 (3)	C11—H11C	0.9800
C1—H1	1.0000	C12—H12A	0.9800
C2—C3	1.537 (3)	C12—H12B	0.9800
C2—H2A	0.9900	C12—H12C	0.9800
C2—H2B	0.9900	C13—H13A	0.9800
C3—C4	1.506 (3)	C13—H13B	0.9800
C3—H3A	0.9900	C13—H13C	0.9800
C3—H3B	0.9900		
C5—O2—C6	115.70 (16)	H6A—C6—H6C	109.5
C9—O4—C10	120.21 (15)	H6B—C6—H6C	109.5
C4—N1—C1	115.28 (18)	C4—C7—C8	118.35 (18)
C4—N1—H1N	119.4 (16)	C4—C7—C9	121.41 (17)
C1—N1—H1N	125.2 (16)	C8—C7—C9	120.23 (18)
N1—C1—C5	113.59 (17)	N2—C8—C7	178.6 (2)
N1—C1—C2	102.49 (15)	O3—C9—O4	124.03 (17)
C5—C1—C2	113.24 (15)	O3—C9—C7	123.66 (17)
N1—C1—H1	109.1	O4—C9—C7	112.31 (16)
C5—C1—H1	109.1	O4—C10—C13	109.97 (16)
C2—C1—H1	109.1	O4—C10—C12	109.63 (16)
C3—C2—C1	104.78 (15)	C13—C10—C12	113.13 (18)
C3—C2—H2A	110.8	O4—C10—C11	103.20 (16)
C1—C2—H2A	110.8	C13—C10—C11	110.56 (18)
C3—C2—H2B	110.8	C12—C10—C11	109.90 (18)
C1—C2—H2B	110.8	C10—C11—H11A	109.5
H2A—C2—H2B	108.9	C10—C11—H11B	109.5
C4—C3—C2	103.35 (15)	H11A—C11—H11B	109.5
C4—C3—H3A	111.1	C10—C11—H11C	109.5
C2—C3—H3A	111.1	H11A—C11—H11C	109.5
C4—C3—H3B	111.1	H11B—C11—H11C	109.5
C2—C3—H3B	111.1	C10—C12—H12A	109.5
H3A—C3—H3B	109.1	C10—C12—H12B	109.5
N1—C4—C7	125.43 (18)	H12A—C12—H12B	109.5
N1—C4—C3	109.30 (17)	C10—C12—H12C	109.5
C7—C4—C3	125.26 (17)	H12A—C12—H12C	109.5
O1—C5—O2	124.1 (2)	H12B—C12—H12C	109.5
O1—C5—C1	122.31 (19)	C10—C13—H13A	109.5
O2—C5—C1	113.59 (16)	C10—C13—H13B	109.5
O2—C6—H6A	109.5	H13A—C13—H13B	109.5
O2—C6—H6B	109.5	C10—C13—H13C	109.5

H6A—C6—H6B	109.5	H13A—C13—H13C	109.5
O2—C6—H6C	109.5	H13B—C13—H13C	109.5
C4—N1—C1—C5	109.61 (19)	N1—C1—C5—O2	-26.3 (2)
C4—N1—C1—C2	-12.9 (2)	C2—C1—C5—O2	90.1 (2)
N1—C1—C2—C3	20.43 (19)	C3—C4—C7—C8	-2.4 (3)
C1—N1—C4—C7	-179.84 (18)	N1—C4—C7—C9	-2.1 (3)
C1—N1—C4—C3	-0.6 (2)	C10—O4—C9—O3	-2.1 (3)
C2—C3—C4—N1	14.0 (2)	C4—C7—C9—O3	-1.4 (3)
C6—O2—C5—O1	-2.2 (3)	C8—C7—C9—O4	0.4 (3)
C6—O2—C5—C1	179.93 (16)	C9—O4—C10—C13	61.8 (2)
N1—C1—C5—O1	155.73 (19)		

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>
N1—H1 <i>N</i> ...O3	0.81 (3)	2.13 (2)	2.714 (2)	129 (2)
N1—H1 <i>N</i> ...N2 ⁱ	0.81 (3)	2.33 (2)	2.924 (2)	131 (2)
C11—H11 <i>B</i> ...O2 ⁱⁱ	0.98	2.60	3.565 (3)	169

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+2, y+1/2, -z+3/2$.