

Crystal structure and photoreactive behaviour of *N,N*-diisopropyl(*p*-phenylphenyl)glyoxylamide

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The title compound [systematic name: 2-([1,1'-biphenyl]-4-yl)-2-oxo-*N,N*-bis-(propan-2-yl)acetamide], C₂₀H₂₃NO₂ was synthesized and its photoreactive properties in the crystalline state and in acetonitrile solution were investigated. The compound crystallizes in the chiral space group *P*2₁2₁2₁. The crystal does not react under UV light irradiation, perhaps due to the presence of the biphenyl group. However, the compound is photoreactive in acetonitrile solution to give racemic 3-(*p*-phenylphenyl)-3-hydroxy-*N*-isopropyl-4,4-dimethylazetidin-2-one.

1. Chemical context

The solid-state photochemistry of *N,N*-dialkyl- α -oxoamides has been studied in relation to penicillin chemistry (Aoyama *et al.*, 1979). The amides undergo Norrish type II cyclization giving β -lactams (Aoyama *et al.*, 1978). The achiral molecule *N,N*-diisopropylphenylglyoxylamide **1a** crystallizes in the chiral space group *P*2₁2₁2₁ and is transformed to the optically active β -lactam derivative **2a** upon UV light irradiation (Fig. 1; Toda *et al.*, 1987; Sekine *et al.*, 1989). *N,N*-Diisopropyl(*m*-chloro or *m*-methyl or *o*-methylphenyl)glyoxylamides **1b** and **1c** also form chiral crystals, and photoirradiation in the solid state gives optically active β -lactam derivatives **2b** and **2c**, respectively (Toda & Miyamoto, 1993; Hashizume *et al.*, 1995, 1996, 1998). However, *N,N*-diisopropyl(*p*-chloro or *o*-chloro or *p*-methylphenyl)glyoxylamide **1b** and **1c** do not form chiral crystals, and their photoirradiation in the solid state gives racemic β -lactam derivatives **2b** and **2c**, respectively. Therefore, we synthesized the novel title compound **1d** having a phenyl group and investigated whether optically active β -lactam derivative **2d** could be obtained by photoreaction. It was found that **1d** formed a chiral crystal in the chiral space group *P*2₁2₁2₁, but photoreaction did not proceed in the solid

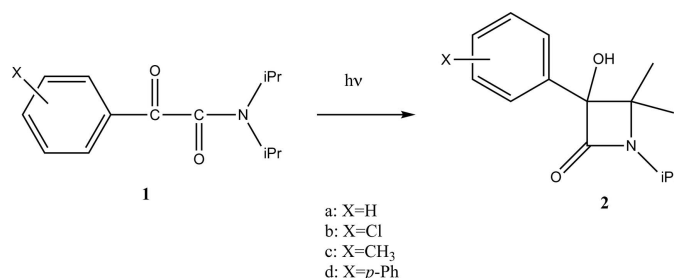
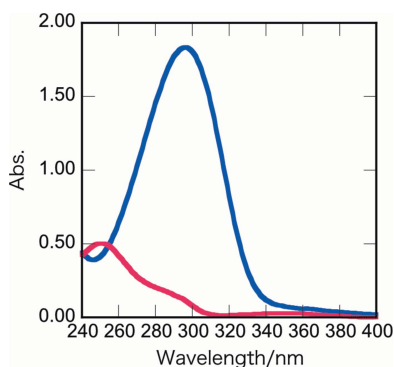


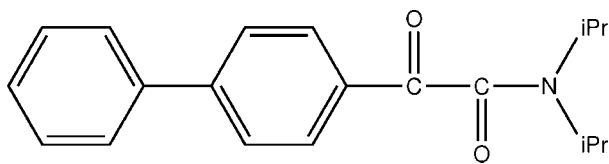
Figure 1
Photoreaction of *N,N*-diisopropylarylglyoxylamide derivatives.

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>
C9—H5···O1	1.00	2.65	3.245 (2)	119
C13—H15···O2	0.98	2.47	3.033 (3)	117
C14—H16···O2	0.98	2.51	3.072 (3)	116
C14—H18···O1 ⁱ	0.98	2.71	3.612 (3)	154
C17—H20···O2 ⁱⁱ	0.95	2.66	3.608 (2)	179

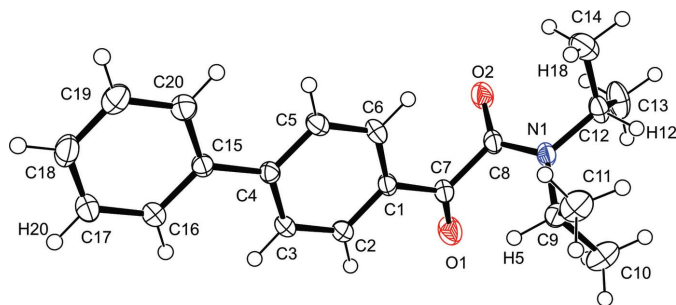
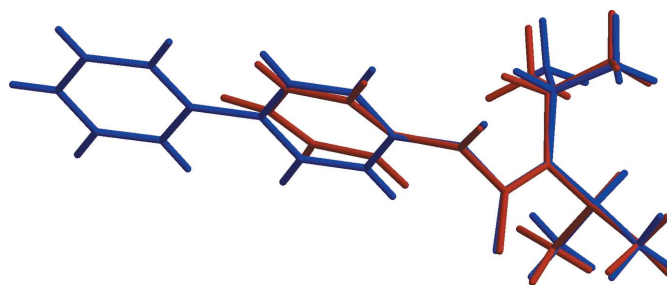
 Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$.

state. However, photoreaction of **1d** in acetonitrile solution proceeded to give racemic 3-(*p*-phenylphenyl)-3-hydroxy-*N*-isopropyl-4,4-dimethylazetididin-2-one **2d** in 26% yield. In this study, although **1d** formed a chiral crystal, the reason why the photoreaction product of **1d** in the solid state was not obtained was clarified by single-crystal X-ray structural analysis, UV spectroscopy and time-dependent density functional theory (TDDFT) calculations.



2. Structural commentary

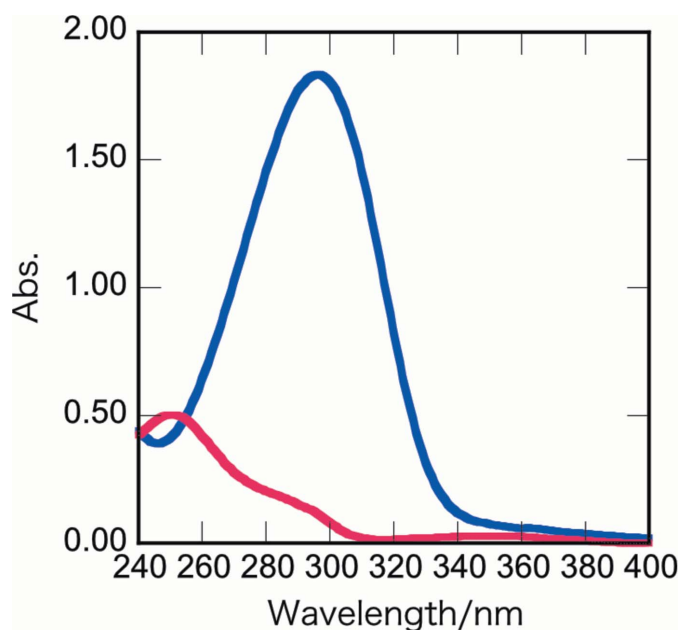
Table 1 summarizes intra and intermolecular hydrogen bonds observed in the title compound. The phenyl rings in the biphenyl group are coplanar with the carbonyl group (C7=O1). The torsion angles C2—C1—C7—O1 and C3—C4—C15—C16 are 7.8 (3) and -0.4 (2)°, respectively, and the torsion angles O1—C7—C8—O2 and C7—C8—N1—C9 are 97.1 (2) and -3.9 (2)°, respectively (Fig. 2). The corresponding torsion angles in **1a** are 88.0 (4) and -5.1 (4)°. In order for the Norrish–Yang reaction to take place, the reacting atoms in the molecular structure must be in close proximity. The Yang cyclization of α -oxoamides to β -lactams starts with abstraction of the γ -hydrogen (with respect to the benzylic carbonyl) by the benzylic carbonyl oxygen in the excited state. In the title compound, there are two γ -hydrogen atoms (H5 on C9 and H12 on C12). The distances between the carbonyl oxygen atom O1 and the respective γ -hydrogen atoms H5 and


Figure 2
 The molecular structure of **1d**. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

Figure 3
 Overlay of molecules **1a** (in red) and **1d** (in blue).

H12 are 2.65 and 5.01 Å. The former interatomic distance is within the ideal value of up to about 2.7 Å, at which photoreaction can proceed in the crystal (Konieczny *et al.*, 2018). Moreover, the distance between the reacting C7 and C9 carbon atoms is 2.840 (2) Å, which is in the range of ideal values of up to about 3.2 Å. The corresponding distances are 2.78 (4) and 2.871 (4) Å in **1a**. As shown in Fig. 3, the geometries of the oxoamide moiety of **1d** and **1a** are almost the same. Despite satisfying the geometry and distance requirements for the photoreaction, the corresponding β -lactam was not detected in the solid-state reaction. From the UV spectrum of **1d**, it is considered that the biphenyl group of **1d** absorbs ultraviolet light preventing the solid-state reaction (Fig. 4). In other words, the photocyclization reaction does not proceed in the solid state for at least 300 h because the irradiated UV light is absorbed by the π - π^* transition of the biphenyl group.

3. DFT calculations

The *GAUSSIAN16* program (Frisch *et al.*, 2016) was used for density functional theory (DFT) calculations. Initial geom-


Figure 4
 UV spectra of **1a** (in red, 51.3×10^{-6} M MeOH solution) and **1d** (in blue, 48.6×10^{-6} M MeOH solution).

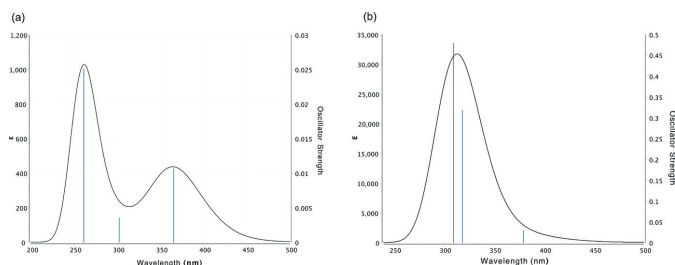


Figure 5
Calculated UV-vis spectra of (a) **1a** and (b) **1d**.

etries of **1a** and **1d** were obtained from XRD data. Hydrogen atoms were optimized at the B3LYP/6-311G(d,p) level (Becke, 1993). The UV-vis spectra of **1a** and **1d** were calculated by the time-dependent density functional theory [TDDFT, B3LYP/6-311G(d,p)] method. In the calculated UV-vis spectra, there were two weak peaks at 254 and 362 nm for **1a**, and there was an intense and broad peak at 310 nm for **1d**. The calculated spectra were similar to the experimental spectra (Fig. 5). For **1a**, the peak at 254 nm corresponds to the π - π^* transition of the Ph group, while that at the longer wavelength of 362 nm is due to n - π^* transitions of the carbonyl groups. For **1d**, the adsorption peak at 376 nm was assigned to n - π^* transitions of carbonyl groups. A very weak absorption peak was observed around 370 nm in the experimental spectrum. A mercury lamp has an intense emission at 365 nm, such that the photoreaction for **1a** proceeds rapidly in the solid state. In contrast, the large and broad absorption prevents the solid-state photoreaction for **1d**. Since the molecules can move freely in solution, light irradiation for 60 h was uniformly performed, and it seemed that the reaction proceeded slightly. It has been reported that an oxoamide derivative having a naphthyl group slows down the photoreaction (Natarajan *et al.*, 2005). The relationship between photoreactivity and irradiation wavelength is under investigation.

4. Supramolecular features

In the crystal, the molecules are linked by weak intermolecular C—H...O (C14—H18...O1, 2.71 Å) interactions forming a 1D chain structure along the *a*-axis direction (Fig. 6*a*), and C—H...O (C17—H20...O2, 2.66 Å) interactions forming a 1D zigzag chain structure along the *b*-axis direction (Fig. 6*b*). Details of these interactions are given in Table 1.

5. Database survey

A search of the Cambridge Structural Database (Version 5.41, last update August 2020; Groom *et al.*, 2016) yielded 18 hits for compounds based on the *N,N*-diisopropylphenylglyoxylamide fragment shown in Fig. 1: no substituent on the phenyl ring (JAGLAE; Sekine *et al.*, 1989), various chiral amido groups on the phenyl ring (KAHWIA, NAHZIG, NAHZUS, NAJBAC,

NAJBEG, NAJBK, NAJBOQ, NAJBW, NAJCAD, and NAJCEH; Natarajan *et al.*, 2005), methyl or dimethyl group(s) on the phenyl ring (WIQKUC, YOWVUB, YOWVUF, and YOWWAI; Hashizume *et al.*, 1995), and a chlorine atom on the phenyl ring (ZOHNIT, ZOHNOZ, and ZOHNUF; Hashizume *et al.*, 1996).

6. Synthesis and crystallization

The title compound was prepared according to a reported method (Toda *et al.*, 1987; Sekine *et al.*, 1989), *i.e.*, chlorination of 2-oxo-2-(4-phenylphenyl)acetic acid with thionyl chloride followed by reaction with *N,N*-diisopropylamine. Thus, to an ice-cooled solution of *N,N*-diisopropylamine (16 mL, 0.11 mol) in dry diethyl ether (45 mL) was added a solution of 4-phenylbenzoylformyl chloride (13.8 g, 0.0564 mol) in dry diethyl ether (45 mL), and the reaction mixture was stirred for 10 h at room temperature. After filtration of *N,N*-diisopropylammonium chloride, the filtrate was washed with dilute HCl and aqueous NaHCO₃ and dried over MgSO₄. The crude product was purified by silica gel column chromatography (toluene:ethyl acetate = 9:1) and recrystallized from toluene to give **1d** as colorless prisms (1.02 g, 5.8% yield, m.p. 397–398 K); IR (KBr): ν_{\max} 1640, 1680 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.01 (*d*, *J* = 8.0 Hz, 2H), 7.73 (*d*, *J* = 8.0 Hz, 2H), 7.63 (*d*, *J* = 8.0 Hz, 2H), 7.50–7.39 (*m*, 3H), 3.75 (*sept*, *J* = 6.9 Hz, 1H), 3.61 (*sept*, *J* = 6.9 Hz, 1H), 1.60 (*d*, *J* = 6.9 Hz, 6H), 1.20 (*d*, *J* = 6.6 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 190.7, 167.0,

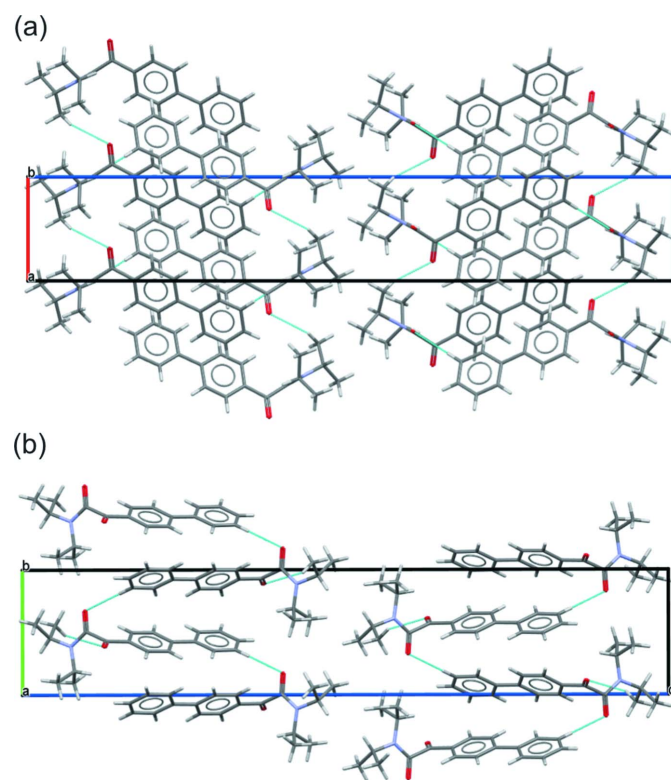


Figure 6
Packing diagrams for **1d** viewed (a) along the *b* axis and (b) along the *a* axis, showing intermolecular C—H...O interactions as dotted blue lines.

147.1, 139.7, 132.1, 130.1, 129.0, 128.5, 127.6, 127.4, 50.2, 46.1, 20.6, 20.4; ESIMS m/z : calculated for $C_{20}H_{23}NNaO_2$ [$M + Na$]⁺, 322.1621; found, 322.1586. Single crystals of **1d** suitable for X-ray diffraction analysis were grown from a toluene solution.

7. Photoreaction

1d (0.100 g, 0.323 mmol) was pulverized in a mortar and irradiated with a 400 W high-pressure mercury lamp for 300 h. No reaction took place, as determined by TLC, IR and NMR spectroscopies. **1d** (0.1368 g, 0.442 mmol) in acetonitrile (10 mL) was irradiated with a 400 W high-pressure mercury lamp for 60 h. The crude product was purified by silica gel column chromatography (toluene:ethyl acetate = 4:1) to give 3-(*p*-phenylphenyl)-3-hydroxy-*N*-isopropyl-4,4-dimethylazetidid-2-one **2d** as a colorless powder (0.035 g, 26% yield, m.p. 467–469 K); IR (KBr): ν_{\max} 3200, 1720 cm^{-1} ; ¹H NMR (60 MHz, CDCl₃): δ 7.60–7.00 (*m*, 9H), 4.64 (*s*, 1H), 3.57 (*sept*, *J* = 7.0 Hz, 1H), 1.44 (*d*, *J* = 7.0 Hz, 6H), 1.27 (*s*, 3H), 0.87 (*s*, 3H); ESIMS m/z : calculated for $C_{20}H_{23}NNaO_2$ [$M + Na$]⁺, 322.1621; found, 322.1569.

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned in geometrically calculated positions (C–H = 0.95–0.98 Å) and refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}(C\text{-methyl})$. The Flack parameter *x* is 0.1 (4) as shown in Table 2. The standard uncertainty is large. The Flack and Hooft (Hooft *et al.*, 2008) parameters are strongly indicative of the correct absolute configuration, even when the standard uncertainties are large (Thompson & Watkin, 2011). Hooft [0.19 (16)] and Parsons parameters [0.2 (3)] (Parsons *et al.*, 2013) were calculated using *PLATON* (Spek, 2020).

Acknowledgements

Theoretical calculations were performed at the Super Computer System of Academic Centre for Computing and Media Studies, Kyoto University.

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Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{23}NO_2$
M_r	309.39
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.1313 (2), 7.3710 (2), 38.1143 (11)
<i>V</i> (Å ³)	1722.53 (9)
<i>Z</i>	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.08
Crystal size (mm)	0.31 × 0.29 × 0.29
Data collection	
Diffractometer	Rigaku Saturn 724+ CCD
Absorption correction	Numerical (<i>CrystalClear-SM Expert</i> ; Rigaku, 2009)
T_{\min} , T_{\max}	0.985, 0.985
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16094, 3877, 3614
R_{int}	0.021
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.660
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.036, 0.080, 1.05
No. of reflections	3877
No. of parameters	212
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.16, -0.15
Absolute structure	Flack <i>x</i> determined using 1346 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.1 (4)

Computer programs: *CrystalClear-SM Expert* (Rigaku, 2009), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

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Crystal structure and photoreactive behaviour of *N,N*-diisopropyl(*p*-phenylphenyl)glyoxylamide

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Computing details

Data collection: *CrystalClear-SM Expert* (Rigaku, 2009); cell refinement: *CrystalClear-SM Expert* (Rigaku, 2009); data reduction: *CrystalClear-SM Expert* (Rigaku, 2009); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

2-([1,1'-Biphenyl]-4-yl)-2-oxo-*N,N*-bis(propan-2-yl)acetamide

Crystal data

$C_{20}H_{23}NO_2$

$M_r = 309.39$

Orthorhombic, $P2_12_12_1$

$a = 6.1313$ (2) Å

$b = 7.3710$ (2) Å

$c = 38.1143$ (11) Å

$V = 1722.53$ (9) Å³

$Z = 4$

$F(000) = 664$

$D_x = 1.193$ Mg m⁻³

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

Cell parameters from 2939 reflections

$\theta = 3.4$ – 27.5°

$\mu = 0.08$ mm⁻¹

$T = 173$ K

Prism, colorless

$0.31 \times 0.29 \times 0.29$ mm

Data collection

Rigaku Saturn 724+ CCD
diffractometer

Radiation source: sealed tube

Detector resolution: 28.5714 pixels mm⁻¹

profile data from ω -scans

Absorption correction: numerical

(*CrystalClear-SM Expert*; Rigaku, 2009)

$T_{\min} = 0.985$, $T_{\max} = 0.985$

16094 measured reflections

3877 independent reflections

3614 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 28.0^\circ$, $\theta_{\min} = 3.4^\circ$

$h = -8 \rightarrow 7$

$k = -9 \rightarrow 9$

$l = -48 \rightarrow 48$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.080$

$S = 1.05$

3877 reflections

212 parameters

0 restraints

Primary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 0.3778P]$

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

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

$\Delta\rho_{\max} = 0.16$ e Å⁻³

$\Delta\rho_{\min} = -0.15$ e Å⁻³

Absolute structure: Flack x determined using
 1346 quotients $[(F^+)-(F^-)]/[(F^+)+(F^-)]$ (Parsons *et al.*, 2013)
 Absolute structure parameter: 0.1 (4)

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	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5093 (3)	0.5728 (2)	0.66469 (4)	0.0240 (3)
C2	0.6161 (3)	0.6491 (2)	0.69356 (4)	0.0264 (4)
H1	0.757076	0.700514	0.690769	0.032*
C3	0.5171 (3)	0.6499 (2)	0.72609 (4)	0.0256 (3)
H2	0.591743	0.702783	0.745390	0.031*
C4	0.3097 (3)	0.5750 (2)	0.73146 (4)	0.0231 (3)
O1	0.8128 (2)	0.6133 (2)	0.62656 (3)	0.0413 (3)
O2	0.4869 (2)	0.32629 (16)	0.59665 (3)	0.0381 (3)
N1	0.4188 (2)	0.61084 (19)	0.57509 (4)	0.0276 (3)
C5	0.2040 (3)	0.5007 (2)	0.70210 (5)	0.0282 (4)
H3	0.062937	0.449217	0.704797	0.034*
C6	0.3012 (3)	0.5011 (2)	0.66922 (4)	0.0287 (4)
H4	0.225190	0.452194	0.649669	0.034*
C7	0.6227 (3)	0.5697 (2)	0.63028 (4)	0.0284 (4)
C8	0.4985 (3)	0.4927 (2)	0.59863 (4)	0.0281 (4)
C9	0.4364 (3)	0.8099 (2)	0.58034 (5)	0.0318 (4)
H5	0.497384	0.829750	0.604367	0.038*
C10	0.5949 (4)	0.8947 (3)	0.55449 (6)	0.0470 (5)
H6	0.736401	0.833410	0.556225	0.070*
H7	0.612914	1.023717	0.559944	0.070*
H8	0.537864	0.881506	0.530604	0.070*
C11	0.2145 (4)	0.9013 (3)	0.57929 (6)	0.0424 (5)
H9	0.156583	0.896594	0.555338	0.064*
H10	0.229103	1.028114	0.586642	0.064*
H11	0.114502	0.838140	0.595205	0.064*
C12	0.3111 (3)	0.5445 (2)	0.54250 (4)	0.0309 (4)
H12	0.270143	0.654227	0.528562	0.037*
C13	0.4680 (4)	0.4345 (3)	0.51993 (5)	0.0466 (5)
H13	0.601203	0.504937	0.515886	0.070*
H14	0.398812	0.406781	0.497376	0.070*
H15	0.504725	0.321214	0.532000	0.070*
C14	0.1007 (4)	0.4442 (3)	0.55063 (6)	0.0434 (5)
H16	0.134408	0.331101	0.563027	0.065*
H17	0.024513	0.416204	0.528682	0.065*
H18	0.007510	0.520425	0.565414	0.065*

C15	0.2068 (3)	0.5729 (2)	0.76699 (4)	0.0242 (3)
C16	0.3150 (3)	0.6450 (2)	0.79631 (5)	0.0327 (4)
H19	0.454724	0.698538	0.793378	0.039*
C17	0.2219 (4)	0.6397 (3)	0.82944 (5)	0.0385 (5)
H20	0.299212	0.687471	0.848972	0.046*
C18	0.0172 (4)	0.5653 (3)	0.83418 (5)	0.0387 (5)
H21	-0.047408	0.563386	0.856828	0.046*
C19	-0.0930 (3)	0.4937 (3)	0.80572 (5)	0.0360 (4)
H22	-0.233437	0.441822	0.808872	0.043*
C20	0.0005 (3)	0.4972 (2)	0.77263 (5)	0.0295 (4)
H23	-0.077146	0.447082	0.753360	0.035*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0285 (8)	0.0234 (7)	0.0201 (8)	0.0024 (7)	-0.0035 (6)	0.0011 (6)
C2	0.0249 (8)	0.0275 (8)	0.0267 (9)	-0.0027 (7)	-0.0031 (7)	0.0002 (7)
C3	0.0275 (8)	0.0278 (8)	0.0216 (8)	-0.0033 (7)	-0.0061 (7)	-0.0022 (6)
C4	0.0267 (8)	0.0202 (7)	0.0223 (8)	0.0028 (7)	-0.0031 (6)	0.0009 (6)
O1	0.0359 (7)	0.0594 (9)	0.0286 (7)	-0.0063 (7)	0.0036 (6)	-0.0020 (6)
O2	0.0598 (9)	0.0259 (6)	0.0285 (6)	0.0030 (6)	-0.0079 (6)	0.0004 (5)
N1	0.0376 (8)	0.0255 (7)	0.0198 (7)	0.0002 (6)	-0.0016 (6)	-0.0001 (6)
C5	0.0252 (8)	0.0313 (8)	0.0283 (9)	-0.0048 (8)	-0.0037 (7)	-0.0017 (7)
C6	0.0303 (9)	0.0334 (9)	0.0224 (8)	-0.0006 (8)	-0.0081 (7)	-0.0034 (7)
C7	0.0338 (10)	0.0271 (8)	0.0244 (8)	0.0000 (7)	-0.0023 (7)	0.0021 (7)
C8	0.0365 (10)	0.0284 (8)	0.0194 (8)	0.0010 (8)	0.0007 (7)	0.0000 (7)
C9	0.0442 (11)	0.0264 (8)	0.0248 (9)	-0.0025 (8)	-0.0018 (8)	0.0011 (7)
C10	0.0446 (11)	0.0382 (11)	0.0581 (13)	-0.0029 (10)	0.0089 (10)	0.0104 (10)
C11	0.0506 (12)	0.0316 (9)	0.0451 (11)	0.0038 (9)	0.0135 (10)	-0.0045 (9)
C12	0.0421 (10)	0.0311 (9)	0.0195 (8)	0.0074 (8)	-0.0050 (7)	-0.0020 (7)
C13	0.0593 (14)	0.0570 (13)	0.0234 (9)	0.0184 (12)	-0.0023 (9)	-0.0081 (9)
C14	0.0476 (12)	0.0433 (11)	0.0395 (11)	-0.0028 (10)	-0.0093 (10)	-0.0081 (9)
C15	0.0293 (8)	0.0193 (7)	0.0240 (8)	0.0019 (7)	-0.0004 (7)	-0.0002 (6)
C16	0.0396 (10)	0.0323 (9)	0.0260 (9)	-0.0076 (8)	0.0005 (8)	-0.0016 (7)
C17	0.0568 (12)	0.0351 (10)	0.0238 (9)	-0.0080 (9)	0.0009 (9)	-0.0033 (8)
C18	0.0555 (13)	0.0322 (9)	0.0285 (9)	0.0005 (9)	0.0126 (9)	0.0031 (8)
C19	0.0360 (10)	0.0348 (9)	0.0373 (10)	-0.0009 (8)	0.0090 (9)	0.0038 (8)
C20	0.0305 (9)	0.0281 (8)	0.0300 (9)	0.0011 (8)	-0.0023 (7)	0.0000 (7)

Geometric parameters (Å, °)

C1—C6	1.392 (3)	C11—H9	0.9800
C1—C2	1.398 (2)	C11—H10	0.9800
C1—C7	1.485 (2)	C11—H11	0.9800
C2—C3	1.380 (2)	C12—C14	1.519 (3)
C2—H1	0.9500	C12—C13	1.524 (3)
C3—C4	1.401 (2)	C12—H12	1.0000
C3—H2	0.9500	C13—H13	0.9800

C4—C5	1.404 (2)	C13—H14	0.9800
C4—C15	1.494 (2)	C13—H15	0.9800
O1—C7	1.217 (2)	C14—H16	0.9800
O2—C8	1.231 (2)	C14—H17	0.9800
N1—C8	1.342 (2)	C14—H18	0.9800
N1—C9	1.485 (2)	C15—C20	1.399 (3)
N1—C12	1.489 (2)	C15—C16	1.404 (2)
C5—C6	1.388 (2)	C16—C17	1.386 (3)
C5—H3	0.9500	C16—H19	0.9500
C6—H4	0.9500	C17—C18	1.382 (3)
C7—C8	1.535 (2)	C17—H20	0.9500
C9—C10	1.519 (3)	C18—C19	1.382 (3)
C9—C11	1.519 (3)	C18—H21	0.9500
C9—H5	1.0000	C19—C20	1.385 (3)
C10—H6	0.9800	C19—H22	0.9500
C10—H7	0.9800	C20—H23	0.9500
C10—H8	0.9800		
C6—C1—C2	118.98 (15)	H9—C11—H10	109.5
C6—C1—C7	122.22 (15)	C9—C11—H11	109.5
C2—C1—C7	118.80 (15)	H9—C11—H11	109.5
C3—C2—C1	120.18 (15)	H10—C11—H11	109.5
C3—C2—H1	119.9	N1—C12—C14	111.50 (15)
C1—C2—H1	119.9	N1—C12—C13	111.46 (16)
C2—C3—C4	121.88 (15)	C14—C12—C13	113.10 (17)
C2—C3—H2	119.1	N1—C12—H12	106.8
C4—C3—H2	119.1	C14—C12—H12	106.8
C3—C4—C5	117.15 (15)	C13—C12—H12	106.8
C3—C4—C15	121.29 (14)	C12—C13—H13	109.5
C5—C4—C15	121.56 (15)	C12—C13—H14	109.5
C8—N1—C9	121.65 (14)	H13—C13—H14	109.5
C8—N1—C12	120.38 (14)	C12—C13—H15	109.5
C9—N1—C12	117.97 (14)	H13—C13—H15	109.5
C6—C5—C4	121.36 (16)	H14—C13—H15	109.5
C6—C5—H3	119.3	C12—C14—H16	109.5
C4—C5—H3	119.3	C12—C14—H17	109.5
C5—C6—C1	120.44 (15)	H16—C14—H17	109.5
C5—C6—H4	119.8	C12—C14—H18	109.5
C1—C6—H4	119.8	H16—C14—H18	109.5
O1—C7—C1	123.19 (16)	H17—C14—H18	109.5
O1—C7—C8	118.74 (16)	C20—C15—C16	117.12 (16)
C1—C7—C8	117.87 (15)	C20—C15—C4	121.66 (15)
O2—C8—N1	125.77 (17)	C16—C15—C4	121.21 (16)
O2—C8—C7	116.41 (16)	C17—C16—C15	121.34 (18)
N1—C8—C7	117.78 (15)	C17—C16—H19	119.3
N1—C9—C10	111.42 (16)	C15—C16—H19	119.3
N1—C9—C11	111.71 (16)	C18—C17—C16	120.26 (18)
C10—C9—C11	111.97 (16)	C18—C17—H20	119.9

N1—C9—H5	107.1	C16—C17—H20	119.9
C10—C9—H5	107.1	C17—C18—C19	119.54 (17)
C11—C9—H5	107.1	C17—C18—H21	120.2
C9—C10—H6	109.5	C19—C18—H21	120.2
C9—C10—H7	109.5	C18—C19—C20	120.33 (19)
H6—C10—H7	109.5	C18—C19—H22	119.8
C9—C10—H8	109.5	C20—C19—H22	119.8
H6—C10—H8	109.5	C19—C20—C15	121.40 (17)
H7—C10—H8	109.5	C19—C20—H23	119.3
C9—C11—H9	109.5	C15—C20—H23	119.3
C9—C11—H10	109.5		
C6—C1—C2—C3	1.2 (2)	C1—C7—C8—N1	104.20 (19)
C7—C1—C2—C3	-178.37 (15)	C8—N1—C9—C10	110.4 (2)
C1—C2—C3—C4	0.3 (2)	C12—N1—C9—C10	-69.1 (2)
C2—C3—C4—C5	-1.0 (2)	C8—N1—C9—C11	-123.57 (18)
C2—C3—C4—C15	178.55 (15)	C12—N1—C9—C11	57.0 (2)
C3—C4—C5—C6	0.2 (3)	C8—N1—C12—C14	65.9 (2)
C15—C4—C5—C6	-179.27 (16)	C9—N1—C12—C14	-114.69 (18)
C4—C5—C6—C1	1.2 (3)	C8—N1—C12—C13	-61.6 (2)
C2—C1—C6—C5	-1.9 (2)	C9—N1—C12—C13	117.88 (18)
C7—C1—C6—C5	177.64 (16)	C3—C4—C15—C20	-179.53 (16)
C6—C1—C7—O1	-171.73 (18)	C5—C4—C15—C20	-0.1 (2)
C2—C1—C7—O1	7.8 (3)	C3—C4—C15—C16	-0.4 (2)
C6—C1—C7—C8	3.1 (2)	C5—C4—C15—C16	179.07 (17)
C2—C1—C7—C8	-177.40 (15)	C20—C15—C16—C17	0.6 (3)
C9—N1—C8—O2	178.42 (19)	C4—C15—C16—C17	-178.57 (17)
C12—N1—C8—O2	-2.2 (3)	C15—C16—C17—C18	-1.1 (3)
C9—N1—C8—C7	-3.9 (2)	C16—C17—C18—C19	1.0 (3)
C12—N1—C8—C7	175.50 (16)	C17—C18—C19—C20	-0.3 (3)
O1—C7—C8—O2	97.1 (2)	C18—C19—C20—C15	-0.2 (3)
C1—C7—C8—O2	-77.9 (2)	C16—C15—C20—C19	0.0 (2)
O1—C7—C8—N1	-80.7 (2)	C4—C15—C20—C19	179.20 (16)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9—H5 \cdots O1	1.00	2.65	3.245 (2)	119
C13—H15 \cdots O2	0.98	2.47	3.033 (3)	117
C14—H16 \cdots O2	0.98	2.51	3.072 (3)	116
C14—H18 \cdots O1 ⁱ	0.98	2.71	3.612 (3)	154
C17—H20 \cdots O2 ⁱⁱ	0.95	2.66	3.608 (2)	179

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