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3′,6′-Bis(diethylamino)-2-(prop-2-ynyl)spiro-[isoindoline-1,9′-xanthen]-3-one

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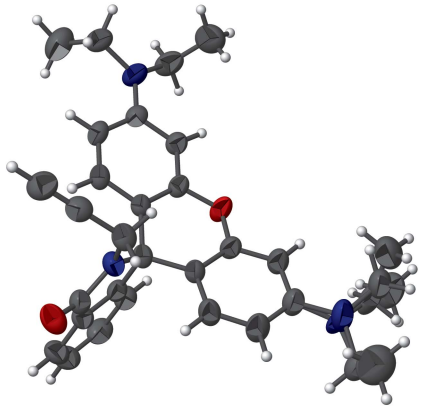
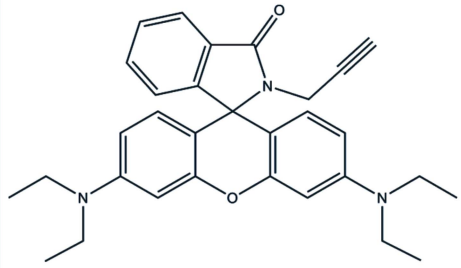
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{31}H_{33}N_3O_2$, the spiropyrrolidine ring has a twisted conformation on the C_{spiro}—N bond, whereas the tetrahydropyran ring adopts a sofa confirmation. The spiro joined fragments are almost orthogonal, with a dihedral angle of 89.1 (2)° between the mean planes of the pyrrolidine and tetrahydropyran rings. In the diethylamine group, the ethanamine portion is disordered over the two positions, with a refined occupancy ratio of 0.73 (1):0.27 (1). In the crystal, molecules are linked by pairs of C—H···O hydrogen bonds, forming inversion dimers with an $R_2^2(10)$ ring motif. The dimers are linked by further C—H···O hydrogen bonds, forming slabs parallel to (100).

3D view



Chemical scheme



Structure description

Rhodamine-based dyes, known for their excellent spectroscopic properties having a large molar extinction coefficient and high fluorescence quantum yield (Wu *et al.*, 2007), have found applications in the study of complex biological systems and environmental analysis as molecular probes. Rhodamine B derivatives are known to have excellent photophysical properties, such as long absorption and emission wavelengths elongated to the visible region. They have therefore been extensively used as fluorescent chemosensors for heavy and transition metal ions, such as copper(II) (Zhang *et al.*, 2007) and mercury(II) (Soh *et al.*, 2007) chemical sensors.

The main skeleton of the title compound is formed by a xanthene ring and a spirolactam ring, as illustrated in Fig. 1. The spiro pyrrolidine ring (C13/C14/C19/C20/N1) adopts a twisted confirmation on the C13—N1 bond [puckering parameters: q_2 = 0.068 (3) Å and φ_2 = 198 (2)°]. The six-membered tetrahydropyran ring (C1/C6/O1/C7/C12/C13) of the xanthene ring system adopts a sofa confirmation [puckering parameters:

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

D—H···A	D—H	H···A	D···A	D—H···A
C21—H21A···O2^{i}	0.97	2.59	3.483 (3)	153
C23—H23···O2^{ii}	0.93	2.36	3.246 (4)	159

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

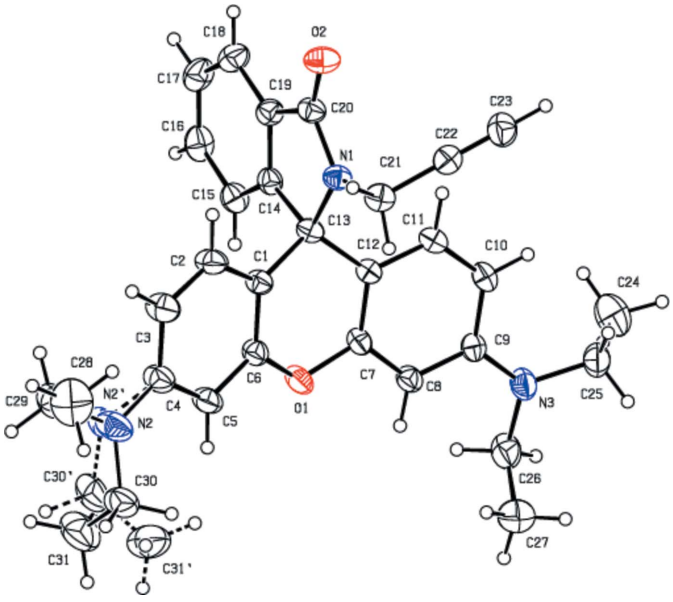


Figure 1
The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

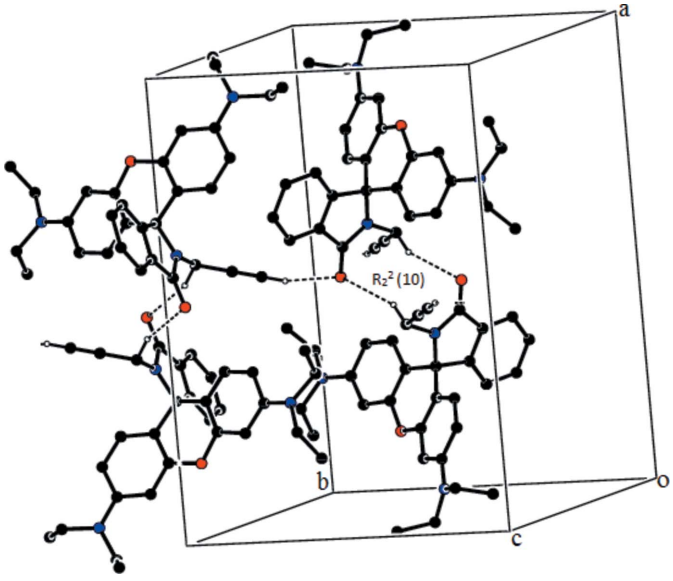


Figure 2
A partial view of the crystal packing of the title compound, showing the formation of hydrogen-bonded dimers (dashed lines; see Table 1). The minor components of the disordered atoms and H atoms not involved in hydrogen bonding have been omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{31}H_{33}N_3O_2$
M_r	479.60
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	18.0701 (8), 16.2611 (7), 9.0801 (4)
β (°)	97.645 (2)
V (Å^3)	2644.4 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.35 × 0.25 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.977, 0.985
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	40635, 4654, 3350
R_{int}	0.037
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.594
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.153, 1.09
No. of reflections	4654
No. of parameters	354
No. of restraints	72
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.38, −0.18

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker, 2004), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

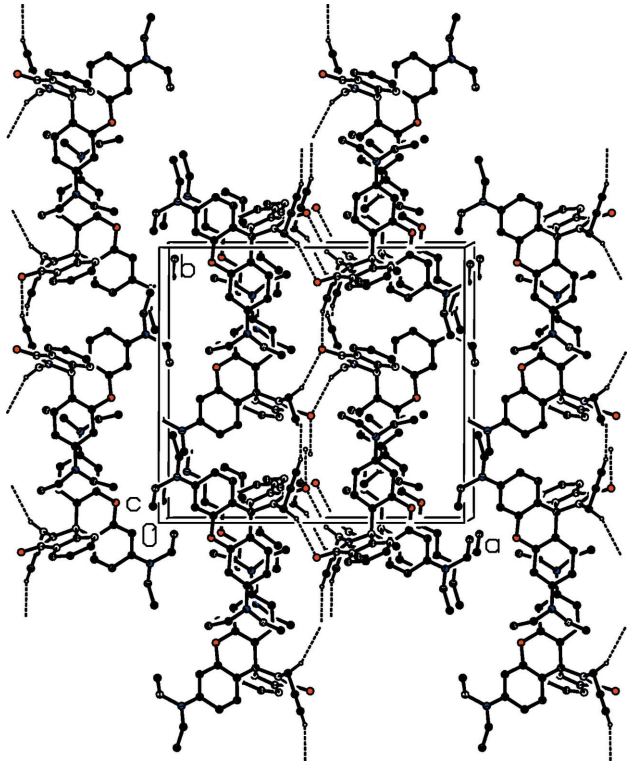


Figure 3
A view along the c axis of the crystal packing of the title compound. The hydrogen bonds (see Table 1) are shown as dashed lines. The minor components of the disordered atoms and H atoms not involved in hydrogen bonding have been omitted for clarity.

Q = 0.261 (2) Å, Θ = 80.3 (7)° and φ = 184.5 (6)°]. The pyrrolidine ring mean plane is orthogonal to the mean plane of the tetrahydropyran ring with a dihedral angle of 89.1 (2)°. The dihedral angle between the benzene rings in the xanthene fragment is 17.3 (1)°.

In the crystal, molecules are linked by pairs of C—H···O hydrogen bonds, forming inversion dimers with an $R_2^2(10)$ ring motif (Table 1 and Fig. 2). The dimers are linked by further C—H···O hydrogen bonds, forming slabs parallel to the *bc* plane (Table 1 and Fig. 3).

Synthesis and crystallization

To a solution of rhodamine B (5.76 g, 12 mmol) in anhydrous dichloromethane (20 ml) was added sequentially 2-(1*H*-benzotriazol-1-yl-1,1,3,3-tetramethyluronium hexafluorophosphate (5.45 g, 14.4 mmol), propargylamine (0.925 ml, 14.4 mmol) and triethylamine (2.5 ml, 14.4 mmol). The reaction mixture was stirred at room temperature overnight until TLC indicated the disappearance of the starting products. The reaction mixture was diluted with dichloromethane (200 ml) and then washed with brine. The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (hexane:EtOAc, 4:1) to yield the title compound as a pale-pink solid. Pink block-like crystals were obtained by slow evaporation of a solution in chloroform/ethanol/acetonitrile in a (2:1:1) ratio.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. In the diethylamine group, one of the NCH_2CH_3 group of atoms is disordered over the two positions (N2/N2′, C30/C30′ and C31/C31′), with a refined occupancy ratio of 0.73 (1):0.27 (1).

Acknowledgements

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References

Bruker (2004). *APEX2*, *SAINT*, *XPREP* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Soh, J. H., Swamy, K. M. K., Kim, S. K., Kim, S., Lee, S. H. & Yoon, J. (2007). *Tetrahedron Lett.* **48**, 5966–5969.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Wu, D., Huang, W., Duan, C. Y., Lin, Z. H. & Meng, Q. J. (2007). *Inorg. Chem.* **46**, 1538–1540.
Zhang, X., Shiraishi, Y. & Hirai, T. (2007). *Org. Lett.* **9**, 5039–5042.

full crystallographic data

IUCrData (2016). **1**, x160772 [doi:10.1107/S2414314616007720]

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Crystal data

$C_{31}H_{33}N_3O_2$
M_r = 479.60
Monoclinic, $P2_1/c$
a = 18.0701 (8) Å
b = 16.2611 (7) Å
c = 9.0801 (4) Å
β = 97.645 (2)°
V = 2644.4 (2) Å^3
Z = 4
$F(000)$ = 1024
D_x = 1.205 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3350 reflections
θ = 2.3–25.0°
μ = 0.08 mm^{-1}
T = 293 K
Block, pink
0.35 × 0.25 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
ω and φ scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.977, T_{max} = 0.985
40635 measured reflections
4654 independent reflections
3350 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 25.0°, θ_{min} = 2.3°
h = −21→21
k = −19→19
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.153
S = 1.09
4654 reflections
354 parameters
72 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
$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 2.114P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0061 (8)

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}	Occ. (<1)
C1	0.29699 (12)	0.55506 (14)	0.4059 (3)	0.0400 (5)	
C2	0.35508 (15)	0.60419 (16)	0.3708 (3)	0.0540 (7)	
H2	0.3987	0.5790	0.3497	0.065*	
C3	0.35069 (15)	0.68822 (16)	0.3658 (4)	0.0601 (8)	
H3	0.3911	0.7185	0.3417	0.072*	
C4	0.28656 (15)	0.72918 (16)	0.3964 (3)	0.0566 (7)	
C5	0.22779 (15)	0.68068 (16)	0.4334 (3)	0.0555 (7)	
H5	0.1844	0.7056	0.4561	0.067*	
C6	0.23396 (13)	0.59608 (15)	0.4363 (3)	0.0436 (6)	
C7	0.17976 (13)	0.47332 (14)	0.5134 (3)	0.0412 (6)	
C8	0.12177 (13)	0.44161 (15)	0.5811 (3)	0.0447 (6)	
H8	0.0807	0.4744	0.5917	0.054*	
C9	0.12425 (13)	0.36132 (14)	0.6335 (3)	0.0410 (6)	
C10	0.18786 (13)	0.31512 (15)	0.6149 (3)	0.0442 (6)	
H10	0.1923	0.2616	0.6513	0.053*	
C11	0.24385 (13)	0.34752 (14)	0.5440 (3)	0.0426 (6)	
H11	0.2847	0.3147	0.5314	0.051*	
C12	0.24146 (12)	0.42754 (14)	0.4904 (3)	0.0373 (5)	
C13	0.29979 (12)	0.46205 (14)	0.4032 (3)	0.0391 (5)	
C14	0.29140 (13)	0.43066 (14)	0.2440 (3)	0.0401 (5)	
C15	0.23015 (15)	0.43577 (16)	0.1353 (3)	0.0492 (6)	
H15	0.1854	0.4588	0.1553	0.059*	
C16	0.23772 (17)	0.40540 (17)	−0.0046 (3)	0.0585 (7)	
H16	0.1972	0.4077	−0.0793	0.070*	
C17	0.30422 (17)	0.37172 (18)	−0.0353 (3)	0.0604 (8)	
H17	0.3079	0.3523	−0.1304	0.072*	
C18	0.36521 (16)	0.36645 (17)	0.0729 (3)	0.0553 (7)	
H18	0.4100	0.3439	0.0526	0.066*	
C19	0.35730 (14)	0.39608 (15)	0.2131 (3)	0.0436 (6)	
C20	0.41227 (14)	0.39862 (14)	0.3487 (3)	0.0431 (6)	
C21	0.41217 (14)	0.44670 (16)	0.6068 (3)	0.0476 (6)	
H21A	0.4547	0.4827	0.6024	0.057*	
H21B	0.3776	0.4748	0.6626	0.057*	
C22	0.43761 (14)	0.37143 (17)	0.6847 (3)	0.0484 (6)	
C23	0.45786 (16)	0.3112 (2)	0.7474 (3)	0.0624 (8)	
H23	0.4740	0.2632	0.7974	0.075*	
N1	0.37558 (10)	0.43172 (12)	0.4563 (2)	0.0412 (5)	
N3	0.06666 (12)	0.32915 (14)	0.7002 (3)	0.0552 (6)	
O1	0.17142 (9)	0.55466 (10)	0.4709 (2)	0.0564 (5)	
O2	0.47756 (10)	0.37691 (12)	0.3659 (2)	0.0570 (5)	
C25	0.07600 (17)	0.25489 (18)	0.7890 (3)	0.0618 (8)	
H25A	0.0476	0.2605	0.8719	0.074*	
H25B	0.1282	0.2497	0.8296	0.074*	
C26	−0.00442 (16)	0.3710 (2)	0.6930 (4)	0.0693 (9)	
H26A	−0.0432	0.3302	0.6979	0.083*	

H26B	−0.0147	0.3985	0.5977	0.083*	
C24	0.0522 (2)	0.1779 (2)	0.7072 (5)	0.0911 (11)	
H24A	0.0601	0.1319	0.7735	0.137*	
H24B	0.0001	0.1816	0.6689	0.137*	
H24C	0.0809	0.1708	0.6264	0.137*	
C27	−0.0086 (2)	0.4336 (3)	0.8147 (5)	0.1045 (14)	
H27A	−0.0571	0.4585	0.8025	0.157*	
H27B	0.0001	0.4068	0.9097	0.157*	
H27C	0.0287	0.4751	0.8094	0.157*	
C28	0.3992 (3)	0.8913 (3)	0.4442 (5)	0.1125 (14)	
H28A	0.4341	0.9241	0.3987	0.169*	
H28C	0.3791	0.9233	0.5185	0.169*	
H28B	0.4243	0.8439	0.4898	0.169*	
C29	0.33793 (18)	0.86470 (19)	0.3299 (4)	0.0703 (9)	
H29A	0.3124	0.9123	0.2829	0.084*	
H29B	0.3577	0.8326	0.2541	0.084*	
N2	0.2856 (5)	0.8146 (6)	0.4037 (10)	0.073 (2)	0.730 (10)
C30	0.2286 (3)	0.8579 (3)	0.4703 (8)	0.0714 (17)	0.730 (10)
H30A	0.2492	0.9091	0.5123	0.086*	0.730 (10)
H30B	0.2143	0.8249	0.5510	0.086*	0.730 (10)
C31	0.1602 (4)	0.8765 (4)	0.3633 (8)	0.106 (2)	0.730 (10)
H31A	0.1246	0.9051	0.4141	0.159*	0.730 (10)
H31B	0.1736	0.9102	0.2842	0.159*	0.730 (10)
H31C	0.1386	0.8260	0.3229	0.159*	0.730 (10)
N2′	0.2711 (11)	0.8100 (15)	0.358 (3)	0.060 (4)	0.270 (10)
C30′	0.1995 (10)	0.8497 (8)	0.3683 (19)	0.075 (4)	0.270 (10)
H30C	0.1595	0.8178	0.3140	0.090*	0.270 (10)
H30D	0.1990	0.9042	0.3247	0.090*	0.270 (10)
C31′	0.1881 (12)	0.8558 (10)	0.5277 (18)	0.103 (6)	0.270 (10)
H31D	0.1411	0.8819	0.5349	0.155*	0.270 (10)
H31E	0.1883	0.8017	0.5700	0.155*	0.270 (10)
H31F	0.2277	0.8878	0.5807	0.155*	0.270 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0367 (12)	0.0351 (12)	0.0485 (14)	0.0002 (10)	0.0066 (10)	−0.0021 (10)
C2	0.0440 (14)	0.0443 (15)	0.0771 (19)	0.0025 (12)	0.0201 (13)	−0.0055 (13)
C3	0.0462 (15)	0.0426 (15)	0.095 (2)	−0.0087 (12)	0.0213 (15)	−0.0040 (15)
C4	0.0509 (16)	0.0399 (15)	0.082 (2)	0.0005 (12)	0.0181 (14)	0.0014 (13)
C5	0.0472 (15)	0.0407 (14)	0.083 (2)	0.0081 (12)	0.0231 (14)	0.0074 (13)
C6	0.0385 (13)	0.0383 (13)	0.0549 (15)	0.0005 (10)	0.0099 (11)	0.0055 (11)
C7	0.0387 (13)	0.0362 (13)	0.0477 (14)	0.0025 (10)	0.0020 (11)	0.0062 (10)
C8	0.0381 (13)	0.0429 (14)	0.0531 (15)	0.0056 (11)	0.0060 (11)	0.0072 (11)
C9	0.0395 (13)	0.0414 (13)	0.0407 (13)	−0.0027 (10)	−0.0002 (10)	0.0037 (10)
C10	0.0488 (14)	0.0335 (12)	0.0478 (14)	−0.0011 (11)	−0.0027 (11)	0.0041 (10)
C11	0.0393 (13)	0.0370 (13)	0.0500 (14)	0.0041 (10)	0.0000 (11)	−0.0038 (11)
C12	0.0359 (12)	0.0340 (12)	0.0413 (13)	0.0011 (10)	0.0028 (10)	−0.0009 (10)

C13	0.0350 (12)	0.0368 (12)	0.0444 (13)	0.0030 (10)	0.0015 (10)	−0.0033 (10)
C14	0.0455 (13)	0.0321 (12)	0.0421 (13)	−0.0043 (10)	0.0037 (11)	−0.0002 (10)
C15	0.0496 (15)	0.0467 (15)	0.0494 (15)	−0.0010 (12)	−0.0004 (12)	0.0014 (12)
C16	0.0691 (19)	0.0565 (17)	0.0453 (15)	−0.0097 (14)	−0.0091 (14)	0.0007 (13)
C17	0.074 (2)	0.0657 (19)	0.0413 (15)	−0.0093 (15)	0.0080 (14)	−0.0076 (13)
C18	0.0602 (17)	0.0582 (17)	0.0492 (15)	−0.0023 (13)	0.0140 (13)	−0.0089 (13)
C19	0.0466 (14)	0.0420 (13)	0.0423 (13)	−0.0018 (11)	0.0060 (11)	−0.0044 (11)
C20	0.0422 (14)	0.0370 (13)	0.0504 (15)	0.0006 (11)	0.0071 (11)	−0.0039 (11)
C21	0.0460 (14)	0.0484 (15)	0.0467 (14)	−0.0021 (12)	−0.0004 (11)	−0.0091 (12)
C22	0.0442 (14)	0.0555 (17)	0.0448 (14)	−0.0026 (12)	0.0034 (11)	−0.0019 (13)
C23	0.0612 (18)	0.065 (2)	0.0599 (18)	0.0009 (15)	0.0045 (14)	0.0101 (15)
N1	0.0384 (11)	0.0424 (11)	0.0419 (11)	0.0032 (9)	0.0020 (9)	−0.0066 (9)
N3	0.0489 (13)	0.0508 (13)	0.0665 (15)	0.0008 (10)	0.0108 (11)	0.0190 (11)
O1	0.0408 (10)	0.0399 (10)	0.0914 (14)	0.0083 (8)	0.0200 (9)	0.0207 (9)
O2	0.0406 (10)	0.0644 (12)	0.0661 (12)	0.0049 (9)	0.0072 (9)	−0.0151 (10)
C25	0.0676 (19)	0.0595 (18)	0.0589 (17)	−0.0004 (14)	0.0114 (14)	0.0160 (14)
C26	0.0486 (16)	0.071 (2)	0.090 (2)	−0.0004 (14)	0.0149 (16)	0.0262 (18)
C24	0.100 (3)	0.061 (2)	0.110 (3)	−0.0123 (19)	0.003 (2)	0.009 (2)
C27	0.111 (3)	0.096 (3)	0.117 (3)	0.032 (2)	0.052 (3)	0.021 (3)
C28	0.122 (4)	0.107 (3)	0.105 (3)	−0.018 (3)	−0.001 (3)	−0.003 (3)
C29	0.075 (2)	0.0487 (17)	0.088 (2)	−0.0019 (15)	0.0143 (18)	0.0119 (16)
N2	0.067 (4)	0.039 (2)	0.116 (6)	0.001 (3)	0.026 (4)	−0.004 (3)
C30	0.078 (4)	0.043 (2)	0.098 (4)	0.001 (2)	0.029 (3)	−0.003 (3)
C31	0.071 (4)	0.092 (4)	0.156 (6)	0.024 (3)	0.019 (4)	0.034 (4)
N2′	0.053 (7)	0.034 (6)	0.100 (10)	−0.004 (5)	0.033 (7)	0.021 (7)
C30′	0.072 (8)	0.040 (6)	0.112 (9)	−0.011 (6)	0.011 (8)	0.015 (7)
C31′	0.112 (12)	0.074 (9)	0.136 (13)	−0.003 (8)	0.060 (11)	−0.016 (9)

Geometric parameters (Å, º)

C1—C6	1.379 (3)	C21—N1	1.457 (3)
C1—C2	1.390 (3)	C21—H21A	0.9700
C1—C13	1.514 (3)	C21—H21B	0.9700
C2—C3	1.369 (4)	C22—C23	1.167 (4)
C2—H2	0.9300	C23—H23	0.9300
C3—C4	1.396 (4)	N3—C26	1.447 (4)
C3—H3	0.9300	N3—C25	1.449 (3)
C4—N2′	1.38 (2)	C25—C24	1.489 (4)
C4—N2	1.391 (10)	C25—H25A	0.9700
C4—C5	1.399 (4)	C25—H25B	0.9700
C5—C6	1.380 (3)	C26—C27	1.512 (5)
C5—H5	0.9300	C26—H26A	0.9700
C6—O1	1.387 (3)	C26—H26B	0.9700
C7—C12	1.379 (3)	C24—H24A	0.9600
C7—O1	1.380 (3)	C24—H24B	0.9600
C7—C8	1.383 (3)	C24—H24C	0.9600
C8—C9	1.388 (3)	C27—H27A	0.9600
C8—H8	0.9300	C27—H27B	0.9600

C9—N3	1.375 (3)	C27—H27C	0.9600
C9—C10	1.402 (3)	C28—C29	1.478 (5)
C10—C11	1.375 (3)	C28—H28A	0.9600
C10—H10	0.9300	C28—H28C	0.9600
C11—C12	1.388 (3)	C28—H28B	0.9600
C11—H11	0.9300	C29—N2	1.474 (10)
C12—C13	1.508 (3)	C29—N2′	1.55 (2)
C13—N1	1.475 (3)	C29—H29A	0.9700
C13—C14	1.521 (3)	C29—H29B	0.9700
C14—C19	1.379 (3)	N2—C30	1.446 (8)
C14—C15	1.384 (3)	C30—C31	1.497 (8)
C15—C16	1.386 (4)	C30—H30A	0.9700
C15—H15	0.9300	C30—H30B	0.9700
C16—C17	1.382 (4)	C31—H31A	0.9600
C16—H16	0.9300	C31—H31B	0.9600
C17—C18	1.378 (4)	C31—H31C	0.9600
C17—H17	0.9300	N2′—C30′	1.459 (15)
C18—C19	1.386 (3)	C30′—C31′	1.492 (15)
C18—H18	0.9300	C30′—H30C	0.9700
C19—C20	1.476 (3)	C30′—H30D	0.9700
C20—O2	1.221 (3)	C31′—H31D	0.9600
C20—N1	1.362 (3)	C31′—H31E	0.9600
C21—C22	1.457 (4)	C31′—H31F	0.9600

C6—C1—C2	115.9 (2)	C20—N1—C13	114.64 (19)
C6—C1—C13	121.1 (2)	C21—N1—C13	122.43 (19)
C2—C1—C13	122.9 (2)	C9—N3—C26	121.4 (2)
C3—C2—C1	122.6 (2)	C9—N3—C25	121.5 (2)
C3—C2—H2	118.7	C26—N3—C25	117.0 (2)
C1—C2—H2	118.7	C7—O1—C6	117.82 (18)
C2—C3—C4	121.0 (2)	N3—C25—C24	114.7 (3)
C2—C3—H3	119.5	N3—C25—H25A	108.6
C4—C3—H3	119.5	C24—C25—H25A	108.6
N2′—C4—C3	123.4 (8)	N3—C25—H25B	108.6
N2—C4—C3	120.1 (4)	C24—C25—H25B	108.6
N2′—C4—C5	117.6 (8)	H25A—C25—H25B	107.6
N2—C4—C5	122.5 (4)	N3—C26—C27	114.4 (3)
C3—C4—C5	117.1 (2)	N3—C26—H26A	108.7
C6—C5—C4	120.3 (2)	C27—C26—H26A	108.7
C6—C5—H5	119.8	N3—C26—H26B	108.7
C4—C5—H5	119.8	C27—C26—H26B	108.7
C1—C6—C5	123.0 (2)	H26A—C26—H26B	107.6
C1—C6—O1	122.0 (2)	C25—C24—H24A	109.5
C5—C6—O1	115.0 (2)	C25—C24—H24B	109.5
C12—C7—O1	122.3 (2)	H24A—C24—H24B	109.5
C12—C7—C8	122.8 (2)	C25—C24—H24C	109.5
O1—C7—C8	114.9 (2)	H24A—C24—H24C	109.5
C7—C8—C9	120.7 (2)	H24B—C24—H24C	109.5

C7—C8—H8	119.6	C26—C27—H27A	109.5
C9—C8—H8	119.6	C26—C27—H27B	109.5
N3—C9—C8	121.1 (2)	H27A—C27—H27B	109.5
N3—C9—C10	122.0 (2)	C26—C27—H27C	109.5
C8—C9—C10	116.9 (2)	H27A—C27—H27C	109.5
C11—C10—C9	121.2 (2)	H27B—C27—H27C	109.5
C11—C10—H10	119.4	C29—C28—H28A	109.5
C9—C10—H10	119.4	C29—C28—H28C	109.5
C10—C11—C12	122.2 (2)	H28A—C28—H28C	109.5
C10—C11—H11	118.9	C29—C28—H28B	109.5
C12—C11—H11	118.9	H28A—C28—H28B	109.5
C7—C12—C11	116.2 (2)	H28C—C28—H28B	109.5
C7—C12—C13	120.9 (2)	N2—C29—C28	108.0 (5)
C11—C12—C13	122.8 (2)	C28—C29—N2′	125.4 (10)
N1—C13—C12	112.79 (19)	N2—C29—H29A	110.1
N1—C13—C1	111.12 (18)	C28—C29—H29A	110.1
C12—C13—C1	109.62 (19)	N2—C29—H29B	110.1
N1—C13—C14	99.74 (18)	C28—C29—H29B	110.1
C12—C13—C14	112.69 (19)	H29A—C29—H29B	108.4
C1—C13—C14	110.59 (19)	C4—N2—C30	121.3 (7)
C19—C14—C15	120.6 (2)	C4—N2—C29	121.2 (6)
C19—C14—C13	110.5 (2)	C30—N2—C29	117.2 (7)
C15—C14—C13	128.8 (2)	N2—C30—C31	113.6 (8)
C14—C15—C16	117.7 (3)	N2—C30—H30A	108.9
C14—C15—H15	121.1	C31—C30—H30A	108.9
C16—C15—H15	121.1	N2—C30—H30B	108.9
C17—C16—C15	121.3 (3)	C31—C30—H30B	108.9
C17—C16—H16	119.3	H30A—C30—H30B	107.7
C15—C16—H16	119.3	C30—C31—H31A	109.5
C18—C17—C16	121.0 (3)	C30—C31—H31B	109.5
C18—C17—H17	119.5	H31A—C31—H31B	109.5
C16—C17—H17	119.5	C30—C31—H31C	109.5
C17—C18—C19	117.6 (3)	H31A—C31—H31C	109.5
C17—C18—H18	121.2	H31B—C31—H31C	109.5
C19—C18—H18	121.2	C4—N2′—C30′	123.9 (15)
C14—C19—C18	121.7 (2)	C4—N2′—C29	117.0 (12)
C14—C19—C20	108.8 (2)	C30′—N2′—C29	118.2 (16)
C18—C19—C20	129.5 (2)	N2′—C30′—C31′	109 (2)
O2—C20—N1	125.2 (2)	N2′—C30′—H30C	109.9
O2—C20—C19	129.1 (2)	C31′—C30′—H30C	109.9
N1—C20—C19	105.8 (2)	N2′—C30′—H30D	109.9
C22—C21—N1	112.9 (2)	C31′—C30′—H30D	109.9
C22—C21—H21A	109.0	H30C—C30′—H30D	108.3
N1—C21—H21A	109.0	C30′—C31′—H31D	109.5
C22—C21—H21B	109.0	C30′—C31′—H31E	109.5
N1—C21—H21B	109.0	H31D—C31′—H31E	109.5
H21A—C21—H21B	107.8	C30′—C31′—H31F	109.5
C23—C22—C21	179.8 (3)	H31D—C31′—H31F	109.5

C22—C23—H23	180.0	H31E—C31′—H31F	109.5
C20—N1—C21	122.4 (2)		
C6—C1—C2—C3	−0.1 (4)	C15—C14—C19—C18	1.0 (4)
C13—C1—C2—C3	176.5 (3)	C13—C14—C19—C18	−176.9 (2)
C1—C2—C3—C4	0.0 (5)	C15—C14—C19—C20	−179.8 (2)
C2—C3—C4—N2′	−163.3 (13)	C13—C14—C19—C20	2.4 (3)
C2—C3—C4—N2	174.3 (5)	C17—C18—C19—C14	−0.8 (4)
C2—C3—C4—C5	0.6 (5)	C17—C18—C19—C20	−179.9 (3)
N2′—C4—C5—C6	163.9 (12)	C14—C19—C20—O2	−177.1 (3)
N2—C4—C5—C6	−174.6 (5)	C18—C19—C20—O2	2.0 (5)
C3—C4—C5—C6	−1.0 (4)	C14—C19—C20—N1	2.4 (3)
C2—C1—C6—C5	−0.3 (4)	C18—C19—C20—N1	−178.5 (3)
C13—C1—C6—C5	−177.0 (2)	O2—C20—N1—C21	1.4 (4)
C2—C1—C6—O1	179.0 (2)	C19—C20—N1—C21	−178.1 (2)
C13—C1—C6—O1	2.3 (4)	O2—C20—N1—C13	173.0 (2)
C4—C5—C6—C1	0.9 (4)	C19—C20—N1—C13	−6.6 (3)
C4—C5—C6—O1	−178.5 (3)	C22—C21—N1—C20	−63.7 (3)
C12—C7—C8—C9	1.8 (4)	C22—C21—N1—C13	125.4 (2)
O1—C7—C8—C9	−178.0 (2)	C12—C13—N1—C20	127.4 (2)
C7—C8—C9—N3	−179.6 (2)	C1—C13—N1—C20	−109.1 (2)
C7—C8—C9—C10	0.3 (4)	C14—C13—N1—C20	7.6 (2)
N3—C9—C10—C11	178.0 (2)	C12—C13—N1—C21	−61.1 (3)
C8—C9—C10—C11	−1.9 (3)	C1—C13—N1—C21	62.5 (3)
C9—C10—C11—C12	1.5 (4)	C14—C13—N1—C21	179.1 (2)
O1—C7—C12—C11	177.6 (2)	C8—C9—N3—C26	12.2 (4)
C8—C7—C12—C11	−2.2 (4)	C10—C9—N3—C26	−167.7 (3)
O1—C7—C12—C13	−6.2 (4)	C8—C9—N3—C25	−163.6 (2)
C8—C7—C12—C13	174.1 (2)	C10—C9—N3—C25	16.5 (4)
C10—C11—C12—C7	0.5 (3)	C12—C7—O1—C6	−15.2 (3)
C10—C11—C12—C13	−175.7 (2)	C8—C7—O1—C6	164.6 (2)
C7—C12—C13—N1	147.4 (2)	C1—C6—O1—C7	17.1 (4)
C11—C12—C13—N1	−36.6 (3)	C5—C6—O1—C7	−163.6 (2)
C7—C12—C13—C1	23.0 (3)	C9—N3—C25—C24	−95.0 (3)
C11—C12—C13—C1	−161.0 (2)	C26—N3—C25—C24	89.1 (4)
C7—C12—C13—C14	−100.6 (2)	C9—N3—C26—C27	−87.4 (3)
C11—C12—C13—C14	75.4 (3)	C25—N3—C26—C27	88.6 (3)
C6—C1—C13—N1	−146.5 (2)	C3—C4—N2—C30	−164.4 (6)
C2—C1—C13—N1	37.1 (3)	C5—C4—N2—C30	9.0 (11)
C6—C1—C13—C12	−21.1 (3)	C3—C4—N2—C29	22.2 (10)
C2—C1—C13—C12	162.4 (2)	C5—C4—N2—C29	−164.5 (5)
C6—C1—C13—C14	103.7 (3)	C28—C29—N2—C4	−100.9 (7)
C2—C1—C13—C14	−72.7 (3)	C28—C29—N2—C30	85.4 (8)
N1—C13—C14—C19	−5.7 (2)	C4—N2—C30—C31	−88.3 (9)
C12—C13—C14—C19	−125.6 (2)	C29—N2—C30—C31	85.3 (7)
C1—C13—C14—C19	111.4 (2)	C3—C4—N2′—C30′	170.0 (16)
N1—C13—C14—C15	176.7 (2)	C5—C4—N2′—C30′	6 (3)
C12—C13—C14—C15	56.8 (3)	C3—C4—N2′—C29	−21 (2)

C1—C13—C14—C15	−66.2 (3)	C5—C4—N2′—C29	175.3 (11)
C19—C14—C15—C16	−0.3 (4)	C28—C29—N2′—C4	−68 (2)
C13—C14—C15—C16	177.1 (2)	C28—C29—N2′—C30′	101.3 (18)
C14—C15—C16—C17	−0.5 (4)	C4—N2′—C30′—C31′	67 (3)
C15—C16—C17—C18	0.6 (4)	C29—N2′—C30′—C31′	−102.4 (18)
C16—C17—C18—C19	0.0 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C21—H21*A*···O2^{i}	0.97	2.59	3.483 (3)	153
C23—H23···O2^{ii}	0.93	2.36	3.246 (4)	159

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