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(*R*)-2-{2-[(*S*)-(2′-Benzoyloxy-1,1′-binaphthyl-2-yl)oxycarbonylamino]-3-phenylpropanamidomethyl}pyridinium picrate acetone solvate

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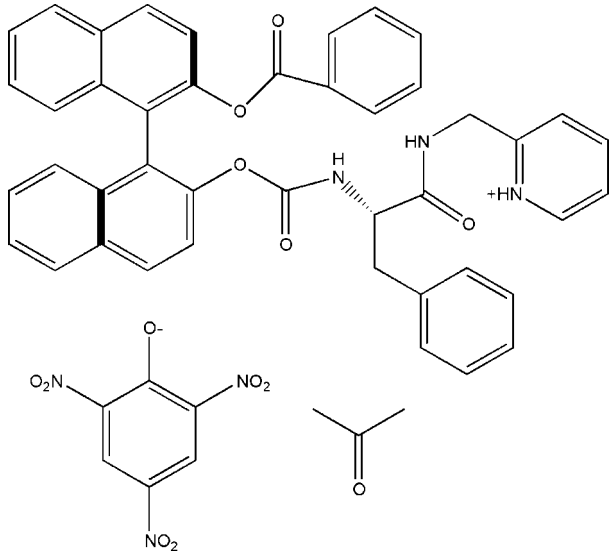
Key indicators: single-crystal X-ray study; T = 110 K; mean σ(C–C) = 0.006 Å; R factor = 0.035; wR factor = 0.061; data-to-parameter ratio = 8.5.

In the crystal structure of the title compound, $C_{43}H_{34}N_3O_5^+\cdot C_6H_2N_3O_7^-\cdot C_3H_6O$, the large dimension and shape of the cation are responsible for the elongation of the orthorhombic unit cell. The ions and acetone molecules are linked together by a system of hydrogen bonds involving an intermolecular hydrogen bond between one N atom of the cation and the O atom of acetone and two intermolecular hydrogen bonds between the cation N atoms and the O atoms of the picrate anion. No intramolecular hydrogen bonds exist in the structure. The dihedral angle between the two naphthalene ring systems is 76.16 (13)°. The chiral C atom has a known *R* configuration, but this cannot be confirmed from this X-ray analysis.

Related literature

For general background, see: Secco *et al.* (2004); Hušek & Šimek (2006); Freimueller & Altorfer (2002); Fransson & Ragnarsson (1998); Christenssen *et al.* (1995); Latypov *et al.* (1999); Fukushi *et al.* (1994*a*,*b*); Růžička *et al.* (2000); Vodička *et al.* (2003).



Experimental

Crystal data

$C_{43}H_{34}N_3O_5^+\cdot C_6H_2N_3O_7^-\cdot C_3H_6O$
M_r = 958.9
Orthorhombic, $P2_12_12_1$
a = 8.5021 (19) Å
b = 10.6178 (19) Å
c = 51.189 (10) Å
V = 4621.0 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 110 K
0.24 × 0.12 × 0.06 mm

Data collection

Oxford Diffraction Xcalibur2 diffractometer with Sapphire2 CCD detector
Absorption correction: none
8240 measured reflections
4723 independent reflections
2429 reflections with $I > 3\sigma(I)$
R_{int} = 0.063

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.061
S = 1.11
4723 reflections
557 parameters
H-atom parameters not refined
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O58	0.87	1.98	2.800 (4)	159
N8—H8···O67	0.87	2.09	2.873 (4)	149
N12—H10···O71^{i}	0.87	2.27	3.106 (4)	160

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *JANA2006*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2075).

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(*R*)-2-{2-[(*S*)-(2′-Benzoyloxy-1,1′-binaphthyl-2-yl)oxycarbonylamino]-3-phenylpropanamidomethyl}pyridinium picrate acetone solvate

Ludvík Streinz, Petr Hartvich, Jan Ondráček, Petr Šimek, Karla Fejfarová and Michal Dušek

S1. Comment

Chiral derivatizing agents are relatively very efficient substances for derivatization of enantiomers to enable their separation by HPLC and/or spectral determination (Secco *et al.*, 2004). Among them, the alkylchloroformates are very popular for analysis of *e.g.* peptides, amines or alcohols, because of their ability to react under mild conditions giving stable and largely well determined diastereomers (Hušek *et al.*, 2006). (-)-Menthyl chloroformate or (+)-[(1-(9-fluorenyl)-ethyl]-chloroformates are good examples of such agents (Freimueller *et al.*, 2002; Fransson *et al.*, 1998; Christenssen *et al.*, 1995). In order to expand the available chiral chloroformate derivatives, we have elaborated the synthesis of chloroformate containing 1-(2-hydroxynaphtha-len-1-yl)naphthalen-2-yl benzoate as a chiral auxiliary. In the bi-naphthyl auxiliary, the presence of voluminous aromatic groups and their spatial orientation massively affects the NMR chemical shifts of particular diastereomers, yielding relatively large differences of $\Delta\delta$ in spectra (Latypov *et al.*, 1999; Fukushi *et al.*, 1994*a*,b). Thus chiral analysis is very effective. Since the orientation of aromatic rings as well as the configuration of the molecular skeleton play an important role in the chiral analysis, the knowledge of spatial orientation of particular substituents is important for *e.g.* deduction of general rules useful for prediction of the absolute configuration (Růžička *et al.*,2000). *X* ray analysis may be of great benefit in this effort (Vodička *et al.*, 2003).

The crystal structure of the title compound is linked together by a system of hydrogen bonds (Table 1). For NMR analyses, positions of hydrogen atoms H8, H17 and H18 in relation to aromatic rings C15*a*—C24*a* (forming the plane A), C15*b*—C24*b* (plane B) and C46—C51 (plane C) are particularly important. Mutual angles between planes defined by these aromatic rings are 76.16 (13)° (A—B), 90.60 (13)° (B—C) and 69.30 (13)° (A—C) respectively. The distances of H8 from the planes A, B and C are -4.445 (8), 3.977 (9) and -0.825 (12) Å, respectively, while distances to the nearest carbons C15*a*, C15*b* and C47 are 6.307 (3), 6.010 (4) and 3.840 (4) Å. The distances of H17 are -0.642 (10), 6.009 (3) and -0.386 (12) Å from the planes A, B and C, and 5.933 (3), 6.108 (3) and 6.507 (4) Å from the carbons C15*a*, C15*b* and C47. For hydrogen H18 we found distances of -0.806 (10) 6.429 (5) and 0.818 (12) Å from the planes A, B and C and distances 5.883 (3), 6.752 (3) and 6.633 (4) Å to the nearest carbons C15*a*, C15*b* and C47.

S2. Experimental

The title compound was prepared from (*R*)-2′-(chlorocarbonyloxy)-1,1′-binaphtyl-2-yl benzoate (162 mg, 1,06 mmol), pyridine (256 uL, 3,18 mmol) and (*S*)-2-amino-3-phenyl-*N*-(pyridin-2-ylmethyl) propan-amide (512 mg, 1.06 mmol) by mixing under cooling (0°C) in total amount of 12 mL of $CHCl_3$. The reaction mixture was stirred at RT for two hours, and then washed with conc. sodium bicarbonate (12 ml), water (12 ml) and dried over magnesium sulfate. After the evaporation of the solvent, the crude product was filtered through a silica column (15 g) with a mixture of diethyl ether/THF (2/1) giving 616 mg of oily product.

In order to obtain crystals suitable for X-ray analysis, the above mentioned compound (30 mg, 0.044 mmol) was mixed with picric acid (10.2 mg, 0.044 mmol) in 0.5 ml of $CHCl_3$ at room temperature. After 30 min at RT the solvent was removed under reduced vacuum giving 40.2 mg (100%) of product. Pure crystals were obtained by re-crystalization (20 mg) from the mixture of 0.5 ml octane and 1.0 ml acetone at room temperature.

S3. Refinement

Hydrogen atoms were constrained to ideal positions, and isotropic temperature parameters of hydrogen atoms were calculated as $1.2U_{eq}$ of the parent atom.

The 1-(2-(benzoyloxy)naphthalen-1-yl)naphthalen-2-yl fragment was refined as a rigid body with two positions in order to save parameters and to cut high angle mostly unobserved reflections without lowering the observations/parameters ratio. The ADP parameters of the molecule were refined as common to both positions. The validity of using the common ADP parameters has been proven by comparison with TLS refinement which refines independent TLS tenzors for each molecular position. The TLS refinement converged with slightly worse *R* values.

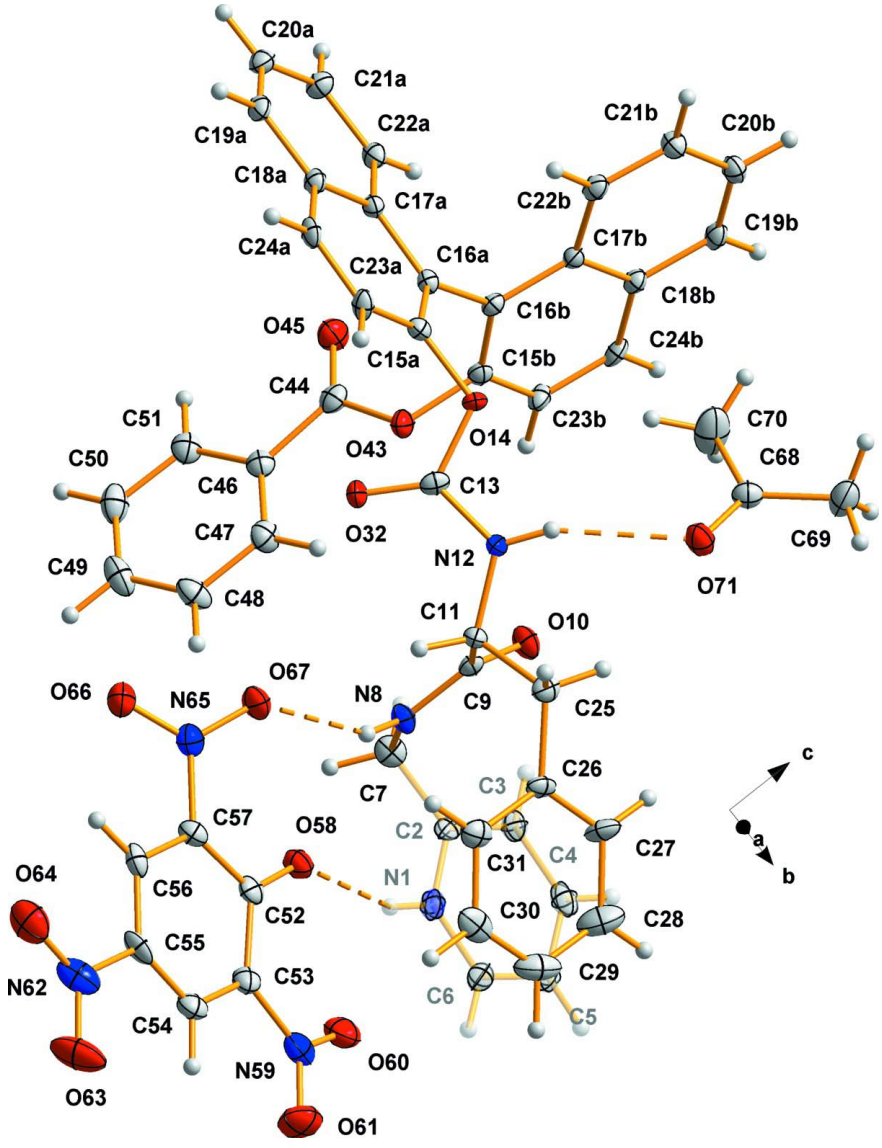

Figure 1

View of the asymmetric unit of the title compound, showing 30% displacement ellipsoids for non-H atoms. [Symmetry codes: (i) 1/2 + *x*, 1.5 - *y*, 1 - *z*]

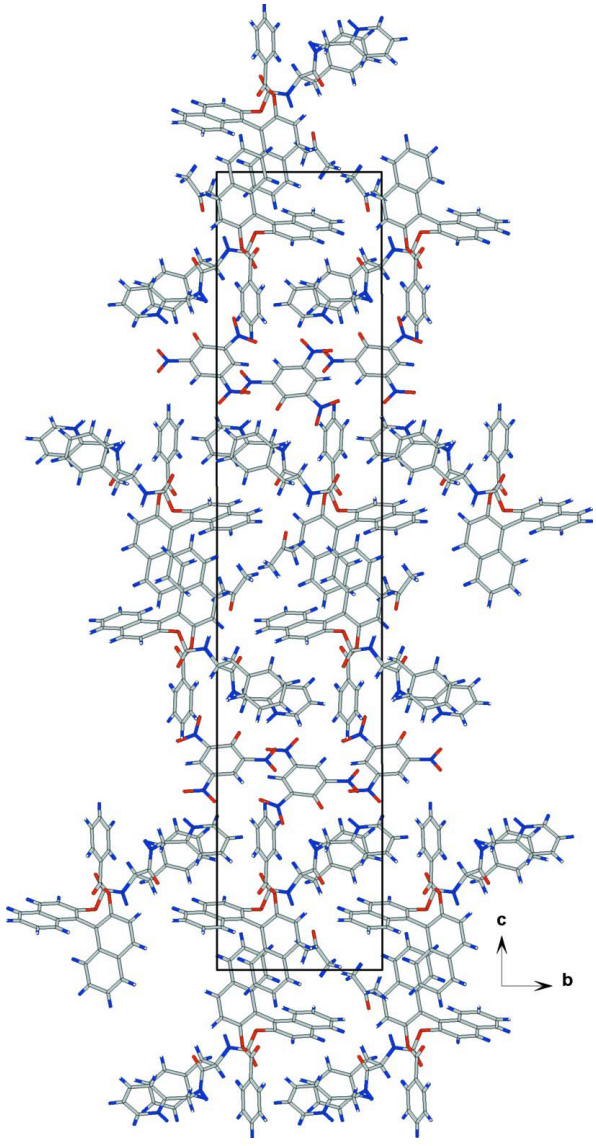

Figure 2

View of the unit cell of the title structure down the axis a.

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Crystal data

$C_{43}H_{34}N_3O_5^+ \cdot C_6H_2N_3O_7^- \cdot C_3H_6O$
$M_r = 958.9$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 8.5021\ (19)$ Å
$b = 10.6178\ (19)$ Å
$c = 51.189\ (10)$ Å
$V = 4621.0\ (16)$ Å^3
$Z = 4$
$F(000) = 2000$
$D_x = 1.378$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8240 reflections
$\theta = 3.3–26.5°$
$\mu = 0.10$ mm^{-1}
$T = 110$ K
Prism, colourless
0.24 × 0.12 × 0.06 mm

Data collection

Oxford Diffraction Xcalibur2 diffractometer with Sapphire2 CCD detector
Radiation source: X-ray tube
Graphite monochromator
Detector resolution: 8.3438 pixels mm^{-1}
Rotation method data acquisition using ω scans
8240 measured reflections
4723 independent reflections
2429 reflections with $I > 3\sigma(I)$
$R_{int} = 0.063$
$\theta_{max} = 25.2°$, $\theta_{min} = 2.5°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -62 \rightarrow 62$

Refinement

Refinement on F^2
$R[F > 3\sigma(F)] = 0.035$
$wR(F) = 0.061$
$S = 1.11$
4723 reflections
557 parameters
0 restraints
144 constraints
H-atom parameters not refined
Weighting scheme based on measured s.u.'s $w = 1/[\sigma^2(I) + 0.0004I^2]$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Special details

Experimental. All tested samples were very weakly diffracting, especially with the used CCD detector Sapphire II. We used an exposure time 100 s / degree but most reflections above resolution 0.9 were unobserved.
Because of the cell parameter c above 50 Å and not very sharp diffraction spots there was danger of overlaps. In order to avoid them we used very fine scan width in omega, 0.5°, and moderate detector-to-sample distance 50 mm. The remaining overlaps were detected by the CrysAlis software using the overlap threshold parameter determined from the overlaps histogram.
Refinement. The refinement was carried out against all reflections. The conventional *R*-factor is always based on *F*. The goodness of fit as well as the weighted *R*-factor are based on *F* and F^2 for refinement carried out on *F* and F^2, respectively. The threshold expression is used only for calculating *R*-factors *etc*. and it is not relevant to the choice of reflections for refinement.
Because the cell parameter c was >50 Å and reflections were not very sharp there was danger of overlaps. In order to avoid this we used a very fine scan width in omega, 0.5°, and moderate detector-to-sample distance 50 mm. The remaining overlaps were detected by the CrysAlis software using the overlap threshold parameter determined from the overlaps histogram.
The program used for refinement, Jana2006, uses a weighting scheme based on the experimental expectations, see _refine_ls_weighting_details, that does not force *S* to be one. Therefore the values of *S* are usually larger then the ones from the *SHELX* program.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.3735 (3)	1.3560 (3)	0.32138 (5)	0.0337 (13)
H1	0.417543	1.301486	0.311015	0.0405*
C2	0.2671 (4)	1.3147 (4)	0.33910 (7)	0.0272 (15)
C3	0.1960 (4)	1.4012 (4)	0.35516 (7)	0.0324 (15)
H2	0.119075	1.374372	0.367696	0.0389*
C4	0.2353 (5)	1.5260 (4)	0.35325 (7)	0.0402 (17)
H3	0.187013	1.586377	0.364683	0.0482*
C5	0.3437 (4)	1.5653 (4)	0.33497 (8)	0.0392 (16)
H4	0.369876	1.652853	0.333315	0.047*
C6	0.4135 (5)	1.4773 (4)	0.31920 (7)	0.0362 (15)
H5	0.490964	1.50267	0.306619	0.0434*
C7	0.2335 (4)	1.1751 (3)	0.33999 (6)	0.0340 (15)
H6	0.14437	1.159785	0.351051	0.030 (10)*

H7	0.202357	1.146694	0.322957	0.0409*
N8	0.3653 (3)	1.1014 (3)	0.34897 (5)	0.0282 (11)
H8	0.424543	1.063187	0.337605	0.0338*
C9	0.3985 (4)	1.0904 (3)	0.37464 (7)	0.0258 (14)
O10	0.3226 (3)	1.1421 (2)	0.39173 (4)	0.0372 (9)
C11	0.5425 (4)	1.0092 (3)	0.38071 (6)	0.0235 (13)
H9	0.566699	0.95978	0.365529	0.0282*
N12	0.5082 (3)	0.9289 (3)	0.40280 (5)	0.0247 (10)
H10	0.533311	0.954186	0.41842	0.0297*
C13	0.4387 (4)	0.8163 (3)	0.39979 (7)	0.0247 (14)
O14	0.4071 (2)	0.7660 (2)	0.42428 (4)	0.0240 (8)
C25	0.6838 (4)	1.0914 (3)	0.38759 (6)	0.0319 (13)
H17	0.668559	1.128007	0.404554	0.0383*
H18	0.774322	1.039038	0.390368	0.0383*
C26	0.7238 (4)	1.1933 (4)	0.36832 (7)	0.0271 (15)
C27	0.6969 (4)	1.3165 (4)	0.37471 (7)	0.0396 (16)
H19	0.650774	1.336815	0.391309	0.0475*
C28	0.7352 (5)	1.4119 (4)	0.35755 (10)	0.061 (2)
H20	0.714979	1.497968	0.362195	0.0728*
C29	0.8017 (5)	1.3842 (5)	0.33407 (9)	0.055 (2)
H21	0.828495	1.45084	0.322194	0.0661*
C30	0.8307 (4)	1.2612 (5)	0.32730 (7)	0.0459 (17)
H22	0.877967	1.241976	0.310744	0.0551*
C31	0.7914 (4)	1.1641 (4)	0.34448 (8)	0.0357 (15)
H23	0.811092	1.077964	0.339817	0.0429*
O32	0.4080 (3)	0.7645 (2)	0.37962 (4)	0.0327 (9)
O43	0.0559 (3)	0.8465 (2)	0.40354 (4)	0.0296 (9)
C44	−0.0722 (5)	0.7933 (3)	0.39202 (7)	0.0315 (15)
O45	−0.1811 (3)	0.7526 (2)	0.40388 (4)	0.0429 (10)
C46	−0.0580 (5)	0.7975 (3)	0.36292 (7)	0.0306 (14)
C47	0.0724 (5)	0.8455 (3)	0.35052 (7)	0.0368 (15)
H30	0.156578	0.881113	0.3606	0.0441*
C48	0.0826 (5)	0.8424 (4)	0.32338 (7)	0.0420 (16)
H31	0.173715	0.875138	0.314635	0.0504*
C49	−0.0404 (5)	0.7915 (4)	0.30918 (7)	0.0458 (17)
H32	−0.034668	0.789746	0.290459	0.055*
C50	−0.1704 (5)	0.7437 (4)	0.32153 (7)	0.0444 (17)
H33	−0.253974	0.7066	0.311534	0.0533*
C51	−0.1806 (5)	0.7491 (3)	0.34856 (7)	0.0375 (16)
H34	−0.273306	0.718949	0.357244	0.0451*
C52	0.5784 (5)	1.0890 (4)	0.28160 (7)	0.0307 (15)
C53	0.6813 (5)	1.1589 (4)	0.26370 (7)	0.0332 (15)
C54	0.7792 (5)	1.1038 (4)	0.24614 (7)	0.0354 (17)
H35	0.843302	1.154969	0.234926	0.0424*
C55	0.7864 (4)	0.9765 (4)	0.24445 (7)	0.0359 (16)
C56	0.6964 (4)	0.8991 (4)	0.26019 (7)	0.0342 (15)
H36	0.700608	0.80915	0.258342	0.0411*
C57	0.6013 (4)	0.9541 (4)	0.27847 (7)	0.0299 (15)

O58	0.4836 (3)	1.1358 (2)	0.29746 (4)	0.0362 (9)
N59	0.6788 (4)	1.2958 (4)	0.26340 (6)	0.0442 (16)
O60	0.5793 (3)	1.3525 (2)	0.27646 (5)	0.0524 (11)
O61	0.7751 (3)	1.3524 (3)	0.25004 (5)	0.0641 (13)
N62	0.8880 (4)	0.9174 (4)	0.22507 (7)	0.0558 (16)
O63	0.9632 (4)	0.9864 (3)	0.21057 (5)	0.0797 (14)
O64	0.8937 (3)	0.8008 (3)	0.22376 (5)	0.0649 (13)
N65	0.5155 (4)	0.8671 (3)	0.29508 (6)	0.0368 (13)
O66	0.4882 (3)	0.7597 (3)	0.28651 (4)	0.0474 (10)
O67	0.4813 (3)	0.8977 (2)	0.31746 (5)	0.0444 (10)
C68	0.0373 (4)	0.3993 (4)	0.52921 (7)	0.0334 (15)
C69	0.0980 (4)	0.3221 (3)	0.50723 (7)	0.0528 (17)
H37	0.025861	0.254702	0.503659	0.0634*
H38	0.198687	0.287718	0.511846	0.0634*
H39	0.108779	0.373922	0.491967	0.0634*
C70	−0.1201 (4)	0.4574 (4)	0.52564 (7)	0.069 (2)
H40	−0.130183	0.48723	0.508013	0.0826*
H41	−0.200164	0.395803	0.529065	0.0826*
H42	−0.131761	0.52671	0.537522	0.0826*
O71	0.1143 (3)	0.4176 (2)	0.54866 (4)	0.0409 (9)
C15a	0.3259 (3)	0.6511 (3)	0.42482 (5)	0.0248 (10)
C16a	0.1794 (5)	0.6530 (4)	0.43568 (8)	0.0209 (9)
C17a	0.0956 (5)	0.5364 (4)	0.43687 (8)	0.0215 (9)
C18a	0.1660 (5)	0.4242 (4)	0.42779 (8)	0.0231 (10)
C19a	0.0801 (6)	0.3101 (4)	0.42842 (8)	0.0269 (10)
H11a	0.1277	0.2336	0.42228	0.0322*
C20a	−0.0698 (6)	0.3085 (4)	0.43771 (9)	0.0286 (10)
H12a	−0.1278	0.2309	0.43789	0.0343*
C21a	−0.1399 (5)	0.4181 (4)	0.44696 (8)	0.0287 (10)
H13a	−0.2452	0.4153	0.45369	0.0344*
C22a	−0.0602 (5)	0.5298 (4)	0.44654 (8)	0.0268 (10)
H14a	−0.1104	0.6047	0.45290	0.0321*
C23a	0.3987 (5)	0.5408 (4)	0.41606 (8)	0.0270 (10)
H15a	0.5036	0.5438	0.40915	0.0324*
C24a	0.3204 (6)	0.4292 (4)	0.41736 (8)	0.0271 (10)
H16a	0.3698	0.3536	0.41119	0.0325*
C15b	0.0516 (3)	0.8620 (3)	0.43089 (5)	0.0248 (11)
C16b	0.1091 (5)	0.7695 (4)	0.44672 (8)	0.0209 (10)
C17b	0.1053 (5)	0.7916 (4)	0.47426 (8)	0.0215 (10)
C18b	0.0396 (5)	0.9038 (4)	0.48427 (8)	0.0231 (10)
C19b	0.0405 (5)	0.9261 (4)	0.51154 (9)	0.0269 (11)
H11b	−0.0042	1.0022	0.51840	0.0322*
C20b	0.1047 (5)	0.8398 (4)	0.52804 (9)	0.0286 (11)
H12b	0.1060	0.8559	0.54649	0.0343*
C21b	0.1684 (5)	0.7283 (4)	0.51844 (9)	0.0287 (11)
H13b	0.2119	0.6677	0.53034	0.0344*
C22b	0.1696 (5)	0.7043 (4)	0.49224 (9)	0.0268 (11)
H14b	0.2145	0.6272	0.48592	0.0321*

C23b	−0.0161 (5)	0.9730 (4)	0.44039 (8)	0.0270 (11)
H15b	−0.0585	1.0339	0.42847	0.0324*
C24b	−0.0215 (5)	0.9942 (4)	0.46659 (8)	0.0271 (11)
H16b	−0.0670	1.0707	0.47313	0.0325*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.041 (2)	0.028 (2)	0.032 (2)	0.0049 (18)	−0.0024 (18)	−0.0063 (18)
C2	0.028 (2)	0.023 (3)	0.031 (2)	0.002 (2)	−0.009 (2)	0.006 (2)
C3	0.033 (3)	0.032 (3)	0.032 (2)	0.005 (2)	0.000 (2)	−0.004 (2)
C4	0.049 (3)	0.040 (3)	0.032 (3)	0.013 (2)	−0.004 (2)	−0.005 (2)
C5	0.049 (3)	0.029 (3)	0.039 (2)	0.004 (3)	−0.012 (2)	−0.003 (3)
C6	0.039 (3)	0.029 (3)	0.040 (3)	−0.004 (2)	−0.002 (2)	−0.004 (2)
C7	0.024 (2)	0.043 (3)	0.036 (2)	0.005 (2)	0.000 (2)	0.001 (2)
N8	0.026 (2)	0.036 (2)	0.0231 (19)	0.0045 (16)	0.0053 (15)	−0.0057 (16)
C9	0.025 (2)	0.026 (2)	0.027 (2)	−0.011 (2)	0.002 (2)	0.000 (2)
O10	0.0399 (16)	0.0430 (17)	0.0286 (14)	0.0077 (15)	0.0084 (13)	−0.0083 (14)
C11	0.030 (2)	0.022 (2)	0.019 (2)	−0.003 (2)	−0.0011 (18)	0.0032 (19)
N12	0.0325 (18)	0.023 (2)	0.0185 (16)	−0.0074 (17)	−0.0045 (15)	0.0029 (16)
C13	0.015 (2)	0.026 (3)	0.033 (2)	−0.001 (2)	0.002 (2)	0.004 (2)
O14	0.0300 (14)	0.0196 (14)	0.0223 (13)	−0.0077 (12)	0.0032 (11)	0.0036 (12)
C25	0.030 (2)	0.031 (2)	0.034 (2)	−0.003 (2)	−0.007 (2)	0.005 (2)
C26	0.019 (2)	0.032 (3)	0.030 (2)	−0.009 (2)	−0.0017 (18)	0.009 (2)
C27	0.039 (3)	0.028 (3)	0.051 (3)	−0.008 (2)	0.013 (2)	0.010 (3)
C28	0.053 (3)	0.040 (3)	0.089 (4)	−0.001 (3)	0.007 (3)	0.019 (3)
C29	0.038 (3)	0.060 (4)	0.067 (4)	−0.005 (3)	−0.003 (3)	0.035 (3)
C30	0.020 (2)	0.081 (4)	0.037 (3)	−0.013 (3)	−0.005 (2)	0.006 (3)
C31	0.025 (2)	0.044 (3)	0.039 (3)	−0.007 (2)	−0.004 (2)	0.006 (3)
O32	0.0446 (17)	0.0328 (16)	0.0207 (13)	−0.0119 (14)	−0.0040 (13)	−0.0044 (14)
O43	0.0301 (15)	0.0312 (16)	0.0274 (14)	−0.0045 (14)	−0.0067 (12)	−0.0016 (13)
C44	0.033 (3)	0.022 (3)	0.039 (3)	0.005 (2)	−0.002 (2)	−0.001 (2)
O45	0.0346 (16)	0.0524 (19)	0.0418 (15)	−0.0073 (16)	−0.0002 (14)	−0.0011 (15)
C46	0.033 (3)	0.027 (2)	0.032 (2)	0.006 (2)	−0.003 (2)	0.001 (2)
C47	0.031 (3)	0.043 (3)	0.036 (3)	0.002 (2)	−0.007 (2)	0.001 (2)
C48	0.034 (3)	0.061 (3)	0.031 (3)	0.005 (3)	−0.001 (2)	0.008 (2)
C49	0.052 (3)	0.057 (3)	0.029 (2)	0.023 (3)	−0.006 (3)	−0.008 (2)
C50	0.042 (3)	0.047 (3)	0.044 (3)	0.007 (3)	−0.016 (2)	−0.010 (2)
C51	0.038 (3)	0.036 (3)	0.038 (3)	0.004 (2)	−0.006 (2)	0.000 (2)
C52	0.033 (3)	0.037 (3)	0.023 (2)	0.001 (2)	−0.009 (2)	0.003 (2)
C53	0.043 (3)	0.029 (3)	0.028 (2)	0.005 (3)	−0.006 (2)	0.003 (2)
C54	0.038 (3)	0.041 (3)	0.027 (2)	0.001 (2)	−0.003 (2)	0.007 (2)
C55	0.035 (3)	0.053 (3)	0.020 (2)	0.014 (2)	0.008 (2)	−0.004 (2)
C56	0.039 (3)	0.042 (3)	0.022 (2)	0.006 (2)	−0.008 (2)	−0.007 (2)
C57	0.030 (2)	0.035 (3)	0.025 (2)	0.003 (2)	0.000 (2)	0.004 (2)
O58	0.0394 (16)	0.0388 (17)	0.0303 (14)	0.0044 (14)	0.0078 (13)	−0.0018 (13)
N59	0.044 (3)	0.061 (3)	0.028 (2)	−0.001 (2)	−0.001 (2)	0.000 (2)
O60	0.071 (2)	0.047 (2)	0.0388 (17)	0.0078 (19)	0.0080 (17)	0.0090 (15)

O61	0.056 (2)	0.064 (2)	0.073 (2)	−0.0160 (18)	0.0239 (18)	0.0065 (18)
N62	0.054 (3)	0.072 (3)	0.042 (3)	0.020 (3)	0.009 (2)	0.013 (3)
O63	0.081 (2)	0.095 (3)	0.063 (2)	0.028 (2)	0.0428 (19)	0.027 (2)
O64	0.064 (2)	0.076 (2)	0.0542 (19)	0.019 (2)	0.0184 (17)	−0.010 (2)
N65	0.034 (2)	0.042 (2)	0.035 (2)	0.0005 (19)	−0.0021 (18)	−0.005 (2)
O66	0.0566 (19)	0.0454 (19)	0.0402 (16)	−0.0083 (16)	−0.0009 (14)	−0.0101 (16)
O67	0.0567 (19)	0.0448 (18)	0.0317 (15)	0.0014 (15)	0.0130 (15)	−0.0084 (14)
C68	0.030 (3)	0.034 (3)	0.036 (2)	−0.001 (2)	−0.002 (2)	0.003 (2)
C69	0.052 (3)	0.046 (3)	0.060 (3)	0.013 (3)	−0.009 (2)	−0.018 (3)
C70	0.040 (3)	0.092 (4)	0.075 (3)	0.020 (3)	−0.014 (3)	−0.030 (3)
O71	0.0362 (16)	0.0541 (18)	0.0324 (15)	0.0070 (15)	−0.0060 (13)	−0.0062 (15)
C15a	0.0317 (18)	0.0246 (18)	0.0181 (15)	−0.0010 (15)	−0.0014 (13)	0.0017 (14)
C16a	0.0219 (16)	0.0226 (15)	0.0181 (14)	0.0018 (13)	−0.0014 (12)	−0.0009 (12)
C17a	0.0258 (17)	0.0206 (17)	0.0182 (15)	0.0008 (14)	−0.0001 (13)	−0.0014 (13)
C18a	0.0256 (17)	0.0206 (17)	0.0232 (15)	0.0033 (14)	0.0011 (13)	−0.0035 (13)
C19a	0.0370 (18)	0.0181 (17)	0.0254 (16)	0.0036 (14)	−0.0015 (14)	−0.0030 (13)
C20a	0.0319 (18)	0.0217 (18)	0.0320 (17)	−0.0031 (14)	−0.0021 (15)	0.0025 (14)
C21a	0.0262 (18)	0.0250 (17)	0.0348 (17)	0.0014 (15)	0.0027 (14)	−0.0006 (15)
C22a	0.0337 (18)	0.0221 (17)	0.0246 (16)	0.0059 (14)	0.0022 (14)	−0.0013 (13)
C23a	0.0216 (16)	0.0320 (18)	0.0275 (16)	0.0002 (15)	0.0038 (13)	−0.0115 (14)
C24a	0.0336 (18)	0.0261 (18)	0.0216 (16)	0.0078 (15)	−0.0009 (14)	−0.0098 (13)
C15b	0.0237 (19)	0.0249 (18)	0.026 (2)	−0.0060 (13)	0.0037 (13)	−0.0009 (13)
C16b	0.0188 (17)	0.0194 (16)	0.0245 (17)	−0.0014 (11)	−0.0002 (12)	−0.0006 (12)
C17b	0.0221 (17)	0.0189 (17)	0.0235 (18)	−0.0024 (12)	0.0017 (12)	−0.0019 (12)
C18b	0.0249 (18)	0.0184 (18)	0.0262 (19)	0.0015 (12)	0.0011 (13)	−0.0031 (13)
C19b	0.0279 (19)	0.0233 (18)	0.0294 (19)	−0.0008 (13)	0.0058 (13)	−0.0084 (13)
C20b	0.0291 (19)	0.0342 (19)	0.0224 (19)	−0.0001 (13)	0.0029 (14)	−0.0035 (14)
C21b	0.0314 (19)	0.0280 (19)	0.0266 (19)	0.0057 (13)	0.0003 (14)	−0.0005 (13)
C22b	0.0279 (19)	0.0208 (18)	0.0317 (19)	0.0011 (13)	0.0061 (13)	−0.0033 (13)
C23b	0.0342 (18)	0.0164 (18)	0.0305 (19)	0.0017 (13)	−0.0090 (13)	−0.0007 (13)
C24b	0.0276 (19)	0.0152 (18)	0.038 (2)	−0.0009 (13)	0.0000 (13)	−0.0075 (13)

Geometric parameters (Å, º)

N1—H1	0.870	C53—C54	1.357 (5)
N1—C2	1.354 (5)	C53—N59	1.454 (6)
N1—C6	1.336 (5)	C54—H35	0.960
C2—C3	1.373 (5)	C54—C55	1.356 (6)
C2—C7	1.510 (5)	C55—C56	1.382 (5)
C3—H2	0.960	C55—N62	1.458 (5)
C3—C4	1.370 (6)	C56—H36	0.960
C4—H3	0.960	C56—C57	1.368 (5)
C4—C5	1.378 (5)	C57—N65	1.452 (5)
C5—H4	0.960	N59—O60	1.235 (5)
C5—C6	1.370 (5)	N59—O61	1.224 (5)
C6—H5	0.960	N62—O63	1.223 (5)
C7—H6	0.960	N62—O64	1.241 (6)
C7—H7	0.960	N65—O66	1.243 (4)

C7—N8	1.442 (5)	N65—O67	1.226 (4)
N8—H8	0.870	C68—C69	1.485 (5)
N8—C9	1.349 (4)	C68—C70	1.485 (5)
C9—O10	1.218 (4)	C68—O71	1.207 (4)
C9—C11	1.529 (5)	C69—H37	0.960
C11—H9	0.960	C69—H38	0.960
C11—N12	1.445 (4)	C69—H39	0.960
C11—C25	1.527 (5)	C70—H40	0.960
N12—H10	0.870	C70—H41	0.960
N12—C13	1.342 (4)	C70—H42	0.960
C13—O14	1.389 (4)	C15a—C16a	1.364 (5)
C13—O32	1.199 (4)	C15a—C23a	1.399 (5)
O14—C15a	1.402 (3)	C16a—C17a	1.430 (6)
C25—H17	0.960	C16a—C16b	1.485 (6)
C25—H18	0.960	C17a—C18a	1.412 (6)
C25—C26	1.503 (5)	C17a—C22a	1.416 (6)
C26—C27	1.368 (6)	C18a—C19a	1.416 (6)
C26—C31	1.384 (5)	C18a—C24a	1.418 (7)
C27—H19	0.960	C19a—H11a	0.960
C27—C28	1.380 (6)	C19a—C20a	1.360 (7)
C28—H20	0.960	C20a—H12a	0.960
C28—C29	1.361 (7)	C20a—C21a	1.391 (7)
C29—H21	0.960	C21a—H13a	0.960
C29—C30	1.374 (7)	C21a—C22a	1.365 (7)
C30—H22	0.960	C22a—H14a	0.960
C30—C31	1.395 (6)	C23a—H15a	0.960
C31—H23	0.960	C23a—C24a	1.361 (6)
O43—C44	1.361 (5)	C24a—H16a	0.960
O43—C15b	1.410 (3)	C15b—C16b	1.364 (5)
C44—O45	1.189 (5)	C15b—C23b	1.399 (5)
C44—C46	1.495 (5)	C16b—C17b	1.430 (6)
C46—C47	1.375 (5)	C17b—C18b	1.412 (6)
C46—C51	1.375 (5)	C17b—C22b	1.416 (6)
C47—H30	0.960	C18b—C19b	1.416 (6)
C47—C48	1.393 (5)	C18b—C24b	1.418 (6)
C48—H31	0.960	C19b—H11b	0.960
C48—C49	1.383 (6)	C19b—C20b	1.360 (7)
C49—H32	0.960	C20b—H12b	0.960
C49—C50	1.371 (6)	C20b—C21b	1.391 (7)
C50—H33	0.960	C21b—H13b	0.960
C50—C51	1.387 (5)	C21b—C22b	1.365 (6)
C51—H34	0.960	C22b—H14b	0.960
C52—C53	1.468 (5)	C23b—H15b	0.960
C52—C57	1.454 (6)	C23b—C24b	1.361 (6)
C52—O58	1.248 (4)	C24b—H16b	0.960
H1—N1—C2	118.7	C53—C54—C55	119.9 (4)
H1—N1—C6	118.7	H35—C54—C55	120.0

C2—N1—C6	122.5 (3)	C54—C55—C56	122.1 (4)
N1—C2—C3	118.6 (3)	C54—C55—N62	120.0 (4)
N1—C2—C7	117.7 (3)	C56—C55—N62	117.9 (4)
C3—C2—C7	123.8 (3)	C55—C56—H36	120.9
C2—C3—H2	120.1	C55—C56—C57	118.1 (4)
C2—C3—C4	119.8 (3)	H36—C56—C57	120.9
H2—C3—C4	120.1	C52—C57—C56	125.1 (3)
C3—C4—H3	119.9	C52—C57—N65	119.7 (3)
C3—C4—C5	120.3 (4)	C56—C57—N65	115.2 (3)
H3—C4—C5	119.9	C53—N59—O60	119.5 (3)
C4—C5—H4	120.5	C53—N59—O61	119.2 (3)
C4—C5—C6	118.9 (4)	O60—N59—O61	121.3 (4)
H4—C5—C6	120.5	C55—N62—O63	117.7 (4)
N1—C6—C5	119.9 (3)	C55—N62—O64	119.3 (4)
N1—C6—H5	120.1	O63—N62—O64	123.0 (4)
C5—C6—H5	120.1	C57—N65—O66	118.1 (3)
C2—C7—H6	109.5	C57—N65—O67	119.8 (3)
C2—C7—H7	109.5	O66—N65—O67	121.9 (3)
C2—C7—N8	113.3 (3)	C69—C68—C70	116.7 (3)
H6—C7—H7	105.3	C69—C68—O71	121.7 (3)
H6—C7—N8	109.5	C70—C68—O71	121.6 (3)
H7—C7—N8	109.5	C68—C69—H37	109.5
C7—N8—H8	119.3	C68—C69—H38	109.5
C7—N8—C9	121.3 (3)	C68—C69—H39	109.5
H8—N8—C9	119.3	H37—C69—H38	109.5
N8—C9—O10	123.4 (3)	H37—C69—H39	109.5
N8—C9—C11	114.5 (3)	H38—C69—H39	109.5
O10—C9—C11	122.2 (3)	C68—C70—H40	109.5
C9—C11—H9	108.4	C68—C70—H41	109.5
C9—C11—N12	109.3 (3)	C68—C70—H42	109.5
C9—C11—C25	110.7 (3)	H40—C70—H41	109.5
H9—C11—N12	110.8	H40—C70—H42	109.5
H9—C11—C25	109.3	H41—C70—H42	109.5
N12—C11—C25	108.4 (2)	O14—C15a—C16a	116.4 (3)
C11—N12—H10	119.2	O14—C15a—C23a	120.3 (3)
C11—N12—C13	121.6 (3)	C16a—C15a—C23a	123.2 (3)
H10—N12—C13	119.2	C15a—C16a—C17a	117.4 (4)
N12—C13—O14	108.9 (3)	C15a—C16a—C16b	122.3 (4)
N12—C13—O32	127.1 (3)	C17a—C16a—C16b	120.3 (4)
O14—C13—O32	123.9 (3)	C16a—C17a—C18a	120.3 (4)
C13—O14—C15a	116.6 (2)	C16a—C17a—C22a	121.6 (4)
C11—C25—H17	109.5	C18a—C17a—C22a	118.0 (4)
C11—C25—H18	109.5	C17a—C18a—C19a	119.7 (4)
C11—C25—C26	116.0 (3)	C17a—C18a—C24a	119.0 (4)
H17—C25—H18	102.1	C19a—C18a—C24a	121.2 (4)
H17—C25—C26	109.5	C18a—C19a—H11a	119.9
H18—C25—C26	109.5	C18a—C19a—C20a	120.2 (4)
C25—C26—C27	119.6 (3)	H11a—C19a—C20a	119.9

C25—C26—C31	120.8 (3)	C19a—C20a—H12a	119.7
C27—C26—C31	119.7 (4)	C19a—C20a—C21a	120.6 (4)
C26—C27—H19	119.7	H12a—C20a—C21a	119.7
C26—C27—C28	120.7 (4)	C20a—C21a—H13a	119.7
H19—C27—C28	119.7	C20a—C21a—C22a	120.6 (4)
C27—C28—H20	119.9	H13a—C21a—C22a	119.7
C27—C28—C29	120.2 (4)	C17a—C22a—C21a	120.9 (4)
H20—C28—C29	119.9	C17a—C22a—H14a	119.6
C28—C29—H21	119.9	C21a—C22a—H14a	119.6
C28—C29—C30	120.2 (4)	C15a—C23a—H15a	120.1
H21—C29—C30	119.9	C15a—C23a—C24a	119.8 (4)
C29—C30—H22	120.0	H15a—C23a—C24a	120.1
C29—C30—C31	120.0 (4)	C18a—C24a—C23a	120.3 (4)
H22—C30—C31	120.0	C18a—C24a—H16a	119.9
C26—C31—C30	119.3 (4)	C23a—C24a—H16a	119.9
C26—C31—H23	120.3	O43—C15b—C16b	119.8 (3)
C30—C31—H23	120.3	O43—C15b—C23b	117.0 (3)
C44—O43—C15b	117.3 (2)	C16b—C15b—C23b	123.2 (3)
O43—C44—O45	123.5 (3)	C16a—C16b—C15b	121.2 (3)
O43—C44—C46	110.8 (3)	C16a—C16b—C17b	121.4 (4)
O45—C44—C46	125.7 (4)	C15b—C16b—C17b	117.4 (4)
C44—C46—C47	122.4 (3)	C16b—C17b—C18b	120.3 (4)
C44—C46—C51	117.4 (3)	C16b—C17b—C22b	121.6 (4)
C47—C46—C51	120.2 (3)	C18b—C17b—C22b	118.0 (4)
C46—C47—H30	119.9	C17b—C18b—C19b	119.7 (4)
C46—C47—C48	120.1 (3)	C17b—C18b—C24b	119.0 (4)
H30—C47—C48	119.9	C19b—C18b—C24b	121.2 (4)
C47—C48—H31	120.5	C18b—C19b—H11b	119.9
C47—C48—C49	119.1 (4)	C18b—C19b—C20b	120.2 (4)
H31—C48—C49	120.4	H11b—C19b—C20b	119.9
C48—C49—H32	119.6	C19b—C20b—H12b	119.7
C48—C49—C50	120.8 (4)	C19b—C20b—C21b	120.6 (4)
H32—C49—C50	119.6	H12b—C20b—C21b	119.7
C49—C50—H33	120.2	C20b—C21b—H13b	119.7
C49—C50—C51	119.6 (4)	C20b—C21b—C22b	120.6 (4)
H33—C50—C51	120.2	H13b—C21b—C22b	119.7
C46—C51—C50	120.1 (4)	C17b—C22b—C21b	120.9 (4)
C46—C51—H34	120.0	C17b—C22b—H14b	119.6
C50—C51—H34	120.0	C21b—C22b—H14b	119.6
C53—C52—C57	110.5 (3)	C15b—C23b—H15b	120.1
C53—C52—O58	126.1 (4)	C15b—C23b—C24b	119.8 (4)
C57—C52—O58	123.4 (3)	H15b—C23b—C24b	120.1
C52—C53—C54	124.1 (4)	C18b—C24b—C23b	120.3 (4)
C52—C53—N59	120.2 (3)	C18b—C24b—H16b	119.9
C54—C53—N59	115.6 (3)	C23b—C24b—H16b	119.9
C53—C54—H35	120.0		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O58	0.87	1.98	2.800 (4)	159
N8—H8···O67	0.87	2.09	2.873 (4)	149
N12—H10···O71^{i}	0.87	2.27	3.106 (4)	160

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