Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

A sterically constrained bis(2,2′:6′,2″-terpyridine) ligand

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Key indicators

Single-crystal synchrotron study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.051
wR factor = 0.138
Data-to-parameter ratio = 14.0

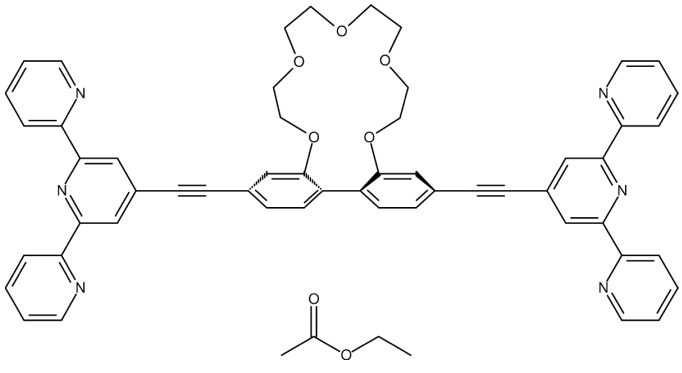
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 22 November 2004
Accepted 23 November 2004
Online 27 November 2004

The title compound, 4,4′-bis[(2,2′:6′,2″-terpyridin-4-yl)ethynyl]-2,2′-(3,6,9-trioxaundecane-1,11-diyldioxy)-1,1′-biphenyl-ethyl acetate solvate, $C_{54}H_{42}N_6O_5\cdot C_4H_8O_2$, is a sterically constrained ligand based on the well-known chelator 2,2′:6′,2″-terpyridine (terpy). Two terpy units are linked by ethynyl bridges to a central 2,2′-biphenyl unit, in which the two rings are connected by a polyether strand. The torsion angle between the two rings of the biphenyl unit is 113.25 (17)°. The crown ether ring is flexible and capable of complexing metal cations, and the two terpy units may be reorganized from their observed *trans-trans* configuration to act as terdentate ligands for transition metal ions.

Comment

Crystal structures have been reported of the terdentate ligand 2,2′:6′,2″-terpyridine (terpy) and its complexes (Constable, 1986); the Cambridge Structural Database (Version 5.25; Allen, 2002) contains 13 entries with uncomplexed and unsubstituted terpy and over 600 of its metal complexes. Linking together two terpy ligands *via* a bridging unit leads to the possibility of producing dinuclear and bimetallic complexes (Sauvage *et al.*, 1994). When the bridge is or contains a 2,2′-biphenyl unit, there exists the opportunity to control the torsion angle between the two rings if they are further connected (Lindsten *et al.*, 1987). The title compound, (I), represents such a constrained derivative, in which the two benzene rings of biphenyl are coupled *via* a pentaoxa cyclic polyether linker, itself capable of acting as a multidentate ligand to provide a third coordination site. In order to find the torsion angle of the biphenyl unit, crystals were grown and the molecular structure obtained crystallographically.



(I)

The molecular structure of (I), as an ethyl acetate solvate, is illustrated in Fig. 1. The N atoms of the terpy segments adopt the sterically preferred *trans–trans* arrangement generally

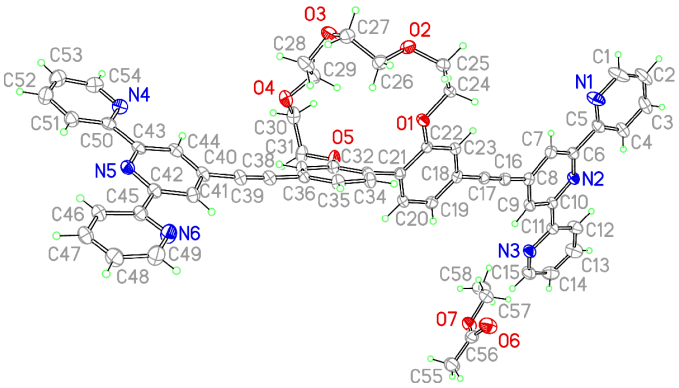


Figure 1
The molecular structure of the asymmetric unit of (I), showing atom labels and 50% probability ellipsoids for non-H atoms. Unlabelled atoms C32 and C37 are obscured by other atoms.

found when terpy is uncoordinated. The length of the C—C bond joining the benzene rings of the biphenyl unit is 1.490 (2) Å, similar to that found in 2,2′-biphenol monohydrate [1.491 (3) Å; Chen *et al.*, 1996]. The spanning polyether chain is sufficiently long and flexible to allow the biphenyl unit to adopt a twisted configuration with almost perpendicular rings. The torsion angle C22—C21—C33—C32 is 113.25 (17)°. There is only one previously reported example of a biphenyl unit with rings linked by such a pentaoxa polyether strand in this way (Costero *et al.*, 1996); it has two polyether strands, one of them uncomplexed and the other binding a mercury(II) ion, thus demonstrating the capability of this crown ether ring to serve as a ligand. The two polyether strands have very different conformations: the complexed one is *gauche* for all O—C—C—O linkages and *anti* for each C—O—C—C segment, in order to bring the O atoms into an essentially coplanar arrangement for coordination, but the uncomplexed one has a wide range of torsion angles, not all of which approximate to *gauche* or *anti*. A similarly unsystematic sequence of torsion angles is found in the title compound (Table 1), reflecting the flexibility of the uncomplexed polyether strand. The torsion angle for the biphenyl unit is similar in the two compounds (110.4° for the mercury complex).

All bond lengths and angles are normal. The skeleton of the molecule, comprising the central rings of the terpy units, the ethynyl bridges and the biphenyl unit, is close to linear, with little bending induced by steric or crystal packing interactions. There are no significant intermolecular interactions, and it is surprising that the ethyl acetate is retained in the crystal structure during recrystallization from a different solvent.

Experimental

The title compound was synthesized by a literature procedure (Benniston *et al.*, 2003). ^{1}H NMR spectroscopy indicated that it was an ethyl acetate solvate. Crystals suitable for X-ray diffraction were grown by slow vapour diffusion of diethyl ether into a chloroform solution; the ethyl acetate is retained in the crystal structure during this process.

Crystal data

$C_{54}H_{42}N_6O_5\cdot C_4H_8O_2$
M_r = 943.04
Monoclinic, $P2_1/c$
a = 8.5942 (12) Å
b = 42.288 (6) Å
c = 13.8795 (19) Å
β = 101.839 (3)°
V = 4936.9 (12) Å^3
Z = 4
D_x = 1.269 Mg m^{-3}
Synchrotron radiation
λ = 0.6948 Å
Cell parameters from 10 431 reflections
θ = 2.5–29.2°
μ = 0.09 mm^{-1}
T = 120 (2) K
Block, colourless
0.10 × 0.05 × 0.02 mm

Data collection

Bruker SMART 1K CCD diffractometer
Thin-slice ω scans
Absorption correction: none
18651 measured reflections
8957 independent reflections
7604 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 25.0°
$h = -10 \rightarrow 10$
$k = -50 \rightarrow 45$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.138
S = 1.02
8957 reflections
642 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 1.7718P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected torsion angles (°).

N1—C5—C6—N2	172.56 (16)	C30—O4—C29—C28	−169.44 (15)
N2—C10—C11—N3	−174.29 (15)	O3—C28—C29—O4	−168.47 (15)
C24—O1—C22—C21	−176.50 (13)	C29—O4—C30—C31	107.96 (17)
C33—C21—C22—O1	1.5 (2)	C32—O5—C31—C30	94.08 (18)
C22—O1—C24—C25	−174.97 (13)	O4—C30—C31—O5	−64.32 (18)
C26—O2—C25—C24	101.55 (16)	C31—O5—C32—C33	179.55 (14)
O1—C24—C25—O2	−62.82 (17)	O5—C32—C33—C21	−4.4 (2)
C25—O2—C26—C27	168.42 (14)	C20—C21—C33—C34	109.81 (18)
C28—O3—C27—C26	79.72 (19)	C22—C21—C33—C32	113.25 (17)
O2—C26—C27—O3	66.46 (18)	N5—C42—C45—N6	−172.13 (15)
C27—O3—C28—C29	−136.94 (17)	N5—C43—C50—N4	−177.06 (13)

H atoms were positioned geometrically, with C—H = 0.95–0.99 Å, and refined with a riding model (including free rotation about C—C bonds), with $U_{iso} = 1.2U_{eq}$(C) ($1.5U_{eq}$ for methyl groups).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

We thank the EPSRC for financial support, including the national X-ray crystallography service synchrotron component, and the CCLRC for SRS beamtime allocation and financial support.

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supporting information

Acta Cryst. (2004). E**60**, o2452–o2454 [https://doi.org/10.1107/S1600536804030594]

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Radiation source: Daresbury SRS station 9.8
Silicon 111 monochromator
Detector resolution: 8.192 pixels mm^{-1}
thin–slice ω scans
18651 measured reflections
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R_{int} = 0.044
θ_{max} = 25.0°, θ_{min} = 1.7°
h = −10→10
k = −50→45
l = −16→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.138
S = 1.02
8957 reflections
642 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 1.7718P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

	x	y	z	U_{iso}*/U_{eq}
O1	0.27488 (13)	0.51726 (3)	0.57718 (7)	0.0234 (3)
O2	−0.00657 (13)	0.55587 (3)	0.52087 (8)	0.0281 (3)
O3	−0.16164 (15)	0.55721 (4)	0.68835 (9)	0.0393 (3)

O4	−0.01811 (15)	0.50171 (3)	0.88282 (8)	0.0325 (3)
O5	0.28158 (15)	0.47477 (3)	0.84784 (9)	0.0314 (3)
N1	0.2366 (2)	0.36340 (4)	0.10106 (12)	0.0420 (4)
N2	0.52799 (16)	0.31576 (3)	0.26163 (9)	0.0234 (3)
N3	0.78846 (17)	0.28615 (4)	0.48003 (10)	0.0289 (3)
N4	−0.06015 (16)	0.60372 (3)	1.25970 (10)	0.0271 (3)
N5	0.27350 (15)	0.65750 (3)	1.28664 (9)	0.0222 (3)
N6	0.62846 (18)	0.69696 (4)	1.25005 (11)	0.0340 (4)
C1	0.1557 (3)	0.36270 (6)	0.00742 (17)	0.0538 (6)
H1	0.0803	0.3790	−0.0135	0.065*
C2	0.1743 (3)	0.34003 (6)	−0.06029 (14)	0.0474 (6)
H2	0.1122	0.3406	−0.1253	0.057*
C3	0.2848 (3)	0.31651 (5)	−0.03177 (13)	0.0408 (5)
H3	0.3016	0.3006	−0.0769	0.049*
C4	0.3709 (2)	0.31656 (5)	0.06413 (12)	0.0329 (4)
H4	0.4482	0.3006	0.0859	0.039*
C5	0.3432 (2)	0.34007 (4)	0.12786 (12)	0.0272 (4)
C6	0.43506 (19)	0.34102 (4)	0.23153 (11)	0.0230 (3)
C7	0.42452 (19)	0.36696 (4)	0.29139 (12)	0.0243 (3)
H7	0.3548	0.3840	0.2683	0.029*
C8	0.51861 (19)	0.36741 (4)	0.38617 (11)	0.0230 (3)
C9	0.61632 (19)	0.34133 (4)	0.41795 (11)	0.0236 (3)
H9	0.6818	0.3410	0.4820	0.028*
C10	0.61561 (19)	0.31601 (4)	0.35382 (11)	0.0225 (3)
C11	0.71243 (19)	0.28694 (4)	0.38529 (12)	0.0241 (3)
C12	0.7210 (2)	0.26229 (4)	0.32026 (13)	0.0343 (4)
H12	0.6662	0.2636	0.2536	0.041*
C13	0.8108 (2)	0.23569 (5)	0.35421 (15)	0.0404 (5)
H13	0.8200	0.2187	0.3110	0.049*
C14	0.8863 (2)	0.23449 (5)	0.45219 (15)	0.0388 (5)
H14	0.9470	0.2165	0.4780	0.047*
C15	0.8715 (2)	0.26006 (5)	0.51187 (13)	0.0351 (4)
H15	0.9231	0.2590	0.5792	0.042*
C16	0.51191 (19)	0.39386 (4)	0.44942 (11)	0.0236 (3)
C17	0.49961 (18)	0.41621 (4)	0.50109 (11)	0.0225 (3)
C18	0.48216 (18)	0.44111 (4)	0.56757 (11)	0.0210 (3)
C19	0.56154 (19)	0.43888 (4)	0.66585 (11)	0.0234 (3)
H19	0.6301	0.4215	0.6872	0.028*
C20	0.53950 (19)	0.46217 (4)	0.73192 (11)	0.0233 (3)
H20	0.5914	0.4603	0.7990	0.028*
C21	0.44292 (18)	0.48833 (4)	0.70224 (11)	0.0202 (3)
C22	0.36603 (17)	0.49085 (4)	0.60261 (11)	0.0187 (3)
C23	0.38407 (18)	0.46719 (4)	0.53594 (11)	0.0203 (3)
H23	0.3300	0.4687	0.4691	0.024*
C24	0.18832 (18)	0.51918 (4)	0.47670 (11)	0.0216 (3)
H24A	0.1078	0.5021	0.4634	0.026*
H24B	0.2621	0.5166	0.4310	0.026*
C25	0.10797 (19)	0.55107 (4)	0.46138 (12)	0.0272 (4)

H25A	0.1899	0.5678	0.4763	0.033*
H25B	0.0550	0.5532	0.3913	0.033*
C26	0.0485 (2)	0.57509 (4)	0.60520 (13)	0.0302 (4)
H26A	0.0994	0.5945	0.5862	0.036*
H26B	0.1278	0.5634	0.6541	0.036*
C27	−0.0927 (2)	0.58370 (4)	0.64884 (13)	0.0320 (4)
H27A	−0.0591	0.5995	0.7018	0.038*
H27B	−0.1746	0.5937	0.5973	0.038*
C28	−0.0792 (2)	0.54747 (5)	0.78371 (13)	0.0382 (5)
H28A	−0.1367	0.5548	0.8345	0.046*
H28B	0.0291	0.5566	0.7984	0.046*
C29	−0.0707 (2)	0.51205 (5)	0.78374 (12)	0.0350 (4)
H29A	−0.1767	0.5030	0.7559	0.042*
H29B	0.0046	0.5049	0.7430	0.042*
C30	0.0224 (2)	0.46894 (4)	0.89174 (13)	0.0324 (4)
H30A	−0.0177	0.4583	0.8279	0.039*
H30B	−0.0308	0.4591	0.9412	0.039*
C31	0.1991 (2)	0.46366 (4)	0.92187 (12)	0.0298 (4)
H31A	0.2402	0.4749	0.9845	0.036*
H31B	0.2202	0.4408	0.9332	0.036*
C32	0.34471 (18)	0.50465 (4)	0.85354 (11)	0.0216 (3)
C33	0.42352 (18)	0.51255 (4)	0.77687 (10)	0.0202 (3)
C34	0.4902 (2)	0.54265 (4)	0.77645 (11)	0.0252 (4)
H34	0.5410	0.5484	0.7243	0.030*
C35	0.4839 (2)	0.56448 (4)	0.85050 (12)	0.0265 (4)
H35	0.5320	0.5847	0.8497	0.032*
C36	0.40595 (18)	0.55632 (4)	0.92620 (11)	0.0219 (3)
C37	0.33597 (19)	0.52643 (4)	0.92695 (11)	0.0243 (3)
H37	0.2822	0.5211	0.9780	0.029*
C38	0.39373 (19)	0.57844 (4)	1.00253 (11)	0.0245 (3)
C39	0.37745 (19)	0.59719 (4)	1.06471 (11)	0.0243 (3)
C40	0.34330 (19)	0.61840 (4)	1.13856 (11)	0.0233 (3)
C41	0.4448 (2)	0.64340 (4)	1.17605 (11)	0.0244 (3)
H41	0.5386	0.6474	1.1519	0.029*
C42	0.40455 (19)	0.66227 (4)	1.24966 (11)	0.0235 (3)
C43	0.17591 (18)	0.63344 (4)	1.25009 (11)	0.0217 (3)
C44	0.20599 (19)	0.61379 (4)	1.17559 (11)	0.0227 (3)
H44	0.1336	0.5974	1.1502	0.027*
C45	0.50778 (19)	0.68924 (4)	1.29346 (11)	0.0245 (3)
C46	0.4774 (2)	0.70510 (4)	1.37563 (11)	0.0261 (4)
H46	0.3910	0.6990	1.4047	0.031*
C47	0.5757 (2)	0.73000 (4)	1.41407 (12)	0.0298 (4)
H47	0.5577	0.7413	1.4700	0.036*
C48	0.7003 (2)	0.73824 (5)	1.37002 (13)	0.0346 (4)
H48	0.7696	0.7552	1.3949	0.042*
C49	0.7215 (2)	0.72114 (5)	1.28859 (14)	0.0380 (4)
H49	0.8070	0.7269	1.2583	0.046*
C50	0.03286 (18)	0.62883 (4)	1.29380 (11)	0.0228 (3)

C51	−0.0023 (2)	0.64949 (4)	1.36399 (12)	0.0294 (4)
H51	0.0659	0.6668	1.3869	0.035*
C52	−0.1392 (2)	0.64436 (5)	1.39999 (14)	0.0359 (4)
H52	−0.1666	0.6582	1.4477	0.043*
C53	−0.2357 (2)	0.61878 (5)	1.36572 (14)	0.0355 (4)
H53	−0.3302	0.6148	1.3892	0.043*
C54	−0.1907 (2)	0.59919 (4)	1.29638 (13)	0.0319 (4)
H54	−0.2562	0.5815	1.2735	0.038*
O6	1.04323 (18)	0.21796 (4)	0.70163 (11)	0.0525 (4)
O7	0.98098 (16)	0.17093 (3)	0.75570 (9)	0.0384 (3)
C55	1.1747 (2)	0.20079 (6)	0.86174 (15)	0.0451 (5)
H55A	1.1174	0.2084	0.9115	0.068*
H55B	1.2594	0.2158	0.8562	0.068*
H55C	1.2212	0.1800	0.8813	0.068*
C56	1.0621 (2)	0.19809 (5)	0.76476 (14)	0.0352 (4)
C57	0.8620 (2)	0.16738 (5)	0.66538 (14)	0.0419 (5)
H57A	0.9117	0.1696	0.6074	0.050*
H57B	0.7787	0.1838	0.6615	0.050*
C58	0.7911 (3)	0.13503 (6)	0.66754 (18)	0.0531 (6)
H58A	0.7605	0.1317	0.7310	0.080*
H58B	0.8696	0.1191	0.6587	0.080*
H58C	0.6971	0.1332	0.6143	0.080*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0281 (6)	0.0222 (6)	0.0180 (5)	0.0065 (5)	0.0002 (4)	−0.0015 (4)
O2	0.0216 (6)	0.0285 (7)	0.0333 (6)	0.0013 (5)	0.0038 (4)	−0.0059 (5)
O3	0.0313 (7)	0.0561 (9)	0.0279 (6)	−0.0098 (6)	−0.0003 (5)	0.0082 (6)
O4	0.0428 (7)	0.0318 (7)	0.0228 (6)	−0.0013 (5)	0.0060 (5)	−0.0037 (5)
O5	0.0455 (7)	0.0223 (7)	0.0323 (6)	−0.0105 (5)	0.0217 (5)	−0.0071 (5)
N1	0.0435 (9)	0.0388 (10)	0.0366 (9)	0.0080 (7)	−0.0087 (7)	0.0043 (7)
N2	0.0287 (7)	0.0206 (7)	0.0202 (6)	0.0013 (5)	0.0030 (5)	0.0001 (5)
N3	0.0322 (8)	0.0302 (9)	0.0232 (7)	0.0076 (6)	0.0034 (6)	0.0019 (6)
N4	0.0280 (7)	0.0231 (8)	0.0296 (7)	−0.0025 (6)	0.0042 (6)	0.0014 (6)
N5	0.0243 (7)	0.0207 (7)	0.0207 (6)	−0.0004 (5)	0.0023 (5)	−0.0012 (5)
N6	0.0343 (8)	0.0329 (9)	0.0373 (8)	−0.0104 (7)	0.0134 (6)	−0.0119 (7)
C1	0.0547 (13)	0.0493 (14)	0.0450 (12)	0.0066 (11)	−0.0185 (10)	0.0135 (10)
C2	0.0550 (13)	0.0544 (14)	0.0246 (9)	−0.0128 (10)	−0.0110 (8)	0.0120 (9)
C3	0.0547 (12)	0.0447 (13)	0.0207 (9)	−0.0139 (10)	0.0025 (8)	0.0012 (8)
C4	0.0420 (10)	0.0325 (11)	0.0222 (8)	−0.0018 (8)	0.0017 (7)	0.0009 (7)
C5	0.0303 (9)	0.0261 (9)	0.0235 (8)	−0.0037 (7)	0.0011 (6)	0.0052 (7)
C6	0.0250 (8)	0.0220 (9)	0.0219 (8)	0.0006 (6)	0.0043 (6)	0.0029 (6)
C7	0.0273 (8)	0.0204 (9)	0.0261 (8)	0.0037 (6)	0.0077 (6)	0.0035 (6)
C8	0.0256 (8)	0.0218 (9)	0.0230 (8)	−0.0004 (6)	0.0081 (6)	−0.0011 (6)
C9	0.0270 (8)	0.0235 (9)	0.0198 (7)	0.0005 (6)	0.0034 (6)	−0.0019 (6)
C10	0.0258 (8)	0.0215 (9)	0.0202 (7)	0.0010 (6)	0.0045 (6)	0.0004 (6)
C11	0.0264 (8)	0.0211 (9)	0.0244 (8)	0.0012 (6)	0.0041 (6)	−0.0007 (6)

C12	0.0381 (10)	0.0277 (10)	0.0327 (9)	0.0053 (8)	−0.0030 (7)	−0.0057 (7)
C13	0.0466 (11)	0.0226 (10)	0.0477 (11)	0.0068 (8)	−0.0007 (9)	−0.0080 (8)
C14	0.0374 (10)	0.0268 (10)	0.0488 (11)	0.0079 (8)	0.0009 (8)	0.0068 (8)
C15	0.0372 (10)	0.0365 (11)	0.0297 (9)	0.0105 (8)	0.0020 (7)	0.0063 (8)
C16	0.0259 (8)	0.0223 (9)	0.0234 (8)	0.0023 (6)	0.0065 (6)	0.0009 (6)
C17	0.0228 (8)	0.0232 (9)	0.0227 (8)	0.0013 (6)	0.0072 (6)	0.0028 (6)
C18	0.0225 (8)	0.0194 (8)	0.0230 (8)	−0.0010 (6)	0.0090 (6)	−0.0020 (6)
C19	0.0251 (8)	0.0213 (9)	0.0243 (8)	0.0044 (6)	0.0059 (6)	0.0037 (6)
C20	0.0262 (8)	0.0267 (9)	0.0166 (7)	0.0008 (7)	0.0036 (6)	0.0025 (6)
C21	0.0207 (7)	0.0206 (8)	0.0198 (7)	−0.0022 (6)	0.0053 (6)	−0.0009 (6)
C22	0.0187 (7)	0.0181 (8)	0.0198 (7)	0.0009 (6)	0.0050 (5)	0.0015 (6)
C23	0.0222 (8)	0.0211 (8)	0.0176 (7)	−0.0003 (6)	0.0042 (6)	−0.0003 (6)
C24	0.0216 (8)	0.0253 (9)	0.0170 (7)	0.0019 (6)	0.0014 (6)	0.0004 (6)
C25	0.0269 (8)	0.0292 (10)	0.0247 (8)	0.0060 (7)	0.0036 (6)	0.0024 (7)
C26	0.0250 (8)	0.0305 (10)	0.0343 (9)	−0.0025 (7)	0.0045 (7)	−0.0060 (7)
C27	0.0304 (9)	0.0326 (10)	0.0324 (9)	0.0049 (7)	0.0052 (7)	0.0003 (7)
C28	0.0405 (10)	0.0442 (12)	0.0256 (9)	−0.0066 (9)	−0.0035 (7)	0.0005 (8)
C29	0.0354 (10)	0.0446 (12)	0.0236 (8)	−0.0048 (8)	0.0028 (7)	−0.0030 (8)
C30	0.0410 (10)	0.0283 (10)	0.0307 (9)	−0.0102 (8)	0.0139 (7)	−0.0048 (7)
C31	0.0427 (10)	0.0221 (9)	0.0294 (9)	−0.0059 (7)	0.0182 (7)	−0.0006 (7)
C32	0.0228 (8)	0.0201 (8)	0.0217 (7)	−0.0019 (6)	0.0045 (6)	−0.0011 (6)
C33	0.0219 (8)	0.0216 (9)	0.0160 (7)	0.0020 (6)	0.0013 (5)	0.0000 (6)
C34	0.0325 (9)	0.0242 (9)	0.0204 (8)	−0.0019 (7)	0.0090 (6)	0.0014 (6)
C35	0.0341 (9)	0.0218 (9)	0.0240 (8)	−0.0040 (7)	0.0072 (6)	−0.0012 (6)
C36	0.0247 (8)	0.0226 (9)	0.0171 (7)	0.0000 (6)	0.0014 (6)	−0.0016 (6)
C37	0.0295 (8)	0.0254 (9)	0.0192 (7)	−0.0017 (7)	0.0077 (6)	−0.0007 (6)
C38	0.0282 (8)	0.0239 (9)	0.0209 (8)	−0.0026 (7)	0.0035 (6)	0.0001 (6)
C39	0.0311 (9)	0.0219 (9)	0.0196 (7)	−0.0028 (7)	0.0046 (6)	−0.0003 (6)
C40	0.0314 (9)	0.0199 (9)	0.0168 (7)	0.0002 (6)	0.0011 (6)	0.0007 (6)
C41	0.0289 (8)	0.0223 (9)	0.0223 (8)	−0.0020 (7)	0.0061 (6)	−0.0017 (6)
C42	0.0273 (8)	0.0208 (9)	0.0216 (7)	−0.0014 (6)	0.0029 (6)	−0.0002 (6)
C43	0.0248 (8)	0.0193 (8)	0.0185 (7)	0.0012 (6)	−0.0016 (6)	0.0028 (6)
C44	0.0268 (8)	0.0194 (8)	0.0192 (7)	−0.0013 (6)	−0.0019 (6)	−0.0002 (6)
C45	0.0273 (8)	0.0221 (9)	0.0237 (8)	−0.0012 (7)	0.0040 (6)	−0.0024 (6)
C46	0.0313 (9)	0.0240 (9)	0.0222 (8)	−0.0017 (7)	0.0037 (6)	−0.0011 (6)
C47	0.0360 (9)	0.0269 (10)	0.0253 (8)	−0.0038 (7)	0.0037 (7)	−0.0054 (7)
C48	0.0359 (10)	0.0292 (10)	0.0371 (10)	−0.0090 (8)	0.0037 (7)	−0.0103 (8)
C49	0.0345 (10)	0.0391 (12)	0.0431 (11)	−0.0127 (8)	0.0144 (8)	−0.0122 (8)
C50	0.0240 (8)	0.0213 (9)	0.0212 (7)	0.0008 (6)	0.0000 (6)	0.0053 (6)
C51	0.0306 (9)	0.0301 (10)	0.0271 (8)	−0.0022 (7)	0.0051 (7)	−0.0028 (7)
C52	0.0369 (10)	0.0391 (12)	0.0347 (9)	−0.0013 (8)	0.0142 (7)	−0.0043 (8)
C53	0.0335 (10)	0.0374 (11)	0.0381 (10)	−0.0028 (8)	0.0135 (7)	0.0064 (8)
C54	0.0290 (9)	0.0267 (10)	0.0395 (10)	−0.0041 (7)	0.0059 (7)	0.0050 (7)
O6	0.0486 (9)	0.0557 (10)	0.0499 (9)	−0.0112 (7)	0.0019 (7)	0.0202 (7)
O7	0.0433 (8)	0.0384 (8)	0.0310 (7)	−0.0051 (6)	0.0019 (5)	0.0036 (6)
C55	0.0442 (11)	0.0498 (14)	0.0381 (11)	0.0003 (10)	0.0014 (8)	−0.0037 (9)
C56	0.0310 (9)	0.0389 (11)	0.0363 (10)	−0.0019 (8)	0.0083 (7)	0.0038 (8)
C57	0.0379 (11)	0.0509 (13)	0.0341 (10)	−0.0013 (9)	0.0008 (8)	−0.0034 (9)

C58	0.0472 (13)	0.0440 (14)	0.0624 (14)	−0.0014 (10)	−0.0018 (10)	−0.0129 (11)

Geometric parameters (Å, º)

O1—C22	1.3684 (18)	C26—H26A	0.990
O1—C24	1.4419 (17)	C26—H26B	0.990
O2—C25	1.423 (2)	C26—C27	1.508 (3)
O2—C26	1.424 (2)	C27—H27A	0.990
O3—C27	1.428 (2)	C27—H27B	0.990
O3—C28	1.428 (2)	C28—H28A	0.990
O4—C29	1.425 (2)	C28—H28B	0.990
O4—C30	1.428 (2)	C28—C29	1.499 (3)
O5—C31	1.442 (2)	C29—H29A	0.990
O5—C32	1.371 (2)	C29—H29B	0.990
N1—C1	1.343 (3)	C30—H30A	0.990
N1—C5	1.345 (2)	C30—H30B	0.990
N2—C6	1.348 (2)	C30—C31	1.507 (3)
N2—C10	1.3450 (19)	C31—H31A	0.990
N3—C11	1.343 (2)	C31—H31B	0.990
N3—C15	1.339 (2)	C32—C33	1.414 (2)
N4—C50	1.355 (2)	C32—C37	1.387 (2)
N4—C54	1.338 (2)	C33—C34	1.396 (2)
N5—C42	1.345 (2)	C34—H34	0.950
N5—C43	1.349 (2)	C34—C35	1.390 (2)
N6—C45	1.342 (2)	C35—H35	0.950
N6—C49	1.340 (2)	C35—C36	1.400 (2)
C1—H1	0.950	C36—C37	1.401 (2)
C1—C2	1.375 (3)	C36—C38	1.433 (2)
C2—H2	0.950	C37—H37	0.950
C2—C3	1.376 (3)	C38—C39	1.201 (2)
C3—H3	0.950	C39—C40	1.437 (2)
C3—C4	1.384 (2)	C40—C41	1.401 (2)
C4—H4	0.950	C40—C44	1.394 (2)
C4—C5	1.384 (3)	C41—H41	0.950
C5—C6	1.493 (2)	C41—C42	1.395 (2)
C6—C7	1.390 (2)	C42—C45	1.495 (2)
C7—H7	0.950	C43—C44	1.392 (2)
C7—C8	1.396 (2)	C43—C50	1.491 (2)
C8—C9	1.401 (2)	C44—H44	0.950
C8—C16	1.430 (2)	C45—C46	1.393 (2)
C9—H9	0.950	C46—H46	0.950
C9—C10	1.392 (2)	C46—C47	1.387 (2)
C10—C11	1.498 (2)	C47—H47	0.950
C11—C12	1.391 (2)	C47—C48	1.382 (3)
C12—H12	0.950	C48—H48	0.950
C12—C13	1.390 (3)	C48—C49	1.385 (3)
C13—H13	0.950	C49—H49	0.950
C13—C14	1.382 (3)	C50—C51	1.387 (2)

C14—H14	0.950	C51—H51	0.950
C14—C15	1.384 (3)	C51—C52	1.387 (3)
C15—H15	0.950	C52—H52	0.950
C16—C17	1.204 (2)	C52—C53	1.386 (3)
C17—C18	1.428 (2)	C53—H53	0.950
C18—C19	1.398 (2)	C53—C54	1.384 (3)
C18—C23	1.403 (2)	C54—H54	0.950
C19—H19	0.950	O6—C56	1.201 (2)
C19—C20	1.385 (2)	O7—C56	1.336 (2)
C20—H20	0.950	O7—C57	1.454 (2)
C20—C21	1.394 (2)	C55—H55A	0.980
C21—C22	1.409 (2)	C55—H55B	0.980
C21—C33	1.490 (2)	C55—H55C	0.980
C22—C23	1.393 (2)	C55—C56	1.492 (3)
C23—H23	0.950	C57—H57A	0.990
C24—H24A	0.990	C57—H57B	0.990
C24—H24B	0.990	C57—C58	1.500 (3)
C24—C25	1.510 (2)	C58—H58A	0.980
C25—H25A	0.990	C58—H58B	0.980
C25—H25B	0.990	C58—H58C	0.980

C22—O1—C24	116.74 (11)	O4—C29—C28	108.21 (14)
C25—O2—C26	113.94 (13)	O4—C29—H29A	110.1
C27—O3—C28	114.60 (13)	O4—C29—H29B	110.1
C29—O4—C30	113.88 (13)	C28—C29—H29A	110.1
C31—O5—C32	120.40 (13)	C28—C29—H29B	110.1
C1—N1—C5	116.09 (18)	H29A—C29—H29B	108.4
C6—N2—C10	117.97 (13)	O4—C30—H30A	109.1
C11—N3—C15	117.57 (15)	O4—C30—H30B	109.1
C50—N4—C54	117.39 (15)	O4—C30—C31	112.44 (14)
C42—N5—C43	118.29 (14)	H30A—C30—H30B	107.8
C45—N6—C49	117.33 (15)	H30A—C30—C31	109.1
N1—C1—H1	117.7	H30B—C30—C31	109.1
N1—C1—C2	124.5 (2)	O5—C31—C30	111.65 (14)
H1—C1—C2	117.7	O5—C31—H31A	109.3
C1—C2—H2	120.7	O5—C31—H31B	109.3
C1—C2—C3	118.55 (17)	C30—C31—H31A	109.3
H2—C2—C3	120.7	C30—C31—H31B	109.3
C2—C3—H3	120.8	H31A—C31—H31B	108.0
C2—C3—C4	118.49 (19)	O5—C32—C33	114.80 (14)
H3—C3—C4	120.8	O5—C32—C37	125.04 (15)
C3—C4—H4	120.4	C33—C32—C37	120.17 (15)
C3—C4—C5	119.17 (18)	C21—C33—C32	120.00 (14)
H4—C4—C5	120.4	C21—C33—C34	121.28 (14)
N1—C5—C4	123.16 (15)	C32—C33—C34	118.61 (14)
N1—C5—C6	116.24 (15)	C33—C34—H34	119.2
C4—C5—C6	120.59 (15)	C33—C34—C35	121.60 (15)
N2—C6—C5	116.10 (14)	H34—C34—C35	119.2

N2—C6—C7	123.18 (14)	C34—C35—H35	120.4
C5—C6—C7	120.72 (15)	C34—C35—C36	119.21 (16)
C6—C7—H7	120.7	H35—C35—C36	120.4
C6—C7—C8	118.55 (14)	C35—C36—C37	120.01 (15)
H7—C7—C8	120.7	C35—C36—C38	120.85 (15)
C7—C8—C9	118.68 (14)	C37—C36—C38	119.13 (15)
C7—C8—C16	120.05 (14)	C32—C37—C36	120.39 (15)
C9—C8—C16	121.27 (14)	C32—C37—H37	119.8
C8—C9—H9	120.6	C36—C37—H37	119.8
C8—C9—C10	118.71 (14)	C36—C38—C39	177.45 (17)
H9—C9—C10	120.6	C38—C39—C40	174.61 (18)
N2—C10—C9	122.86 (15)	C39—C40—C41	122.23 (15)
N2—C10—C11	116.09 (14)	C39—C40—C44	119.21 (15)
C9—C10—C11	121.04 (13)	C41—C40—C44	118.55 (15)
N3—C11—C10	115.79 (14)	C40—C41—H41	120.8
N3—C11—C12	122.47 (15)	C40—C41—C42	118.36 (15)
C10—C11—C12	121.73 (14)	H41—C41—C42	120.8
C11—C12—H12	120.5	N5—C42—C41	123.12 (15)
C11—C12—C13	119.07 (16)	N5—C42—C45	115.63 (14)
H12—C12—C13	120.5	C41—C42—C45	121.25 (15)
C12—C13—H13	120.7	N5—C43—C44	122.25 (15)
C12—C13—C14	118.62 (17)	N5—C43—C50	116.52 (14)
H13—C13—C14	120.7	C44—C43—C50	121.23 (14)
C13—C14—H14	120.7	C40—C44—C43	119.40 (15)
C13—C14—C15	118.55 (17)	C40—C44—H44	120.3
H14—C14—C15	120.7	C43—C44—H44	120.3
N3—C15—C14	123.69 (16)	N6—C45—C42	116.85 (14)
N3—C15—H15	118.2	N6—C45—C46	122.85 (15)
C14—C15—H15	118.2	C42—C45—C46	120.30 (15)
C8—C16—C17	177.28 (17)	C45—C46—H46	120.7
C16—C17—C18	175.77 (17)	C45—C46—C47	118.58 (16)
C17—C18—C19	119.07 (14)	H46—C46—C47	120.7
C17—C18—C23	120.90 (13)	C46—C47—H47	120.4
C19—C18—C23	120.01 (14)	C46—C47—C48	119.20 (16)
C18—C19—H19	120.2	H47—C47—C48	120.4
C18—C19—C20	119.51 (14)	C47—C48—H48	120.9
H19—C19—C20	120.2	C47—C48—C49	118.22 (16)
C19—C20—H20	119.2	H48—C48—C49	120.9
C19—C20—C21	121.53 (14)	N6—C49—C48	123.81 (18)
H20—C20—C21	119.2	N6—C49—H49	118.1
C20—C21—C22	118.75 (14)	C48—C49—H49	118.1
C20—C21—C33	119.01 (13)	N4—C50—C43	115.92 (14)
C22—C21—C33	122.24 (14)	N4—C50—C51	122.77 (16)
O1—C22—C21	116.31 (13)	C43—C50—C51	121.31 (15)
O1—C22—C23	123.42 (13)	C50—C51—H51	120.7
C21—C22—C23	120.27 (14)	C50—C51—C52	118.53 (16)
C18—C23—C22	119.89 (13)	H51—C51—C52	120.7
C18—C23—H23	120.1	C51—C52—H52	120.3

C22—C23—H23	120.1	C51—C52—C53	119.38 (17)
O1—C24—H24A	110.0	H52—C52—C53	120.3
O1—C24—H24B	110.0	C52—C53—H53	120.9
O1—C24—C25	108.47 (12)	C52—C53—C54	118.21 (17)
H24A—C24—H24B	108.4	H53—C53—C54	120.9
H24A—C24—C25	110.0	N4—C54—C53	123.72 (17)
H24B—C24—C25	110.0	N4—C54—H54	118.1
O2—C25—C24	113.36 (14)	C53—C54—H54	118.1
O2—C25—H25A	108.9	C56—O7—C57	115.53 (15)
O2—C25—H25B	108.9	H55A—C55—H55B	109.5
C24—C25—H25A	108.9	H55A—C55—H55C	109.5
C24—C25—H25B	108.9	H55A—C55—C56	109.5
H25A—C25—H25B	107.7	H55B—C55—H55C	109.5
O2—C26—H26A	110.1	H55B—C55—C56	109.5
O2—C26—H26B	110.1	H55C—C55—C56	109.5
O2—C26—C27	108.02 (13)	O6—C56—O7	122.90 (17)
H26A—C26—H26B	108.4	O6—C56—C55	124.76 (19)
H26A—C26—C27	110.1	O7—C56—C55	112.33 (16)
H26B—C26—C27	110.1	O7—C57—H57A	110.3
O3—C27—C26	113.34 (15)	O7—C57—H57B	110.3
O3—C27—H27A	108.9	O7—C57—C58	107.08 (17)
O3—C27—H27B	108.9	H57A—C57—H57B	108.6
C26—C27—H27A	108.9	H57A—C57—C58	110.3
C26—C27—H27B	108.9	H57B—C57—C58	110.3
H27A—C27—H27B	107.7	C57—C58—H58A	109.5
O3—C28—H28A	110.2	C57—C58—H58B	109.5
O3—C28—H28B	110.2	C57—C58—H58C	109.5
O3—C28—C29	107.66 (15)	H58A—C58—H58B	109.5
H28A—C28—H28B	108.5	H58A—C58—H58C	109.5
H28A—C28—C29	110.2	H58B—C58—H58C	109.5
H28B—C28—C29	110.2		

C5—N1—C1—C2	0.5 (3)	C32—O5—C31—C30	94.08 (18)
N1—C1—C2—C3	−1.0 (4)	O4—C30—C31—O5	−64.32 (18)
C1—C2—C3—C4	0.7 (3)	C31—O5—C32—C33	179.55 (14)
C2—C3—C4—C5	0.1 (3)	C31—O5—C32—C37	−0.4 (2)
C1—N1—C5—C4	0.4 (3)	O5—C32—C33—C21	−4.4 (2)
C1—N1—C5—C6	179.18 (18)	O5—C32—C33—C34	179.43 (14)
C3—C4—C5—N1	−0.7 (3)	C37—C32—C33—C21	175.57 (14)
C3—C4—C5—C6	−179.40 (16)	C37—C32—C33—C34	−0.7 (2)
C10—N2—C6—C5	178.48 (14)	C20—C21—C33—C32	−66.3 (2)
C10—N2—C6—C7	−0.7 (2)	C20—C21—C33—C34	109.81 (18)
N1—C5—C6—N2	172.56 (16)	C22—C21—C33—C32	113.25 (17)
N1—C5—C6—C7	−8.2 (2)	C22—C21—C33—C34	−70.6 (2)
C4—C5—C6—N2	−8.7 (2)	C21—C33—C34—C35	−174.57 (15)
C4—C5—C6—C7	170.56 (17)	C32—C33—C34—C35	1.6 (2)
N2—C6—C7—C8	2.2 (3)	C33—C34—C35—C36	−1.4 (2)
C5—C6—C7—C8	−176.93 (15)	C34—C35—C36—C37	0.3 (2)

C6—C7—C8—C9	−1.8 (2)	C34—C35—C36—C38	−178.50 (15)
C6—C7—C8—C16	179.40 (16)	O5—C32—C37—C36	179.46 (15)
C7—C8—C9—C10	−0.1 (2)	C33—C32—C37—C36	−0.5 (2)
C16—C8—C9—C10	178.76 (16)	C35—C36—C37—C32	0.7 (2)
C6—N2—C10—C9	−1.3 (2)	C38—C36—C37—C32	179.43 (14)
C6—N2—C10—C11	177.83 (14)	C39—C40—C41—C42	−178.19 (14)
C8—C9—C10—N2	1.7 (3)	C44—C40—C41—C42	0.8 (2)
C8—C9—C10—C11	−177.41 (14)	C43—N5—C42—C41	−0.5 (2)
C15—N3—C11—C10	177.60 (16)	C43—N5—C42—C45	−179.86 (13)
C15—N3—C11—C12	−1.7 (3)	C40—C41—C42—N5	0.3 (2)
N2—C10—C11—N3	−174.29 (15)	C40—C41—C42—C45	179.64 (14)
N2—C10—C11—C12	5.0 (2)	C42—N5—C43—C44	−0.5 (2)
C9—C10—C11—N3	4.8 (2)	C42—N5—C43—C50	179.46 (13)
C9—C10—C11—C12	−175.85 (17)	N5—C43—C44—C40	1.6 (2)
N3—C11—C12—C13	0.3 (3)	C50—C43—C44—C40	−178.30 (14)
C10—C11—C12—C13	−178.98 (17)	C39—C40—C44—C43	177.28 (14)
C11—C12—C13—C14	1.1 (3)	C41—C40—C44—C43	−1.8 (2)
C12—C13—C14—C15	−1.1 (3)	C49—N6—C45—C42	179.86 (16)
C11—N3—C15—C14	1.8 (3)	C49—N6—C45—C46	−0.3 (3)
C13—C14—C15—N3	−0.4 (3)	N5—C42—C45—N6	−172.13 (15)
C17—C18—C19—C20	−176.98 (15)	N5—C42—C45—C46	8.0 (2)
C23—C18—C19—C20	1.6 (2)	C41—C42—C45—N6	8.5 (2)
C18—C19—C20—C21	−1.7 (2)	C41—C42—C45—C46	−171.33 (15)
C19—C20—C21—C22	0.2 (2)	N6—C45—C46—C47	0.2 (3)
C19—C20—C21—C33	179.82 (15)	C42—C45—C46—C47	−179.97 (15)
C24—O1—C22—C21	−176.50 (13)	C45—C46—C47—C48	−0.1 (3)
C24—O1—C22—C23	3.2 (2)	C46—C47—C48—C49	0.1 (3)
C20—C21—C22—O1	−178.92 (14)	C45—N6—C49—C48	0.3 (3)
C20—C21—C22—C23	1.4 (2)	C47—C48—C49—N6	−0.2 (3)
C33—C21—C22—O1	1.5 (2)	C54—N4—C50—C43	−179.04 (14)
C33—C21—C22—C23	−178.19 (15)	C54—N4—C50—C51	0.0 (2)
O1—C22—C23—C18	178.80 (14)	N5—C43—C50—N4	−177.06 (13)
C21—C22—C23—C18	−1.5 (2)	N5—C43—C50—C51	3.9 (2)
C17—C18—C23—C22	178.55 (15)	C44—C43—C50—N4	2.9 (2)
C19—C18—C23—C22	0.0 (2)	C44—C43—C50—C51	−176.19 (15)
C22—O1—C24—C25	−174.97 (13)	N4—C50—C51—C52	−0.6 (2)
C26—O2—C25—C24	101.55 (16)	C43—C50—C51—C52	178.41 (15)
O1—C24—C25—O2	−62.82 (17)	C50—C51—C52—C53	0.5 (3)
C25—O2—C26—C27	168.42 (14)	C51—C52—C53—C54	0.1 (3)
C28—O3—C27—C26	79.72 (19)	C50—N4—C54—C53	0.7 (2)
O2—C26—C27—O3	66.46 (18)	C52—C53—C54—N4	−0.7 (3)
C27—O3—C28—C29	−136.94 (17)	C57—O7—C56—O6	−2.6 (3)
C30—O4—C29—C28	−169.44 (15)	C57—O7—C56—C55	176.54 (17)
O3—C28—C29—O4	−168.47 (15)	C56—O7—C57—C58	177.30 (18)
C29—O4—C30—C31	107.96 (17)		