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4′-(2,5,8,11,14-Pentaoxabicyclo[13.4.0]-nonadeca-15,17,19-trien-17-yloxy)-2,2′:6′,2″-terpyridine: a powder study

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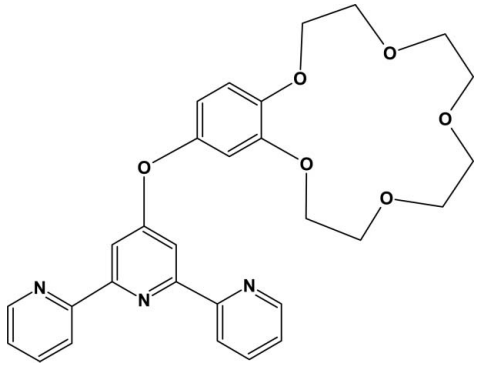
Key indicators: powder X-ray study; T = 295 K; mean σ(C–C) = 0.030 Å; R factor = 0.019; wR factor = 0.024; data-to-parameter ratio = 5.3.

The central pyridine ring of the 2,2′:6′,2″-terpyridine fragment of the title compound, $C_{29}H_{29}N_3O_6$, forms dihedral angles of 5.2 (5), 10.1 (5) and 86.0 (6)°, respectively, with the two outer pyridine rings and the benzene ring of the benzo-15-crown-5 fragment.

Related literature

For related crystal structures determined from synchrotron powder diffraction data, see Dorokhov *et al.* (2007). For useful applications of 2,2′:6′,2"-terpyridine derivatives, see Andres *et al.* (2003). For details of the synthesis of the title compound, see: Constable & Ward (1990); Chitta *et al.* (2004); Kobayashi (2001). For details of the indexing algorithm, see Visser (1969).



Experimental

Crystal data

$C_{29}H_{29}N_3O_6$
M_r = 515.55
Orthorhombic, *Fdd*2
a = 58.347 (11) Å
b = 33.712 (3) Å
c = 5.3211 (8) Å
V = 10467 (3) Å^3
Z = 16
Cu $K\alpha_1$ radiation
λ = 1.54059 Å
μ = 0.76 mm^{-1}
T = 295 (2) K
Specimen shape: flat sheet
15 × 1 × 1 mm
Specimen prepared at 295 (2) K and 101 kPa
Particle morphology: no specific habit, colourless

Data collection

G670 Guinier camera diffractometer
Specimen mounting: thin layer in the specimen holder of the camera
Specimen mounted in transmission mode
Scan method: continuous
Absorption correction: none
$2\theta_{min}$ = 4.5, $2\theta_{max}$ = 75.0°
Increment in 2θ = 0.01°

Refinement

R_p = 0.019
R_{wp} = 0.024
R_{exp} = 0.018
R_B = 0.023
S = 1.36
Excluded region(s): none
Profile function: split-type pseudo-Voigt (Toraya, 1986)
148 parameters
173 restraints
H-atom parameters not refined
Preferred orientation correction: none

Data collection: local program (Huber, 2002); cell refinement: *MRIA* (Zlokazov & Chernyshev, 1992); data reduction: local program (Huber, 2002); program(s) used to solve structure: grid search (Chernyshev & Schenk, 1998); program(s) used to refine structure: *MRIA*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *MRIA*, *SHELXL97* (Sheldrick, 1997).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YA2062).

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supporting information

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4′-(2,5,8,11,14-Pentaoxabicyclo[13.4.0]nonadeca-15,17,19-trien-17-yl-oxy)-2,2′:6′,2″-terpyridine: a powder study

Nadezhda M. Logacheva, Tamara P. Puryaeva, Aslan Yu. Tsivadze, Yurii A. Velikodny and Vladimir V. Chernyshev

S1. Comment

Ability of 2,2′:6′,2"-terpyridines to form complexes with transition metals, such as Zn(II), Fe(II), Co(II), Ni(II) and Ru(II) is widely used in supramolecular chemistry to control self organization processes. Introduction of additional fragments with various coordinating groups to a molecule of 2,2′:6′,2"-terpyridine opens broad prospects for purposeful design of supramolecular compounds (Andres *et al.*, 2003). 4′-(Benzo-15-crown-5) substituted 2,2′:6′,2"-terpyridines represent a new interesting class of compounds involving both terpyridine fragment, which selectively binds the d-element cations, and benzo-15-crown-5 with unique ability for complexation of cations of alkaline, alkaline-earth metals as well as those of organic amines. Compounds of this class offer new opportunities for use of metal-ligand interactions for controllable assembly of the supramolecular complexes. We present here the structure of title compound, (I).

In (I) (Fig. 1), all bond lengths and angles are comparable with those reported earlier for the related compounds (Dorokhov *et al.*, 2007). The six-membered rings N2/C5—C9 (A), N3/C10—C14 (B), N4/C15—C19 (C) and C25—C30 (D) form the following dihedral angles - A/B 5.2 (5)°, A/C 10.1 (5)° and A/D 86.0 (6)°.

S2. Experimental

The synthesis of 2,2′:6′,2"-terpyridine was carried out according to Constable & Ward (1990). 4′-Hydroxy-benzo-15-crown-5 was obtained on the basis of commercially accessible benzo-15-crown-5 by the formylation reaction (Chitta *et al.*, 2004) and the subsequent oxidizing decarbonylation (Kobayashi, 2001). 4′-(4‴-Benzo-15-crown-5)-oxy-2,2′:6′,2″-terpyridine has been synthesized using reaction of nucleophilic replacement of 4′-chloro-2,2′:6′,2″-terpyridine with 4′-hydroxy-benzo-15-crown-5 in the dry DMSO in the presence of a base (KOH).

The synthesis of 4′-(4‴-benzo-15-crown-5)-oxy-2,2′:6′,2″-terpyridine (Scheme 2): to a stirred suspension of powdered KOH (890 mg, 15,90 mmol) in dry DMSO (12 ml) in the argon atmosphere at 70 °C, the 4′-hydroxy-benzo-15-crown-5 (928 mg, 3,269 mmol) was added. After 30 min, 4′-chloro-2,2′:6′,2″-terpyridine (873 mg, 3,269 mmol) was added and the mixture was stirred for 8 h at 70 °C and then poured into 150 ml of ice water. The water phase was extracted with chloroform (150 *x* 100 *x* 50 *x* 50 ml), dried over $MgSO_4$ and evaporated in vacuum. The residue (20 ml) was purified by column chromatography on the neutral Al_2O_3 ($CHCl_3$). After evaporation, the product, obtained as a yellowish oil, was crystallized from diethyl ether, then filtered and washed on the filter by the cooled diethyl ether, recrystallized from methyl alcohol (25 ml) and dried in vacuum at 60 °C. The yield of the target product as white solid was 623 mg (37,2%). (*M*. p. = 151 °C)

S3. Refinement

During the exposure, the specimen was spun in its plane to improve particle statistics. The orthorhombic unit-cell dimensions were determined with the indexing program ITO (Visser, 1969), M_{20}=44, using the first 35 peak positions. The space group Fdd2 was chosen on the basis of systematic extinction rules and confirmed later by the crystal structure solution. The structure of (I) was solved by the systematic grid search procedure (Chernyshev & Schenk, 1998) and refined following the methodology described in detail elsewhere (Dorokhov *et al.*, 2007) by the subsequent bond-restrained Rietveld refinement with the program MRIA (Zlokazov & Chernyshev, 1992). All O atoms were refined isotropically with the overall U_{iso} parameter. The U_{iso} for the rest of non-H atoms were fixed at 0.051 Å^2. All H atoms were placed in geometrically calculated positions and not refined. The diffraction profiles and the differences between the measured and calculated profiles are shown in Fig. 2.

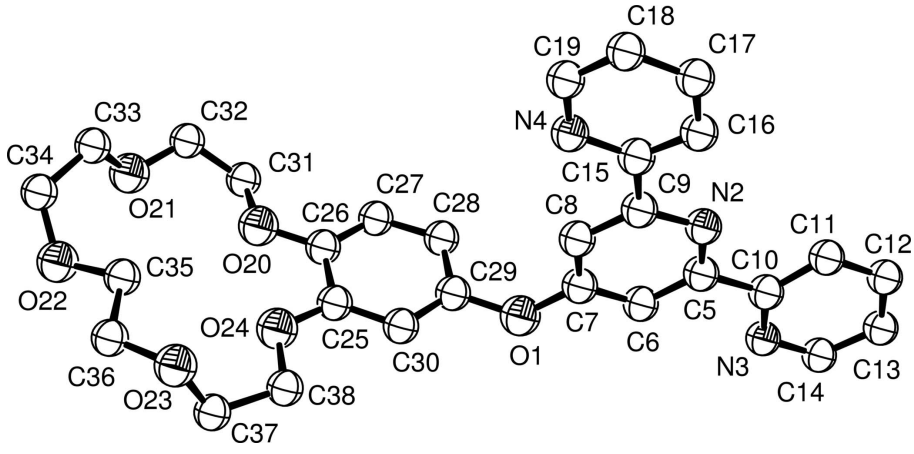

Figure 1

The molecular structure of (I) with the atomic numbering and 50% displacement spheres. H atoms omitted for clarity.

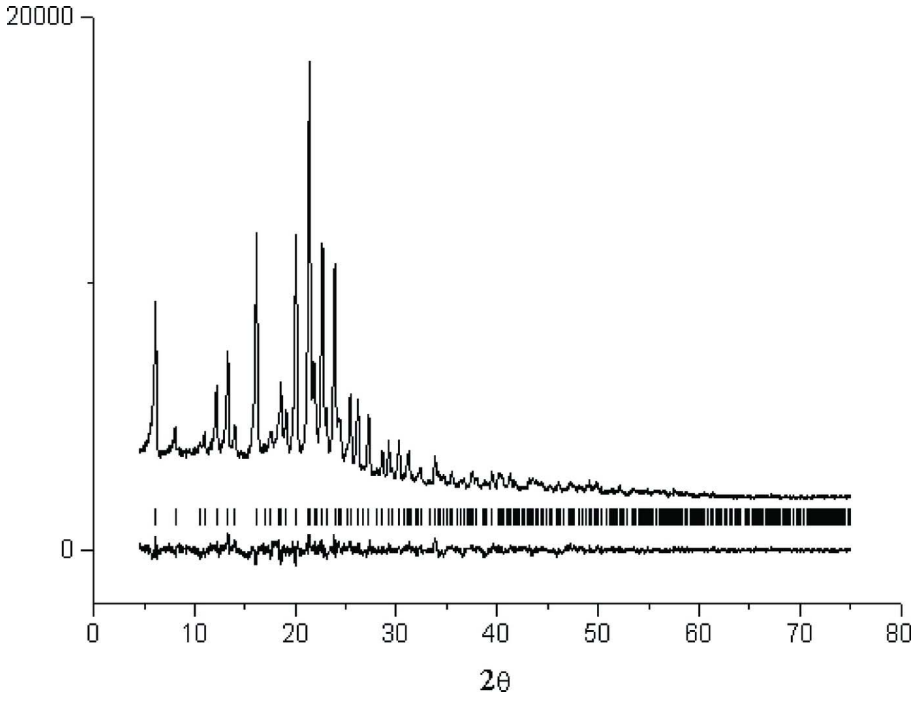

Figure 2

The Rietveld plot, showing the observed and difference profiles for (I). The reflection positions are shown above the difference profile.

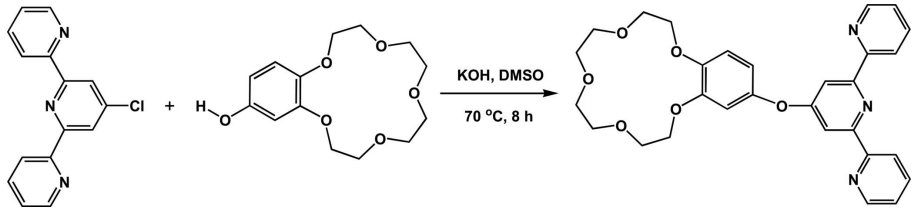

Figure 3

The formation of the title compound.

4′-(2,5,8,11,14-Pentaoxadicyclo[13.4.0]nonadeca-15,17,19-trien-17-yloxy)-\2,2′:6′,2′′-terpyridine

Crystal data

$C_{29}H_{29}N_3O_6$
M_r = 515.55
Orthorhombic, *Fdd*2
a = 58.347 (11) Å
b = 33.712 (3) Å
c = 5.3211 (8) Å
V = 10467 (3) Å^3
Z = 16
F(000) = 4352

D_x = 1.309 Mg m^{-3}
Cu $K\alpha_1$ radiation, λ = 1.54059 Å
μ = 0.76 mm^{-1}
T = 295 K
Particle morphology: no specific habit
colourless
flat_sheet, 15 × 1 mm
Specimen preparation: Prepared at 295 K and 101 kPa

Data collection

Guinier camera G670 diffractometer
Radiation source: line-focus sealed tube
Curved Germanium (111) monochromator
Specimen mounting: thin layer in the specimen holder of the camera
Data collection mode: transmission
Scan method: continuous
$2\theta_{min}$ = 4.50°, $2\theta_{max}$ = 75.00°, $2\theta_{step}$ = 0.01°

Refinement

Refinement on I_{net}
Least-squares matrix: full with fixed elements per cycle
R_p = 0.019
R_{wp} = 0.024
R_{exp} = 0.018
R_{Bragg} = 0.023
7051 data points
Excluded region(s): none
Profile function: split-type pseudo-Voigt (Toraya, 1986)
148 parameters
173 restraints
7 constraints
H-atom parameters not refined
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max}$ = 0.007
Background function: Chebyshev polynomial up to the 5th order
Preferred orientation correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.0046 (3)	0.6614 (4)	0.1346	0.067 (3)*
N2	0.0097 (3)	0.5679 (6)	0.655 (3)	0.051*
N3	0.0633 (3)	0.5704 (6)	0.288 (4)	0.051*
N4	−0.0478 (3)	0.6009 (6)	0.858 (4)	0.051*
C5	0.0253 (4)	0.5800 (7)	0.478 (4)	0.051*
C6	0.0209 (4)	0.6110 (7)	0.301 (4)	0.051*
H6	0.0319	0.6180	0.1824	0.061*
C7	0.0000 (4)	0.6304 (7)	0.310 (4)	0.051*
C8	−0.0160 (4)	0.6196 (7)	0.486 (4)	0.051*
H8	−0.0301	0.6325	0.4940	0.061*
C9	−0.0108 (4)	0.5887 (7)	0.654 (4)	0.051*
C10	0.0482 (4)	0.5595 (7)	0.471 (4)	0.051*
C11	0.0544 (4)	0.5322 (6)	0.660 (4)	0.051*
H11	0.0445	0.5270	0.7934	0.061*
C12	0.0756 (3)	0.5132 (7)	0.645 (4)	0.051*
H12	0.0798	0.4945	0.7643	0.061*
C13	0.0905 (4)	0.5225 (7)	0.448 (4)	0.051*
H13	0.1045	0.5096	0.4299	0.061*
C14	0.0837 (4)	0.5518 (7)	0.278 (4)	0.051*
H14	0.0938	0.5589	0.1510	0.061*
C15	−0.0286 (3)	0.5771 (6)	0.840 (3)	0.051*
C16	−0.0263 (4)	0.5425 (7)	0.984 (4)	0.051*
H16	−0.0137	0.5259	0.9615	0.061*
C17	−0.0431 (4)	0.5332 (7)	1.161 (4)	0.051*
H17	−0.0415	0.5110	1.2628	0.061*
C18	−0.0624 (4)	0.5579 (7)	1.183 (4)	0.051*
H18	−0.0744	0.5516	1.2909	0.061*
C19	−0.0630 (4)	0.5925 (7)	1.035 (4)	0.051*

H19	−0.0748	0.6106	1.0631	0.061*
O20	−0.0608 (2)	0.7962 (4)	0.187 (3)	0.067 (3)*
O21	−0.0911 (2)	0.8612 (4)	0.246 (3)	0.067 (3)*
O22	−0.1263 (3)	0.8329 (4)	−0.111 (3)	0.067 (3)*
O23	−0.1184 (2)	0.7296 (4)	−0.314 (3)	0.067 (3)*
O24	−0.0706 (2)	0.7416 (4)	−0.138 (3)	0.067 (3)*
C25	−0.0511 (4)	0.7344 (7)	−0.001 (4)	0.051*
C26	−0.0454 (4)	0.7653 (7)	0.176 (4)	0.051*
C27	−0.0263 (3)	0.7608 (7)	0.327 (4)	0.051*
H27	−0.0215	0.7816	0.4291	0.061*
C28	−0.0139 (4)	0.7242 (7)	0.325 (4)	0.051*
H28	−0.0025	0.7196	0.4433	0.061*
C29	−0.0190 (4)	0.6956 (8)	0.146 (4)	0.051*
C30	−0.0376 (3)	0.6998 (6)	−0.014 (4)	0.051*
H30	−0.0411	0.6800	−0.1292	0.061*
C31	−0.0540 (4)	0.8312 (7)	0.328 (4)	0.051*
H31A	−0.0444	0.8235	0.4689	0.061*
H31B	−0.0453	0.8490	0.2215	0.061*
C32	−0.0743 (4)	0.8510 (7)	0.419 (4)	0.051*
H32A	−0.0813	0.8341	0.5447	0.061*
H32B	−0.0695	0.8751	0.5038	0.061*
C33	−0.1144 (3)	0.8536 (7)	0.324 (4)	0.051*
H33A	−0.1188	0.8739	0.4437	0.061*
H33B	−0.1147	0.8284	0.4119	0.061*
C34	−0.1324 (4)	0.8524 (7)	0.116 (4)	0.051*
H34A	−0.1460	0.8396	0.1823	0.061*
H34B	−0.1366	0.8795	0.0750	0.061*
C35	−0.1172 (4)	0.7936 (7)	−0.091 (4)	0.051*
H35A	−0.1202	0.7829	0.0754	0.061*
H35B	−0.1008	0.7940	−0.1177	0.061*
C36	−0.1289 (4)	0.7680 (7)	−0.291 (4)	0.051*
H36A	−0.1449	0.7647	−0.2477	0.061*
H36B	−0.1281	0.7815	−0.4518	0.061*
C37	−0.0982 (4)	0.7268 (6)	−0.462 (4)	0.051*
H37A	−0.0945	0.7529	−0.5273	0.061*
H37B	−0.1012	0.7095	−0.6039	0.061*
C38	−0.0776 (4)	0.7110 (6)	−0.319 (4)	0.051*
H38A	−0.0816	0.6867	−0.2314	0.061*
H38B	−0.0651	0.7053	−0.4341	0.061*

Geometric parameters (Å, º)

O1—C7	1.43 (3)	C28—C29	1.39 (3)
O1—C29	1.43 (3)	C29—C30	1.39 (3)
O20—C26	1.38 (3)	C31—C32	1.44 (3)
O20—C31	1.45 (3)	C33—C34	1.53 (3)
O21—C32	1.39 (3)	C35—C36	1.53 (3)
O21—C33	1.45 (2)	C37—C38	1.52 (3)

O22—C34	1.42 (3)	C6—H6	0.93
O22—C35	1.43 (3)	C8—H8	0.93
O23—C36	1.44 (3)	C11—H11	0.93
O23—C37	1.42 (3)	C12—H12	0.93
O24—C25	1.37 (3)	C13—H13	0.93
O24—C38	1.47 (3)	C14—H14	0.93
N2—C5	1.38 (3)	C16—H16	0.93
N2—C9	1.39 (3)	C17—H17	0.93
N3—C10	1.36 (3)	C18—H18	0.93
N3—C14	1.35 (3)	C19—H19	0.93
N4—C15	1.38 (3)	C27—H27	0.93
N4—C19	1.32 (3)	C28—H28	0.93
C5—C6	1.43 (3)	C30—H30	0.93
C5—C10	1.50 (3)	C31—H31A	0.97
C6—C7	1.38 (3)	C31—H31B	0.97
C7—C8	1.37 (3)	C32—H32A	0.97
C8—C9	1.41 (3)	C32—H32B	0.97
C9—C15	1.49 (3)	C33—H33A	0.97
C10—C11	1.41 (3)	C33—H33B	0.97
C11—C12	1.40 (3)	C34—H34A	0.97
C12—C13	1.40 (3)	C34—H34B	0.97
C13—C14	1.39 (3)	C35—H35A	0.97
C15—C16	1.40 (3)	C35—H35B	0.97
C16—C17	1.40 (3)	C36—H36A	0.97
C17—C18	1.41 (3)	C36—H36B	0.97
C18—C19	1.41 (3)	C37—H37A	0.97
C25—C26	1.44 (3)	C37—H37B	0.97
C25—C30	1.41 (3)	C38—H38A	0.97
C26—C27	1.38 (3)	C38—H38B	0.97
C27—C28	1.43 (3)		

C7—O1—C29	132.4 (14)	C11—C12—H12	120
C26—O20—C31	117.3 (16)	C13—C12—H12	120
C32—O21—C33	115.2 (16)	C12—C13—H13	121
C34—O22—C35	117.3 (16)	C14—C13—H13	121
C36—O23—C37	117.4 (15)	N3—C14—H14	118
C25—O24—C38	117.0 (16)	C13—C14—H14	118
C5—N2—C9	114.7 (19)	C15—C16—H16	120
C10—N3—C14	118.3 (19)	C17—C16—H16	120
C15—N4—C19	117.9 (19)	C16—C17—H17	120
N2—C5—C6	123 (2)	C18—C17—H17	121
N2—C5—C10	117.8 (19)	C17—C18—H18	121
C6—C5—C10	118.8 (19)	C19—C18—H18	121
C5—C6—C7	119 (2)	N4—C19—H19	118
O1—C7—C6	119.3 (19)	C18—C19—H19	118
O1—C7—C8	121 (2)	C26—C27—H27	120
C6—C7—C8	120 (2)	C28—C27—H27	120
C7—C8—C9	119 (2)	C27—C28—H28	120

N2—C9—C8	124 (2)	C29—C28—H28	120
N2—C9—C15	117.8 (19)	C25—C30—H30	120
C8—C9—C15	118 (2)	C29—C30—H30	120
N3—C10—C5	117.7 (16)	O20—C31—H31A	110
N3—C10—C11	121 (2)	O20—C31—H31B	110
C5—C10—C11	120.8 (19)	C32—C31—H31A	110
C10—C11—C12	119 (2)	C32—C31—H31B	110
C11—C12—C13	119 (2)	H31A—C31—H31B	108
C12—C13—C14	118 (2)	O21—C32—H32A	108
N3—C14—C13	124 (2)	O21—C32—H32B	108
N4—C15—C9	117.4 (18)	C31—C32—H32A	108
N4—C15—C16	121.5 (18)	C31—C32—H32B	108
C9—C15—C16	121.0 (18)	H32A—C32—H32B	107
C15—C16—C17	119 (2)	O21—C33—H33A	108
C16—C17—C18	119 (2)	O21—C33—H33B	108
C17—C18—C19	118 (2)	C34—C33—H33A	108
N4—C19—C18	124 (2)	C34—C33—H33B	108
O24—C25—C26	114.2 (19)	H33A—C33—H33B	107
O24—C25—C30	125.7 (19)	O22—C34—H34A	108
C26—C25—C30	120 (2)	O22—C34—H34B	108
O20—C26—C25	115.1 (19)	C33—C34—H34A	108
O20—C26—C27	126 (2)	C33—C34—H34B	108
C25—C26—C27	119 (2)	H34A—C34—H34B	107
C26—C27—C28	120 (2)	O22—C35—H35A	110
C27—C28—C29	120 (2)	O22—C35—H35B	110
O1—C29—C28	117.6 (19)	C36—C35—H35A	110
O1—C29—C30	121 (2)	C36—C35—H35B	110
C28—C29—C30	121 (2)	H35A—C35—H35B	108
C25—C30—C29	119 (2)	O23—C36—H36A	109
O20—C31—C32	108.9 (18)	O23—C36—H36B	109
O21—C32—C31	118.0 (18)	C35—C36—H36A	109
O21—C33—C34	116.2 (17)	C35—C36—H36B	109
O22—C34—C33	117.2 (19)	H36A—C36—H36B	108
O22—C35—C36	107.7 (18)	O23—C37—H37A	109
O23—C36—C35	112.1 (18)	O23—C37—H37B	109
O23—C37—C38	113.7 (17)	C38—C37—H37A	109
O24—C38—C37	107.6 (16)	C38—C37—H37B	109
C5—C6—H6	120	H37A—C37—H37B	108
C7—C6—H6	120	O24—C38—H38A	110
C7—C8—H8	120	O24—C38—H38B	110
C9—C8—H8	120	C37—C38—H38A	110
C10—C11—H11	120	C37—C38—H38B	110
C12—C11—H11	120	H38A—C38—H38B	108