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7,11,15,28-Tetrakis(bromomethyl)-1,21,23,25-tetrapentylresorcin[4]arene cavitand 0.415-hydrate

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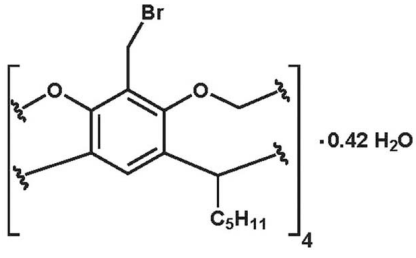
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.006 Å; H-atom completeness 99%; disorder in main residue; R factor = 0.052; wR factor = 0.187; data-to-parameter ratio = 16.5.

The title compound {systematic name: 7,11,15,28-tetrakis-(bromomethyl)-1,21,23,25-tetrapentyl-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocine 0.415-hydrate}, $C_{56}H_{68}Br_4O_8\cdot0.415H_2O$, has been previously synthesized and reported; however, its crystal structure has hitherto not been elucidated. The structure is the first reported example of a resorcin[4]arene cavitand bearing bromomethyl functional groups at the rim of the molecule. The inclusion of Br atoms makes the compound useful as a precursor to a number of synthetically more complex cavitand host molecules.. This is also true of the pentyl 'feet' of the title compound. Two pentyl groups are disordered over two positions; the site occupancy factors are *ca*. 0.68 and 0.32.

Related literature

For related literature, see: Boerrigter *et al.* (1997); Cram *et al.* (1988); Sorrell & Pigge (1993); Tunstad *et al.* (1989).



Experimental

Crystal data

$C_{56}H_{68}Br_4O_8\cdot0.415H_2O$
M_r = 1197.75
Triclinic, $P\overline{1}$
a = 11.5151 (2) Å
b = 11.9323 (2) Å
c = 22.7986 (5) Å
α = 93.655 (1)°
β = 92.921 (1)°
γ = 118.676 (1)°
V = 2730.83 (9) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.00 mm^{-1}
T = 173 (2) K
0.41 × 0.30 × 0.29 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: integration [face-indexed absorption corrections carried out with *XPREP* (Bruker, 2005)]
T_{min} = 0.373, T_{max} = 0.477
42983 measured reflections
10730 independent reflections
7721 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.187
S = 1.12
10730 reflections
649 parameters
102 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.41 e Å^{-3}
$\Delta\rho_{min}$ = −1.41 e Å^{-3}

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-NT* (Bruker, 2005); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Version 1.4.2; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2300).

References

Boerrigter, H., Verboom, W. & Reinhoudt, D. N. (1997). *J. Org. Chem.* **62**, 7148–7155.
Bruker (1999). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2005). *APEX2* (Version 2.0-1) and *SAINT-NT* (Version 6.0; includes *XPREP*). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Cram, D. J., Karbach, S., Kim, H.-E., Knobler, C. B., Maverick, E. F., Ericson, J. L. & Helgeson, R. C. (1988). *J. Am. Chem. Soc.* **110**, 2229–2237.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Sorrell, T. N. & Pigge, F. C. (1993). *J. Org. Chem.* **58**, 784–785.
Tunstad, L. M., Tucker, J. A., Dalcanale, E., Weiser, J., Bryant, J. A., Sherman, J. C., Helgeson, R. C., Knobler, C. B. & Cram, D. J. (1989). *J. Org. Chem.* **54**, 1305–1312.

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supplementary materials

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7,11,15,28-Tetrakis(bromomethyl)-1,21,23,25-tetrapentylresorcin[4]arene cavitand 0.415-hydrate

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Comment

The title compound, (II, Scheme 1), has been previously prepared by Boerrigter *et al.* (1997), as the result of a free radical bromination of (I) using *N*-bromosuccinimide and the radical initiator, AIBN. The synthesis of (II) in this study, however, followed the synthetic conditions as set out by Sorrell & Pigge (1993), which used benzoyl peroxide as the radical initiator. Interestingly, this is despite observations by Boerrigter *et al.* that this protocol did not afford the desired product. Indeed, the conditions of Sorrell & Pigge, in conjunction with the use of white light, yielded 76% of pure (II).

In the title compound the [4]arene moiety is a cyclic tetramer. The labelling scheme for one of the monomers, shown in Fig.1, extends over the whole molecule.

The asymmetric unit of (II) is shown in Fig. 2. The bond lengths and bond angles all fall within the normal ranges and are not discussed further. The four bromine atoms which appear at the upper rim of the molecule are orientated such that all four face inwards towards the molecular cavity. Interestingly, (II) appears with a water molecule of partial (0.42) occupancy inside the molecular cavity. This is despite the hydrophobic nature of the cavity. Such partial occupancy has been reported in related structures; for examples see Tunstad *et al.*, (1989) and Cram *et al.*,(1988).

The bromine atoms give rise to interesting packing arrangements in the crystal structure of (II). As shown in Fig. 3, the individual resorcin[4]arene cavitand molecules pack such that the bromine atoms are in close contact with the corresponding bromine atoms of a neighbouring molecule. This results in alternate layers of bromine atoms, in between the cavities and the 'feet' (pentyl groups) representing the remainder of the cavitand molecules.

In Fig. 4, the feet of (II) are such that two adjacent pentyl groups are linear, while the remaining two are bent. This is due to the interdigitation of a pair of linear chains from one cavitand molecule, with the corresponding chains of a neighbouring cavitand molecule. This results in insufficient space for the remaining pairs of alkyl groups to extend in a linear fashion.

Experimental

Methyl cavitand (I) (1.00 g, 1.15 mmol) and *N*-bromosuccinimide (0.90 g, 5.04 mmol) were added to CCl_4 (100 ml). A catalytic amount of benzoyl peroxide was added to the solution, and the solution allowed to reflux overnight under irradiation of white light. The orange solution accompanied by a succinimide precipitate was then allowed to cool to room temperature. The precipitate was filtered off, and the orange filtrate concentrated on a rotary evaporator. The resulting solid was chromatographed on silica gel using a chloroform mobile phase. The fractions that were collected were concentrated on a rotary evaporator, and the orange solid product stirred in methanol overnight. The solution was then filtered, and the purified product dried overnight to yield the title compound as a dark orange powder. (1.03 g, 76%), mp 553–555 K. ^{1}H NMR [$CDCl_3$, 300 MHz]: δ = 0.89 (t, 12 H, C*H*$_3$), 1.28 − 1.50 (m, 24 H, (C*H*$_2$)$_3$), 2.15 − 2.22 (m, 8 H, C*H*$_2$), 4.40 (s, 8 H, C*H*$_2$Br), 4.55 (d, 4 H, inner of OC*H*$_2$O), 4.76 (t, 4 H, C*H*(CH$_2$)$_4$CH$_3$), 6.02 (d, 4 H, outer of OC*H*$_2$O), 7.11 (s, 4 H, Ar *H*). ^{13}C NMR [$CDCl_3$, 75 MHz]: δ = 153.55, 138.13, 124.55, 121.18, 98.17, 36.87, 32.68, 31.98, 30.08, 27.55, 22.67, 14.10.

Crystals suitable for X-ray crystallography were grown by slow liquid diffusion of methanol into a solution of the title compound in 1:1 e thyl acetate:hexane.

Refinement

Hydrogen atoms, first located in the difference map, were positioned geometrically and allowed to ride on their respective parent atoms, with C—H bond lengths of 1.00 (CH), 0.99 (CH_2), or 0.98 (CH_3). They were then refined with a riding model with U_{iso}(H) = 1.5U_{eq}(CH_3) and U_{iso}(H) = 1.2U_{eq}(X) for X = CH or CH_2. Two of the four pentyl groups are disordered. These were refined over two positions using SIMU, SADI and DELU restraints with the final occupancies being 0.681 (5) for atoms C49—C51, C53—C56 and 0.319 (5) for atoms C49A—C51A, C53A—C56A. In addition, atoms C53—C56 and C53A—C56A were refined isotropically as they did not refine well when refined anisotropically. This is likely due to the presence of further structural disorder which is not fully accounted for by the current disorder model. The atom O1W was introduced into the structural model to account for an electron density feature of approximately 1.4 e/Å^3. Its coordinates and sof were refined with its U_{iso} fixed. This feature is interpreted as the O atom of a water molecule but its low occupancy factor [0.415] has prevented discovery of the associated H atoms which are, therefore, absent from the structural model.

Figures

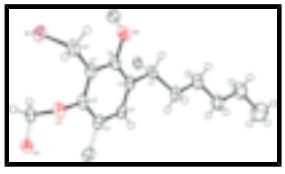


Fig. 1. A view of one component of the cyclic tetramer. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. Dashed bonds indicate links to the neighbouring monomer units. Selected atoms are labelled.

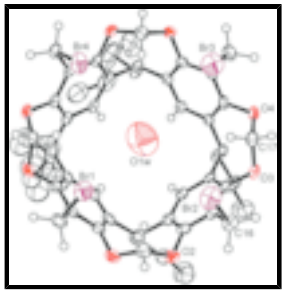


Fig. 2. The asymmetric unit of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms, where shown, are drawn as spheres of arbitrary radii. Selected atoms are labelled. The water molecule of partial occupancy is clearly evident, present in the molecular cavity.

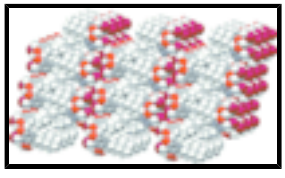


Fig. 3. Packing of the individual cavitand units, showing the close contact between resorcin[4]arene bromine atoms, resulting in layers of bromine atoms in between resorcin[4]arene units.

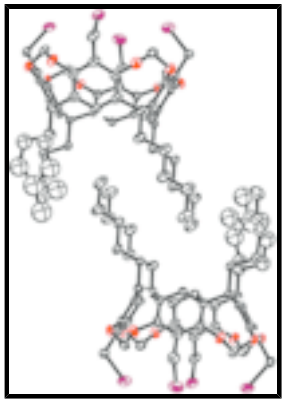


Fig. 4. The relative orientation of the feet of (II) in terms of neighbouring resorcin[4]arene units. Displacement ellipsoids are drawn at the 50% probability. The interdigitation of the feet is clearly shown. Hydrogen atoms and the water molecule in each unit have been omitted.

Fig. 5. The formation of the title compound.

7,11,15,28-tetrakis(bromomethyl)-1,21,23,25-tetrapentyl-2,20:3,19-dimetheno- 1H,21*H*,23H,25*H*-bis[1,3]dioxocino[5,4 – i:5',4'-i']benzo[1,2 – d:5,4 – d']bis[1,3] benzodioxocine stereoisomer

Crystal data

$C_{56}H_{68}Br_4O_8 \cdot 0.415H_2O$	$Z = 2$
$M_r = 1197.75$	$F_{000} = 1224.3$
	$D_x = 1.457$ Mg m^{-3}
Triclinic, $P\bar{1}$	$D_m = 1.454$ Mg m^{-3}
	D_m measured by not measured
Hall symbol: -P 1	Melting point: 553 K
$a = 11.5151$ (2) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 11.9323$ (2) Å	Cell parameters from 7203 reflections
$c = 22.7986$ (5) Å	$\theta = 2.3$–28.2°
$\alpha = 93.655$ (1)°	$\mu = 3.00$ mm^{-1}
$\beta = 92.921$ (1)°	$T = 173$ (2) K
$\gamma = 118.676$ (1)°	Block, colourless
$V = 2730.83$ (9) Å^3	0.41 × 0.30 × 0.29 mm

Data collection

Bruker APEXII CCD area-detector diffractometer	10730 independent reflections
Radiation source: fine-focus sealed tube	7721 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.044$
$T = 173$(2) K	$\theta_{max} = 26.0^\circ$
φ and ω scans	$\theta_{min} = 0.9^\circ$
Absorption correction: integration [face-indexed absorption corrections carried out with XPREP (Bruker, 2005)]	$h = -14 \rightarrow 14$
$T_{min} = 0.373$, $T_{max} = 0.477$	$k = -14 \rightarrow 14$
42983 measured reflections	$l = -28 \rightarrow 28$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.052$	H-atom parameters constrained
$wR(F^2) = 0.187$	$w = 1/[\sigma^2(F_o^2) + (0.113P)^2 + 1.1716P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.12$	$(\Delta/\sigma)_{max} = 0.001$
10730 reflections	$\Delta\rho_{max} = 1.41$ e Å^{-3}
649 parameters	$\Delta\rho_{min} = -1.41$ e Å^{-3}
102 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.2648 (4)	0.3135 (4)	0.83103 (19)	0.0297 (10)	
C2	0.3949 (4)	0.4079 (4)	0.82396 (18)	0.0280 (9)	
C3	0.4596 (4)	0.4022 (4)	0.77546 (18)	0.0271 (9)	
C4	0.3927 (4)	0.2972 (4)	0.73324 (18)	0.0284 (9)	
H4	0.4370	0.2907	0.7002	0.034*	
C5	0.2636 (4)	0.2017 (4)	0.73754 (18)	0.0285 (9)	
C6	0.2009 (4)	0.2118 (4)	0.78623 (19)	0.0294 (9)	
C7	0.1982 (4)	0.3215 (5)	0.88375 (19)	0.0354 (10)	
H7A	0.1008	0.2781	0.8736	0.042*	
H7B	0.2286	0.4126	0.8972	0.042*	
C8	0.0440 (4)	0.0068 (4)	0.8155 (2)	0.0342 (10)	
H8A	−0.0346	−0.0220	0.8383	0.041*	
H8B	0.1211	0.0234	0.8430	0.041*	
C9	0.1912 (4)	0.0826 (4)	0.69345 (18)	0.0294 (9)	
H9	0.0940	0.0537	0.6933	0.035*	
C10	0.1518 (4)	−0.1964 (4)	0.77947 (17)	0.0253 (9)	
C11	0.1310 (4)	−0.1024 (4)	0.75608 (18)	0.0270 (9)	

C12	0.2135 (4)	−0.0228 (4)	0.71655 (17)	0.0256 (9)
C13	0.3202 (4)	−0.0405 (4)	0.70139 (17)	0.0239 (8)
H13	0.3787	0.0140	0.6753	0.029*
C14	0.3437 (4)	−0.1343 (4)	0.72296 (17)	0.0223 (8)
C15	0.2598 (4)	−0.2102 (4)	0.76253 (17)	0.0251 (9)
C16	0.0631 (4)	−0.2791 (4)	0.82210 (19)	0.0335 (10)
H16A	0.0617	−0.3629	0.8190	0.040*
H16B	−0.0286	−0.2951	0.8121	0.040*
C17	0.3759 (4)	−0.2732 (4)	0.83114 (19)	0.0299 (9)
H17A	0.3872	−0.1954	0.8547	0.036*
H17B	0.3467	−0.3432	0.8573	0.036*
C18	0.4623 (4)	−0.1500 (4)	0.70673 (17)	0.0235 (8)
H18	0.4376	−0.2418	0.7099	0.028*
C19	0.6874 (4)	−0.0514 (4)	0.85005 (18)	0.0248 (9)
C20	0.5878 (4)	−0.1207 (4)	0.80484 (19)	0.0254 (9)
C21	0.5767 (4)	−0.0697 (4)	0.75303 (17)	0.0208 (8)
C22	0.6708 (4)	0.0567 (4)	0.74812 (17)	0.0227 (8)
H22	0.6656	0.0938	0.7131	0.027*
C23	0.7723 (4)	0.1315 (4)	0.79198 (17)	0.0217 (8)
C24	0.7765 (4)	0.0762 (4)	0.84305 (17)	0.0231 (8)
C25	0.6987 (5)	−0.1108 (4)	0.9045 (2)	0.0357 (10)
H25A	0.7936	−0.0742	0.9190	0.043*
H25B	0.6614	−0.2044	0.8949	0.043*
C26	0.8615 (4)	0.2342 (4)	0.92645 (18)	0.0301 (10)
H26A	0.8973	0.2351	0.9670	0.036*
H26B	0.7656	0.2061	0.9272	0.036*
C27	0.8734 (4)	0.2700 (4)	0.78705 (17)	0.0232 (8)
H27	0.9546	0.2880	0.8128	0.028*
C28	0.8035 (4)	0.4716 (4)	0.90174 (17)	0.0238 (9)
C29	0.8498 (4)	0.3950 (4)	0.87391 (17)	0.0228 (8)
C30	0.8234 (4)	0.3565 (4)	0.81336 (17)	0.0220 (8)
C31	0.7456 (4)	0.3949 (4)	0.78090 (17)	0.0236 (8)
H31	0.7265	0.3694	0.7397	0.028*
C32	0.6944 (4)	0.4697 (4)	0.80646 (18)	0.0250 (9)
C33	0.7244 (4)	0.5066 (4)	0.86678 (17)	0.0240 (8)
C34	0.8352 (4)	0.5136 (4)	0.96568 (18)	0.0286 (9)
H34A	0.8344	0.5957	0.9740	0.034*
H34B	0.9251	0.5277	0.9783	0.034*
C35	0.5449 (4)	0.5140 (4)	0.91094 (18)	0.0279 (9)
H35A	0.5229	0.4250	0.9174	0.034*
H35B	0.5383	0.5562	0.9485	0.034*
C36	0.6030 (4)	0.5056 (4)	0.77138 (19)	0.0305 (10)
H36	0.6134	0.5865	0.7924	0.037*
C37	0.2275 (5)	0.1072 (5)	0.62994 (18)	0.0360 (11)
H37A	0.3228	0.1331	0.6284	0.043*
H37B	0.2144	0.1793	0.6185	0.043*
C38	0.1437 (5)	−0.0115 (5)	0.58520 (18)	0.0424 (12)
H38A	0.1488	−0.0861	0.5991	0.051*
H38B	0.0496	−0.0315	0.5835	0.051*

C39	0.1889 (5)	0.0076 (5)	0.52436 (18)	0.0475 (13)	
H39A	0.1933	0.0878	0.5125	0.057*	
H39B	0.2800	0.0187	0.5255	0.057*	
C40	0.1015 (6)	−0.1002 (6)	0.47847 (19)	0.0566 (15)	
H40A	0.0102	−0.1120	0.4773	0.068*	
H40B	0.0978	−0.1805	0.4899	0.068*	
C41	0.1496 (7)	−0.0772 (7)	0.4167 (2)	0.080 (2)	
H41A	0.1602	0.0055	0.4064	0.120*	
H41B	0.0842	−0.1462	0.3879	0.120*	
H41C	0.2352	−0.0762	0.4163	0.120*	
C42	0.4991 (4)	−0.1216 (4)	0.64416 (17)	0.0279 (9)	
H42A	0.5816	−0.1262	0.6389	0.033*	
H42B	0.5183	−0.0327	0.6391	0.033*	
C43	0.3914 (4)	−0.2131 (5)	0.59580 (19)	0.0372 (11)	
H43A	0.3669	−0.3026	0.6025	0.045*	
H43B	0.3112	−0.2033	0.5988	0.045*	
C44	0.4348 (5)	−0.1893 (5)	0.5340 (2)	0.0407 (11)	
H44A	0.4597	−0.0994	0.5279	0.049*	
H44B	0.5157	−0.1981	0.5316	0.049*	
C45	0.3352 (6)	−0.2749 (6)	0.4848 (2)	0.0535 (14)	
H45A	0.2546	−0.2653	0.4863	0.064*	
H45B	0.3094	−0.3651	0.4906	0.064*	
C46	0.3868 (6)	−0.2465 (6)	0.4223 (2)	0.0617 (16)	
H46A	0.4129	−0.1573	0.4162	0.093*	
H46B	0.3160	−0.3042	0.3920	0.093*	
H46C	0.4637	−0.2604	0.4197	0.093*	
C47	0.9170 (4)	0.2961 (4)	0.72461 (18)	0.0292 (9)	
H47A	0.9383	0.2294	0.7090	0.035*	
H47B	0.8425	0.2901	0.6985	0.035*	
C48	1.0383 (5)	0.4283 (5)	0.7235 (2)	0.0488 (14)	
H48A	1.0107	0.4941	0.7320	0.059*	
H48B	1.1050	0.4400	0.7559	0.059*	
C49	1.1046 (14)	0.4535 (19)	0.6669 (4)	0.064 (2)	0.681 (5)
H49A	1.1883	0.5363	0.6735	0.077*	0.681 (5)
H49B	1.1283	0.3854	0.6572	0.077*	0.681 (5)
C50	1.0233 (9)	0.4583 (9)	0.6152 (4)	0.076 (2)	0.681 (5)
H50A	1.0735	0.4733	0.5800	0.091*	0.681 (5)
H50B	0.9405	0.3750	0.6071	0.091*	0.681 (5)
C51	0.9896 (11)	0.5626 (10)	0.6269 (5)	0.090 (3)	0.681 (5)
H51A	0.9374	0.5655	0.5923	0.135*	0.681 (5)
H51B	1.0716	0.6450	0.6351	0.135*	0.681 (5)
H51C	0.9375	0.5462	0.6611	0.135*	0.681 (5)
C49A	1.081 (4)	0.462 (4)	0.6627 (9)	0.068 (3)	0.319 (5)
H49C	1.0012	0.4284	0.6340	0.082*	0.319 (5)
H49D	1.1307	0.5565	0.6626	0.082*	0.319 (5)
C50A	1.167 (2)	0.4054 (19)	0.6450 (8)	0.070 (3)	0.319 (5)
H50C	1.2477	0.4468	0.6730	0.084*	0.319 (5)
H50D	1.1187	0.3137	0.6521	0.084*	0.319 (5)
C51A	1.211 (2)	0.411 (2)	0.5848 (8)	0.088 (5)	0.319 (5)

H51D	1.1986	0.3260	0.5702	0.132*	0.319 (5)
H51E	1.3055	0.4743	0.5862	0.132*	0.319 (5)
H51F	1.1589	0.4346	0.5583	0.132*	0.319 (5)
C52	0.6385 (5)	0.5344 (5)	0.7090 (2)	0.0457 (12)	
H52A	0.7363	0.5879	0.7101	0.055*	0.681 (5)
H52B	0.6133	0.4524	0.6851	0.055*	0.681 (5)
H52C	0.6598	0.4683	0.6924	0.055*	0.319 (5)
H52D	0.5580	0.5222	0.6854	0.055*	0.319 (5)
C53	0.5770 (9)	0.5997 (9)	0.6787 (3)	0.067 (2)*	0.681 (5)
H53A	0.6236	0.6910	0.6951	0.080*	0.681 (5)
H53B	0.4839	0.5625	0.6888	0.080*	0.681 (5)
C54	0.5754 (8)	0.5953 (13)	0.6128 (4)	0.115 (3)*	0.681 (5)
H54A	0.5335	0.5044	0.5961	0.138*	0.681 (5)
H54B	0.5193	0.6314	0.5980	0.138*	0.681 (5)
C55	0.7097 (9)	0.6669 (14)	0.5908 (4)	0.124 (3)*	0.681 (5)
H55A	0.7701	0.6400	0.6102	0.149*	0.681 (5)
H55B	0.7462	0.7599	0.6023	0.149*	0.681 (5)
C56	0.7070 (13)	0.6444 (14)	0.5237 (4)	0.122 (4)*	0.681 (5)
H56A	0.7972	0.6936	0.5118	0.183*	0.681 (5)
H56B	0.6489	0.6724	0.5043	0.183*	0.681 (5)
H56C	0.6733	0.5528	0.5122	0.183*	0.681 (5)
C53A	0.7517 (16)	0.6654 (12)	0.7093 (7)	0.072 (5)*	0.319 (5)
H53C	0.8321	0.6666	0.7277	0.086*	0.319 (5)
H53D	0.7339	0.7248	0.7347	0.086*	0.319 (5)
C54A	0.781 (2)	0.7159 (16)	0.6503 (7)	0.103 (4)*	0.319 (5)
H54C	0.7186	0.7469	0.6387	0.123*	0.319 (5)
H54D	0.8722	0.7903	0.6539	0.123*	0.319 (5)
C55A	0.772 (2)	0.620 (3)	0.6022 (8)	0.120 (4)*	0.319 (5)
H55C	0.7929	0.5568	0.6197	0.144*	0.319 (5)
H55D	0.8397	0.6643	0.5746	0.144*	0.319 (5)
C56A	0.635 (2)	0.548 (3)	0.5675 (11)	0.116 (5)*	0.319 (5)
H56D	0.6049	0.4553	0.5637	0.174*	0.319 (5)
H56E	0.6400	0.5774	0.5282	0.174*	0.319 (5)
H56F	0.5714	0.5639	0.5886	0.174*	0.319 (5)
O1	0.0691 (3)	0.1223 (3)	0.79143 (14)	0.0344 (7)	
O2	0.0211 (3)	−0.0925 (3)	0.77090 (13)	0.0326 (7)	
O3	0.2756 (3)	−0.3082 (3)	0.78403 (13)	0.0279 (6)	
O4	0.4997 (3)	−0.2486 (3)	0.81165 (13)	0.0291 (7)	
O5	0.8766 (3)	0.1446 (3)	0.88846 (12)	0.0265 (6)	
O6	0.9272 (3)	0.3609 (3)	0.90898 (12)	0.0256 (6)	
O7	0.6788 (3)	0.5819 (3)	0.89468 (12)	0.0278 (6)	
O8	0.4525 (3)	0.5112 (3)	0.86706 (13)	0.0312 (7)	
Br1	0.24027 (5)	0.23895 (5)	0.94766 (2)	0.04566 (17)	
Br2	0.12420 (6)	−0.19738 (6)	0.90338 (2)	0.05765 (19)	
Br3	0.60254 (6)	−0.07854 (7)	0.96640 (3)	0.0609 (2)	
Br4	0.70324 (6)	0.38183 (5)	1.00981 (2)	0.04434 (17)	
O1W	0.467 (2)	0.126 (2)	0.8609 (10)	0.157 (11)	0.415 (19)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.034 (2)	0.039 (3)	0.029 (2)	0.029 (2)	−0.0028 (18)	−0.0017 (19)
C2	0.036 (2)	0.030 (2)	0.029 (2)	0.026 (2)	−0.0053 (18)	−0.0003 (18)
C3	0.039 (2)	0.027 (2)	0.025 (2)	0.024 (2)	−0.0018 (17)	0.0045 (17)
C4	0.038 (2)	0.033 (2)	0.022 (2)	0.024 (2)	−0.0010 (17)	0.0034 (18)
C5	0.037 (2)	0.036 (2)	0.022 (2)	0.028 (2)	−0.0070 (17)	−0.0017 (18)
C6	0.029 (2)	0.035 (2)	0.031 (2)	0.023 (2)	−0.0047 (17)	−0.0026 (19)
C7	0.035 (2)	0.046 (3)	0.034 (2)	0.029 (2)	−0.0023 (19)	−0.007 (2)
C8	0.034 (2)	0.039 (3)	0.031 (2)	0.020 (2)	0.0049 (19)	−0.005 (2)
C9	0.031 (2)	0.036 (2)	0.024 (2)	0.020 (2)	−0.0050 (17)	−0.0038 (18)
C10	0.0234 (19)	0.024 (2)	0.020 (2)	0.0056 (17)	0.0008 (15)	−0.0059 (17)
C11	0.0211 (19)	0.033 (2)	0.022 (2)	0.0108 (18)	−0.0010 (16)	−0.0082 (18)
C12	0.027 (2)	0.029 (2)	0.0187 (19)	0.0136 (18)	−0.0043 (16)	−0.0073 (17)
C13	0.026 (2)	0.023 (2)	0.0174 (19)	0.0080 (17)	−0.0008 (15)	−0.0043 (16)
C14	0.0183 (18)	0.020 (2)	0.0205 (19)	0.0045 (16)	−0.0036 (15)	−0.0089 (16)
C15	0.0236 (19)	0.019 (2)	0.025 (2)	0.0059 (17)	−0.0020 (16)	−0.0062 (17)
C16	0.032 (2)	0.034 (3)	0.028 (2)	0.010 (2)	0.0076 (18)	−0.0020 (19)
C17	0.032 (2)	0.026 (2)	0.031 (2)	0.0128 (19)	0.0072 (18)	0.0066 (19)
C18	0.0242 (19)	0.018 (2)	0.026 (2)	0.0094 (17)	0.0041 (16)	−0.0031 (16)
C19	0.029 (2)	0.028 (2)	0.025 (2)	0.0196 (19)	0.0029 (16)	0.0027 (17)
C20	0.028 (2)	0.017 (2)	0.034 (2)	0.0124 (17)	0.0074 (17)	0.0008 (17)
C21	0.0228 (19)	0.019 (2)	0.023 (2)	0.0127 (17)	0.0060 (15)	−0.0006 (16)
C22	0.0224 (19)	0.023 (2)	0.023 (2)	0.0109 (17)	0.0065 (15)	−0.0002 (16)
C23	0.0213 (18)	0.024 (2)	0.024 (2)	0.0138 (17)	0.0053 (15)	−0.0037 (16)
C24	0.0196 (18)	0.026 (2)	0.026 (2)	0.0137 (17)	0.0015 (15)	−0.0038 (17)
C25	0.042 (3)	0.033 (3)	0.038 (3)	0.023 (2)	0.001 (2)	0.005 (2)
C26	0.036 (2)	0.034 (2)	0.024 (2)	0.021 (2)	−0.0018 (17)	−0.0047 (18)
C27	0.0205 (18)	0.022 (2)	0.0209 (19)	0.0058 (17)	0.0032 (15)	−0.0032 (16)
C28	0.0202 (18)	0.018 (2)	0.027 (2)	0.0042 (16)	0.0033 (16)	−0.0030 (16)
C29	0.0177 (18)	0.020 (2)	0.024 (2)	0.0035 (16)	0.0043 (15)	−0.0008 (16)
C30	0.0192 (18)	0.0158 (19)	0.0221 (19)	0.0015 (16)	0.0059 (15)	−0.0021 (16)
C31	0.026 (2)	0.0158 (19)	0.0201 (19)	0.0031 (16)	0.0049 (15)	−0.0005 (16)
C32	0.026 (2)	0.0154 (19)	0.028 (2)	0.0050 (17)	0.0048 (16)	0.0051 (17)
C33	0.027 (2)	0.0145 (19)	0.025 (2)	0.0058 (17)	0.0052 (16)	0.0010 (16)
C34	0.031 (2)	0.023 (2)	0.027 (2)	0.0111 (18)	0.0013 (17)	−0.0060 (18)
C35	0.034 (2)	0.031 (2)	0.024 (2)	0.022 (2)	−0.0033 (17)	−0.0066 (18)
C36	0.043 (2)	0.022 (2)	0.029 (2)	0.018 (2)	0.0030 (19)	0.0043 (18)
C37	0.044 (3)	0.044 (3)	0.025 (2)	0.026 (2)	−0.0048 (19)	−0.001 (2)
C38	0.049 (3)	0.050 (3)	0.030 (2)	0.028 (3)	−0.004 (2)	−0.003 (2)
C39	0.048 (3)	0.060 (4)	0.035 (3)	0.028 (3)	−0.003 (2)	−0.004 (2)
C40	0.062 (4)	0.069 (4)	0.039 (3)	0.034 (3)	0.001 (3)	−0.011 (3)
C41	0.097 (5)	0.090 (5)	0.045 (4)	0.041 (4)	0.013 (3)	−0.012 (3)
C42	0.026 (2)	0.026 (2)	0.026 (2)	0.0086 (18)	0.0065 (16)	−0.0047 (18)
C43	0.036 (2)	0.035 (3)	0.029 (2)	0.010 (2)	0.0023 (19)	−0.010 (2)
C44	0.043 (3)	0.038 (3)	0.034 (3)	0.015 (2)	0.005 (2)	−0.007 (2)

C45	0.062 (3)	0.062 (4)	0.030 (3)	0.028 (3)	−0.001 (2)	−0.008 (3)
C46	0.067 (4)	0.072 (4)	0.038 (3)	0.031 (3)	−0.007 (3)	−0.017 (3)
C47	0.027 (2)	0.026 (2)	0.025 (2)	0.0059 (18)	0.0076 (17)	−0.0041 (18)
C48	0.049 (3)	0.037 (3)	0.036 (3)	0.001 (2)	0.015 (2)	−0.001 (2)
C49	0.066 (5)	0.051 (4)	0.053 (3)	0.009 (3)	0.028 (3)	0.007 (3)
C50	0.078 (5)	0.060 (4)	0.053 (3)	0.003 (3)	0.019 (3)	0.011 (3)
C51	0.083 (6)	0.079 (6)	0.083 (6)	0.020 (5)	−0.007 (5)	0.008 (5)
C49A	0.070 (5)	0.052 (4)	0.056 (4)	0.007 (4)	0.027 (4)	0.008 (4)
C50A	0.073 (5)	0.052 (5)	0.062 (4)	0.009 (4)	0.029 (4)	0.008 (4)
C51A	0.098 (9)	0.064 (9)	0.073 (7)	0.013 (7)	0.044 (7)	0.002 (8)
C52	0.065 (3)	0.036 (3)	0.035 (3)	0.023 (3)	0.007 (2)	0.008 (2)
O1	0.0295 (15)	0.0422 (19)	0.0380 (17)	0.0238 (15)	0.0001 (13)	−0.0039 (15)
O2	0.0227 (14)	0.0355 (17)	0.0377 (17)	0.0140 (13)	0.0029 (12)	−0.0073 (14)
O3	0.0290 (15)	0.0151 (14)	0.0335 (16)	0.0062 (12)	0.0019 (12)	0.0001 (12)
O4	0.0298 (15)	0.0166 (14)	0.0405 (17)	0.0103 (12)	0.0067 (13)	0.0052 (13)
O5	0.0255 (14)	0.0285 (16)	0.0263 (15)	0.0156 (13)	−0.0057 (11)	−0.0060 (12)
O6	0.0222 (13)	0.0242 (15)	0.0250 (14)	0.0081 (12)	−0.0030 (11)	−0.0049 (12)
O7	0.0321 (15)	0.0197 (15)	0.0307 (16)	0.0127 (13)	0.0029 (12)	−0.0051 (12)
O8	0.0400 (16)	0.0283 (16)	0.0332 (16)	0.0245 (14)	−0.0036 (13)	−0.0063 (13)
Br1	0.0529 (3)	0.0517 (3)	0.0312 (3)	0.0251 (3)	0.0032 (2)	−0.0019 (2)
Br2	0.0725 (4)	0.0600 (4)	0.0348 (3)	0.0269 (3)	0.0122 (3)	0.0052 (3)
Br3	0.0680 (4)	0.0706 (4)	0.0414 (3)	0.0293 (3)	0.0125 (3)	0.0181 (3)
Br4	0.0657 (3)	0.0457 (3)	0.0279 (3)	0.0309 (3)	0.0146 (2)	0.0047 (2)
O1W	0.149 (17)	0.17 (2)	0.19 (2)	0.095 (15)	0.071 (14)	0.038 (15)

Geometric parameters (Å, °)

C1—C6	1.402 (6)	C37—H37A	0.9900
C1—C2	1.403 (6)	C37—H37B	0.9900
C1—C7	1.480 (6)	C38—C39	1.499 (5)
C2—C3	1.381 (6)	C38—H38A	0.9900
C2—O8	1.386 (5)	C38—H38B	0.9900
C3—C4	1.391 (6)	C39—C40	1.497 (5)
C3—C36	1.527 (6)	C39—H39A	0.9900
C4—C5	1.386 (6)	C39—H39B	0.9900
C4—H4	0.9500	C40—C41	1.532 (6)
C5—C6	1.384 (6)	C40—H40A	0.9900
C5—C9	1.523 (6)	C40—H40B	0.9900
C6—O1	1.392 (5)	C41—H41A	0.9800
C7—Br1	1.974 (5)	C41—H41B	0.9800
C7—H7A	0.9900	C41—H41C	0.9800
C7—H7B	0.9900	C42—C43	1.534 (6)
C8—O1	1.420 (6)	C42—H42A	0.9900
C8—O2	1.423 (5)	C42—H42B	0.9900
C8—H8A	0.9900	C43—C44	1.517 (6)
C8—H8B	0.9900	C43—H43A	0.9900
C9—C12	1.519 (6)	C43—H43B	0.9900
C9—C37	1.535 (6)	C44—C45	1.488 (6)
C9—H9	1.0000	C44—H44A	0.9900

C10—C11	1.385 (6)	C44—H44B	0.9900
C10—C15	1.400 (6)	C45—C46	1.566 (8)
C10—C16	1.489 (6)	C45—H45A	0.9900
C11—O2	1.383 (5)	C45—H45B	0.9900
C11—C12	1.396 (6)	C46—H46A	0.9800
C12—C13	1.398 (6)	C46—H46B	0.9800
C13—C14	1.385 (6)	C46—H46C	0.9800
C13—H13	0.9500	C47—C48	1.528 (6)
C14—C15	1.386 (6)	C47—H47A	0.9900
C14—C18	1.524 (5)	C47—H47B	0.9900
C15—O3	1.382 (5)	C48—C49	1.506 (7)
C16—Br2	1.964 (4)	C48—C49A	1.508 (9)
C16—H16A	0.9900	C48—H48A	0.9900
C16—H16B	0.9900	C48—H48B	0.9900
C17—O4	1.412 (5)	C49—C50	1.488 (9)
C17—O3	1.420 (5)	C49—H49A	0.9900
C17—H17A	0.9900	C49—H49B	0.9900
C17—H17B	0.9900	C50—C51	1.484 (9)
C18—C21	1.512 (5)	C50—H50A	0.9900
C18—C42	1.521 (5)	C50—H50B	0.9900
C18—H18	1.0000	C51—H51A	0.9800
C19—C20	1.387 (6)	C51—H51B	0.9800
C19—C24	1.395 (6)	C51—H51C	0.9800
C19—C25	1.497 (6)	C49A—C50A	1.498 (10)
C20—C21	1.390 (6)	C49A—H49C	0.9900
C20—O4	1.394 (5)	C49A—H49D	0.9900
C21—C22	1.389 (6)	C50A—C51A	1.484 (10)
C22—C23	1.388 (5)	C50A—H50C	0.9900
C22—H22	0.9500	C50A—H50D	0.9900
C23—C24	1.384 (6)	C51A—H51D	0.9800
C23—C27	1.514 (5)	C51A—H51E	0.9800
C24—O5	1.391 (4)	C51A—H51F	0.9800
C25—Br3	1.966 (5)	C52—C53	1.461 (7)
C25—H25A	0.9900	C52—C53A	1.478 (8)
C25—H25B	0.9900	C52—H52A	0.9900
C26—O5	1.414 (5)	C52—H52B	0.9900
C26—O6	1.424 (5)	C52—H52C	0.9900
C26—H26A	0.9900	C52—H52D	0.9900
C26—H26B	0.9900	C53—C54	1.499 (5)
C27—C30	1.512 (5)	C53—H52D	0.8681
C27—C47	1.534 (5)	C53—H53A	0.9900
C27—H27	1.0000	C53—H53B	0.9900
C28—C29	1.397 (6)	C54—C55	1.497 (5)
C28—C33	1.404 (6)	C54—H54A	0.9900
C28—C34	1.479 (5)	C54—H54B	0.9900
C29—O6	1.384 (5)	C55—C56	1.533 (6)
C29—C30	1.397 (5)	C55—H55A	0.9900
C30—C31	1.388 (6)	C55—H55B	0.9900
C31—C32	1.399 (6)	C56—H56A	0.9800

C31—H31	0.9500	C56—H56B	0.9800
C32—C33	1.390 (6)	C56—H56C	0.9800
C32—C36	1.523 (6)	C53A—C54A	1.499 (5)
C33—O7	1.379 (5)	C53A—H53C	0.9900
C34—Br4	1.964 (4)	C53A—H53D	0.9900
C34—H34A	0.9900	C54A—C55A	1.497 (5)
C34—H34B	0.9900	C54A—H54C	0.9900
C35—O8	1.410 (5)	C54A—H54D	0.9900
C35—O7	1.438 (5)	C55A—C56A	1.532 (6)
C35—H35A	0.9900	C55A—H55C	0.9900
C35—H35B	0.9900	C55A—H55D	0.9900
C36—C52	1.516 (6)	C56A—H56D	0.9800
C36—H36	1.0000	C56A—H56E	0.9800
C37—C38	1.544 (6)	C56A—H56F	0.9800
C6—C1—C2	117.3 (4)	C41—C40—H40B	109.0
C6—C1—C7	121.6 (4)	H40A—C40—H40B	107.8
C2—C1—C7	121.1 (4)	C40—C41—H41A	109.5
C3—C2—O8	121.7 (4)	C40—C41—H41B	109.5
C3—C2—C1	122.2 (4)	H41A—C41—H41B	109.5
O8—C2—C1	116.0 (4)	C40—C41—H41C	109.5
C2—C3—C4	117.9 (4)	H41A—C41—H41C	109.5
C2—C3—C36	119.7 (4)	H41B—C41—H41C	109.5
C4—C3—C36	122.3 (4)	C18—C42—C43	114.3 (3)
C5—C4—C3	122.4 (4)	C18—C42—H42A	108.7
C5—C4—H4	118.8	C43—C42—H42A	108.7
C3—C4—H4	118.8	C18—C42—H42B	108.7
C6—C5—C4	118.1 (4)	C43—C42—H42B	108.7
C6—C5—C9	118.7 (4)	H42A—C42—H42B	107.6
C4—C5—C9	123.2 (4)	C44—C43—C42	113.2 (4)
C5—C6—O1	120.6 (4)	C44—C43—H43A	108.9
C5—C6—C1	122.0 (4)	C42—C43—H43A	108.9
O1—C6—C1	117.3 (4)	C44—C43—H43B	108.9
C1—C7—Br1	109.9 (3)	C42—C43—H43B	108.9
C1—C7—H7A	109.7	H43A—C43—H43B	107.8
Br1—C7—H7A	109.7	C45—C44—C43	116.1 (4)
C1—C7—H7B	109.7	C45—C44—H44A	108.3
Br1—C7—H7B	109.7	C43—C44—H44A	108.3
H7A—C7—H7B	108.2	C45—C44—H44B	108.3
O1—C8—O2	112.0 (4)	C43—C44—H44B	108.3
O1—C8—H8A	109.2	H44A—C44—H44B	107.4
O2—C8—H8A	109.2	C44—C45—C46	113.5 (5)
O1—C8—H8B	109.2	C44—C45—H45A	108.9
O2—C8—H8B	109.2	C46—C45—H45A	108.9
H8A—C8—H8B	107.9	C44—C45—H45B	108.9
C12—C9—C5	108.1 (3)	C46—C45—H45B	108.9
C12—C9—C37	113.4 (4)	H45A—C45—H45B	107.7
C5—C9—C37	113.7 (4)	C45—C46—H46A	109.5
C12—C9—H9	107.1	C45—C46—H46B	109.5
C5—C9—H9	107.1	H46A—C46—H46B	109.5

C37—C9—H9	107.1	C45—C46—H46C	109.5
C11—C10—C15	118.1 (4)	H46A—C46—H46C	109.5
C11—C10—C16	121.0 (4)	H46B—C46—H46C	109.5
C15—C10—C16	120.9 (4)	C48—C47—C27	112.2 (3)
O2—C11—C10	118.0 (4)	C48—C47—H47A	109.2
O2—C11—C12	119.8 (4)	C27—C47—H47A	109.2
C10—C11—C12	122.1 (4)	C48—C47—H47B	109.2
C11—C12—C13	117.3 (4)	C27—C47—H47B	109.2
C11—C12—C9	120.9 (4)	H47A—C47—H47B	107.9
C13—C12—C9	121.8 (4)	C49—C48—C47	116.2 (8)
C14—C13—C12	122.6 (4)	C49A—C48—C47	114.4 (18)
C14—C13—H13	118.7	C49—C48—H48A	108.2
C12—C13—H13	118.7	C49A—C48—H48A	97.5
C13—C14—C15	117.9 (4)	C47—C48—H48A	108.2
C13—C14—C18	121.6 (4)	C49—C48—H48B	108.2
C15—C14—C18	120.4 (4)	C49A—C48—H48B	119.9
O3—C15—C14	120.5 (4)	C47—C48—H48B	108.2
O3—C15—C10	117.4 (4)	H48A—C48—H48B	107.4
C14—C15—C10	121.9 (4)	C50—C49—C48	115.0 (8)
C10—C16—Br2	111.0 (3)	C50—C49—H49A	108.5
C10—C16—H16A	109.4	C48—C49—H49A	108.5
Br2—C16—H16A	109.4	C50—C49—H49B	108.5
C10—C16—H16B	109.4	C48—C49—H49B	108.5
Br2—C16—H16B	109.4	H49A—C49—H49B	107.5
H16A—C16—H16B	108.0	C51—C50—C49	110.5 (10)
O4—C17—O3	113.0 (3)	C51—C50—H50A	109.6
O4—C17—H17A	109.0	C49—C50—H50A	109.6
O3—C17—H17A	109.0	C51—C50—H50B	109.6
O4—C17—H17B	109.0	C49—C50—H50B	109.6
O3—C17—H17B	109.0	H50A—C50—H50B	108.1
H17A—C17—H17B	107.8	C50—C51—H51A	109.5
C21—C18—C42	112.9 (3)	C50—C51—H51B	109.5
C21—C18—C14	107.8 (3)	H51A—C51—H51B	109.5
C42—C18—C14	114.4 (3)	C50—C51—H51C	109.5
C21—C18—H18	107.1	H51A—C51—H51C	109.5
C42—C18—H18	107.1	H51B—C51—H51C	109.5
C14—C18—H18	107.1	C50A—C49A—C48	109.9 (14)
C20—C19—C24	117.4 (4)	C50A—C49A—H49C	109.7
C20—C19—C25	121.4 (4)	C48—C49A—H49C	109.7
C24—C19—C25	121.2 (4)	C50A—C49A—H49D	109.7
C19—C20—C21	122.9 (4)	C48—C49A—H49D	109.7
C19—C20—O4	117.3 (4)	H49C—C49A—H49D	108.2
C21—C20—O4	119.7 (4)	C51A—C50A—C49A	122.1 (18)
C22—C21—C20	116.8 (4)	C51A—C50A—H50C	106.8
C22—C21—C18	123.5 (4)	C49A—C50A—H50C	106.8
C20—C21—C18	119.7 (3)	C51A—C50A—H50D	106.8
C23—C22—C21	123.1 (4)	C49A—C50A—H50D	106.8
C23—C22—H22	118.5	H50C—C50A—H50D	106.7
C21—C22—H22	118.5	C50A—C51A—H51D	109.5

C24—C23—C22	117.5 (4)	C50A—C51A—H51E	109.5
C24—C23—C27	119.5 (3)	H51D—C51A—H51E	109.5
C22—C23—C27	123.0 (4)	C50A—C51A—H51F	109.5
C23—C24—O5	120.7 (4)	H51D—C51A—H51F	109.5
C23—C24—C19	122.3 (4)	H51E—C51A—H51F	109.5
O5—C24—C19	116.9 (3)	C53—C52—C53A	78.0 (9)
C19—C25—Br3	110.5 (3)	C53—C52—C36	116.0 (5)
C19—C25—H25A	109.6	C53A—C52—C36	110.2 (7)
Br3—C25—H25A	109.6	C53—C52—H52A	108.3
C19—C25—H25B	109.6	C36—C52—H52A	108.3
Br3—C25—H25B	109.6	C53—C52—H52B	108.3
H25A—C25—H25B	108.1	C53A—C52—H52B	132.7
O5—C26—O6	112.9 (3)	C36—C52—H52B	108.3
O5—C26—H26A	109.0	H52A—C52—H52B	107.4
O6—C26—H26A	109.0	C53—C52—H52C	128.9
O5—C26—H26B	109.0	C53A—C52—H52C	111.8
O6—C26—H26B	109.0	C36—C52—H52C	107.2
H26A—C26—H26B	107.8	H52A—C52—H52C	81.1
C30—C27—C23	109.2 (3)	C53A—C52—H52D	112.7
C30—C27—C47	114.4 (3)	C36—C52—H52D	107.8
C23—C27—C47	113.5 (3)	H52A—C52—H52D	138.5
C30—C27—H27	106.3	H52B—C52—H52D	79.7
C23—C27—H27	106.3	H52C—C52—H52D	107.0
C47—C27—H27	106.3	C52—C53—C54	117.6 (8)
C29—C28—C33	117.5 (4)	C54—C53—H52D	103.1
C29—C28—C34	121.5 (4)	C52—C53—H53A	107.9
C33—C28—C34	121.0 (4)	C54—C53—H53A	107.9
O6—C29—C30	120.8 (3)	H52D—C53—H53A	145.1
O6—C29—C28	116.8 (3)	C52—C53—H53B	107.9
C30—C29—C28	122.4 (4)	C54—C53—H53B	107.9
C31—C30—C29	117.6 (4)	H52D—C53—H53B	77.4
C31—C30—C27	123.3 (3)	H53A—C53—H53B	107.2
C29—C30—C27	119.1 (4)	C55—C54—C53	114.3 (4)
C30—C31—C32	122.6 (4)	C55—C54—H54A	108.7
C30—C31—H31	118.7	C53—C54—H54A	108.7
C32—C31—H31	118.7	C55—C54—H54B	108.7
C33—C32—C31	117.7 (4)	C53—C54—H54B	108.7
C33—C32—C36	119.8 (4)	H54A—C54—H54B	107.6
C31—C32—C36	122.5 (4)	C54—C55—C56	113.0 (5)
O7—C33—C32	120.7 (4)	C54—C55—H55A	109.0
O7—C33—C28	117.1 (3)	C56—C55—H55A	109.0
C32—C33—C28	122.2 (4)	C54—C55—H55B	109.0
C28—C34—Br4	109.6 (3)	C56—C55—H55B	109.0
C28—C34—H34A	109.8	H55A—C55—H55B	107.8
Br4—C34—H34A	109.8	C55—C56—H56A	109.5
C28—C34—H34B	109.8	C55—C56—H56B	109.5
Br4—C34—H34B	109.8	H56A—C56—H56B	109.5
H34A—C34—H34B	108.2	C55—C56—H56C	109.5
O8—C35—O7	111.7 (3)	H56A—C56—H56C	109.5

O8—C35—H35A	109.3	H56B—C56—H56C	109.5
O7—C35—H35A	109.3	C52—C53A—C54A	115.9 (12)
O8—C35—H35B	109.3	C52—C53A—H53C	108.3
O7—C35—H35B	109.3	C54A—C53A—H53C	108.3
H35A—C35—H35B	107.9	C52—C53A—H53D	108.3
C52—C36—C32	114.1 (4)	C54A—C53A—H53D	108.3
C52—C36—C3	114.3 (4)	H53C—C53A—H53D	107.4
C32—C36—C3	108.1 (3)	C55A—C54A—C53A	114.3 (4)
C52—C36—H36	106.6	C55A—C54A—H54C	108.7
C32—C36—H36	106.6	C53A—C54A—H54C	108.7
C3—C36—H36	106.6	C55A—C54A—H54D	108.7
C9—C37—C38	112.8 (4)	C53A—C54A—H54D	108.7
C9—C37—H37A	109.0	H54C—C54A—H54D	107.6
C38—C37—H37A	109.0	C54A—C55A—C56A	113.0 (5)
C9—C37—H37B	109.0	C54A—C55A—H55C	109.0
C38—C37—H37B	109.0	C56A—C55A—H55C	109.0
H37A—C37—H37B	107.8	C54A—C55A—H55D	109.0
C39—C38—C37	112.8 (4)	C56A—C55A—H55D	109.0
C39—C38—H38A	109.0	H55C—C55A—H55D	107.8
C37—C38—H38A	109.0	C55A—C56A—H56D	109.5
C39—C38—H38B	109.0	C55A—C56A—H56E	109.5
C37—C38—H38B	109.0	H56D—C56A—H56E	109.5
H38A—C38—H38B	107.8	C55A—C56A—H56F	109.5
C40—C39—C38	114.3 (4)	H56D—C56A—H56F	109.5
C40—C39—H39A	108.7	H56E—C56A—H56F	109.5
C38—C39—H39A	108.7	C6—O1—C8	117.5 (3)
C40—C39—H39B	108.7	C11—O2—C8	116.6 (3)
C38—C39—H39B	108.7	C15—O3—C17	116.9 (3)
H39A—C39—H39B	107.6	C20—O4—C17	115.8 (3)
C39—C40—C41	113.0 (5)	C24—O5—C26	116.8 (3)
C39—C40—H40A	109.0	C29—O6—C26	115.8 (3)
C41—C40—H40A	109.0	C33—O7—C35	115.4 (3)
C39—C40—H40B	109.0	C2—O8—C35	118.2 (3)
C6—C1—C2—C3	−0.6 (6)	C33—C28—C29—C30	2.0 (6)
C7—C1—C2—C3	179.5 (4)	C34—C28—C29—C30	−178.6 (4)
C6—C1—C2—O8	176.2 (3)	O6—C29—C30—C31	−179.6 (3)
C7—C1—C2—O8	−3.8 (6)	C28—C29—C30—C31	−1.4 (6)
O8—C2—C3—C4	−177.7 (3)	O6—C29—C30—C27	3.8 (5)
C1—C2—C3—C4	−1.2 (6)	C28—C29—C30—C27	−178.0 (3)
O8—C2—C3—C36	5.6 (6)	C23—C27—C30—C31	−89.7 (4)
C1—C2—C3—C36	−177.9 (4)	C47—C27—C30—C31	38.8 (5)
C2—C3—C4—C5	1.9 (6)	C23—C27—C30—C29	86.7 (4)
C36—C3—C4—C5	178.5 (4)	C47—C27—C30—C29	−144.8 (4)
C3—C4—C5—C6	−0.7 (6)	C29—C30—C31—C32	0.2 (6)
C3—C4—C5—C9	−176.8 (4)	C27—C30—C31—C32	176.7 (4)
C4—C5—C6—O1	176.7 (4)	C30—C31—C32—C33	0.4 (6)
C9—C5—C6—O1	−7.1 (6)	C30—C31—C32—C36	−176.6 (4)
C4—C5—C6—C1	−1.2 (6)	C31—C32—C33—O7	179.1 (3)
C9—C5—C6—C1	175.1 (4)	C36—C32—C33—O7	−3.9 (6)

C2—C1—C6—C5	1.8 (6)	C31—C32—C33—C28	0.2 (6)
C7—C1—C6—C5	−178.2 (4)	C36—C32—C33—C28	177.2 (4)
C2—C1—C6—O1	−176.1 (3)	C29—C28—C33—O7	179.8 (3)
C7—C1—C6—O1	3.8 (6)	C34—C28—C33—O7	0.3 (5)
C6—C1—C7—Br1	92.4 (4)	C29—C28—C33—C32	−1.3 (6)
C2—C1—C7—Br1	−87.6 (4)	C34—C28—C33—C32	179.2 (4)
C6—C5—C9—C12	−83.5 (4)	C29—C28—C34—Br4	−86.8 (4)
C4—C5—C9—C12	92.5 (5)	C33—C28—C34—Br4	92.7 (4)
C6—C5—C9—C37	149.7 (4)	C33—C32—C36—C52	145.4 (4)
C4—C5—C9—C37	−34.3 (5)	C31—C32—C36—C52	−37.7 (5)
C15—C10—C11—O2	177.3 (3)	C33—C32—C36—C3	−86.2 (4)
C16—C10—C11—O2	−3.5 (6)	C31—C32—C36—C3	90.7 (5)
C15—C10—C11—C12	0.2 (6)	C2—C3—C36—C52	−148.6 (4)
C16—C10—C11—C12	179.3 (4)	C4—C3—C36—C52	34.9 (6)
O2—C11—C12—C13	−177.6 (3)	C2—C3—C36—C32	83.2 (5)
C10—C11—C12—C13	−0.5 (6)	C4—C3—C36—C32	−93.3 (4)
O2—C11—C12—C9	5.2 (5)	C12—C9—C37—C38	61.2 (5)
C10—C11—C12—C9	−177.7 (4)	C5—C9—C37—C38	−174.7 (4)
C5—C9—C12—C11	86.0 (4)	C9—C37—C38—C39	−173.7 (4)
C37—C9—C12—C11	−146.9 (4)	C37—C38—C39—C40	−174.0 (5)
C5—C9—C12—C13	−91.1 (4)	C38—C39—C40—C41	179.5 (5)
C37—C9—C12—C13	36.0 (5)	C21—C18—C42—C43	172.5 (4)
C11—C12—C13—C14	1.4 (6)	C14—C18—C42—C43	−63.7 (5)
C9—C12—C13—C14	178.6 (3)	C18—C42—C43—C44	−175.5 (4)
C12—C13—C14—C15	−2.0 (5)	C42—C43—C44—C45	179.8 (5)
C12—C13—C14—C18	−178.8 (3)	C43—C44—C45—C46	−179.3 (5)
C13—C14—C15—O3	177.8 (3)	C30—C27—C47—C48	65.3 (5)
C18—C14—C15—O3	−5.4 (5)	C23—C27—C47—C48	−168.4 (4)
C13—C14—C15—C10	1.7 (5)	C27—C47—C48—C49	168.8 (6)
C18—C14—C15—C10	178.5 (3)	C27—C47—C48—C49A	−176.7 (11)
C11—C10—C15—O3	−177.0 (3)	C49A—C48—C49—C50	−19 (9)
C16—C10—C15—O3	3.8 (5)	C47—C48—C49—C50	66.4 (14)
C11—C10—C15—C14	−0.8 (6)	C48—C49—C50—C51	60.5 (15)
C16—C10—C15—C14	−180.0 (4)	C49—C48—C49A—C50A	17 (8)
C11—C10—C16—Br2	−87.0 (4)	C47—C48—C49A—C50A	−83 (3)
C15—C10—C16—Br2	92.2 (4)	C48—C49A—C50A—C51A	173 (2)
C13—C14—C18—C21	91.7 (4)	C32—C36—C52—C53	−165.1 (5)
C15—C14—C18—C21	−85.0 (4)	C3—C36—C52—C53	69.8 (6)
C13—C14—C18—C42	−34.8 (5)	C32—C36—C52—C53A	−78.9 (10)
C15—C14—C18—C42	148.5 (4)	C3—C36—C52—C53A	156.0 (10)
C24—C19—C20—C21	2.2 (6)	C53A—C52—C53—C54	91.1 (9)
C25—C19—C20—C21	−178.1 (4)	C36—C52—C53—C54	−162.2 (6)
C24—C19—C20—O4	179.3 (3)	C52—C53—C54—C55	−67.0 (15)
C25—C19—C20—O4	−1.0 (6)	C53—C54—C55—C56	171.6 (12)
C19—C20—C21—C22	−0.4 (6)	C53—C52—C53A—C54A	−55.5 (16)
O4—C20—C21—C22	−177.5 (3)	C36—C52—C53A—C54A	−169.1 (14)
C19—C20—C21—C18	−177.8 (4)	C52—C53A—C54A—C55A	−42 (2)
O4—C20—C21—C18	5.1 (5)	C53A—C54A—C55A—C56A	93 (2)
C42—C18—C21—C22	35.5 (5)	C5—C6—O1—C8	84.5 (5)

C14—C18—C21—C22	−91.8 (4)	C1—C6—O1—C8	−97.6 (4)
C42—C18—C21—C20	−147.2 (4)	O2—C8—O1—C6	−92.3 (4)
C14—C18—C21—C20	85.4 (4)	C10—C11—O2—C8	100.7 (4)
C20—C21—C22—C23	−0.1 (6)	C12—C11—O2—C8	−82.1 (5)
C18—C21—C22—C23	177.2 (4)	O1—C8—O2—C11	91.4 (4)
C21—C22—C23—C24	−1.2 (6)	C14—C15—O3—C17	80.7 (5)
C21—C22—C23—C27	−178.9 (3)	C10—C15—O3—C17	−103.1 (4)
C22—C23—C24—O5	178.9 (3)	O4—C17—O3—C15	−92.0 (4)
C27—C23—C24—O5	−3.3 (5)	C19—C20—O4—C17	99.4 (4)
C22—C23—C24—C19	3.1 (6)	C21—C20—O4—C17	−83.4 (5)
C27—C23—C24—C19	−179.1 (3)	O3—C17—O4—C20	93.9 (4)
C20—C19—C24—C23	−3.6 (6)	C23—C24—O5—C26	79.7 (5)
C25—C19—C24—C23	176.7 (4)	C19—C24—O5—C26	−104.3 (4)
C20—C19—C24—O5	−179.6 (3)	O6—C26—O5—C24	−94.1 (4)
C25—C19—C24—O5	0.8 (6)	C30—C29—O6—C26	−80.2 (4)
C20—C19—C25—Br3	−92.9 (4)	C28—C29—O6—C26	101.5 (4)
C24—C19—C25—Br3	86.8 (4)	O5—C26—O6—C29	94.3 (4)
C24—C23—C27—C30	−86.5 (4)	C32—C33—O7—C35	82.8 (4)
C22—C23—C27—C30	91.1 (4)	C28—C33—O7—C35	−98.3 (4)
C24—C23—C27—C47	144.4 (4)	O8—C35—O7—C33	−93.6 (4)
C22—C23—C27—C47	−37.9 (5)	C3—C2—O8—C35	−81.4 (5)
C33—C28—C29—O6	−179.8 (3)	C1—C2—O8—C35	101.9 (4)
C34—C28—C29—O6	−0.3 (5)	O7—C35—O8—C2	91.9 (4)

Fig. 1

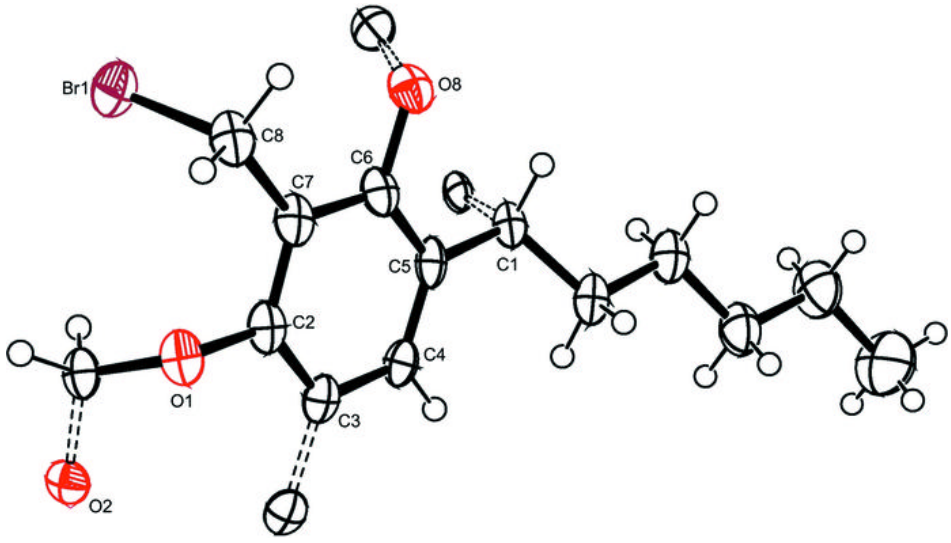


Fig. 2

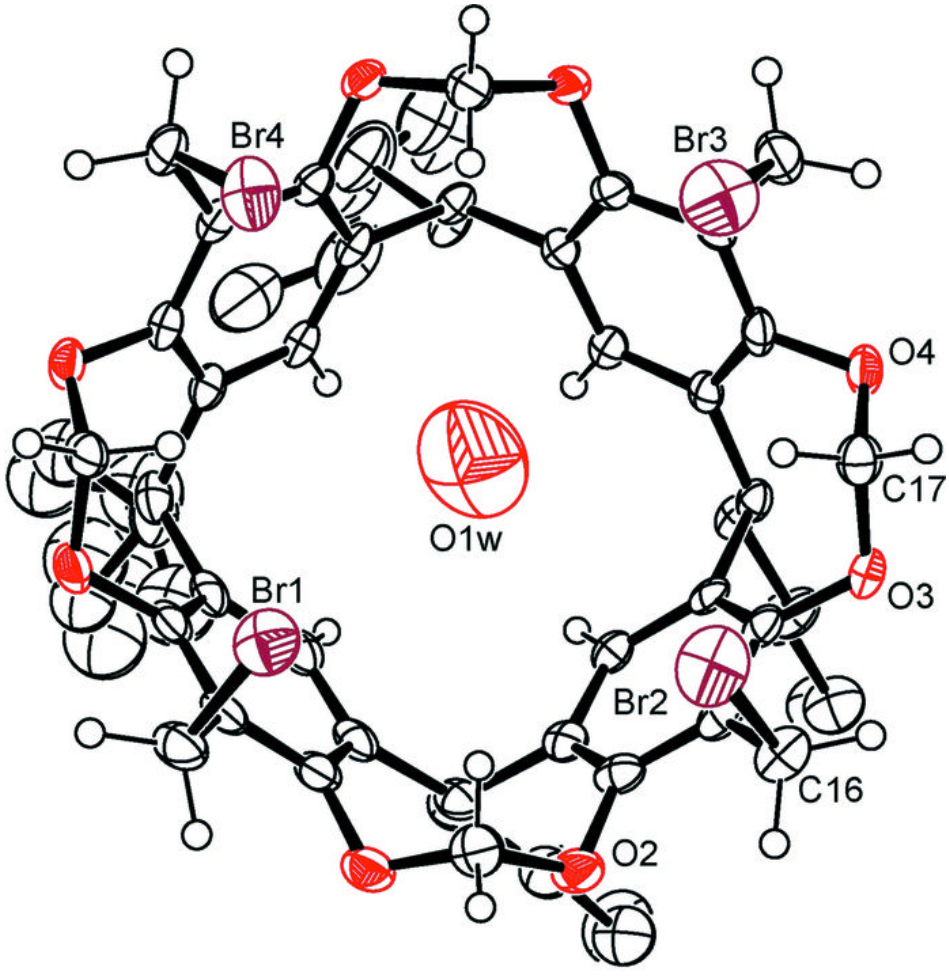


Fig. 3

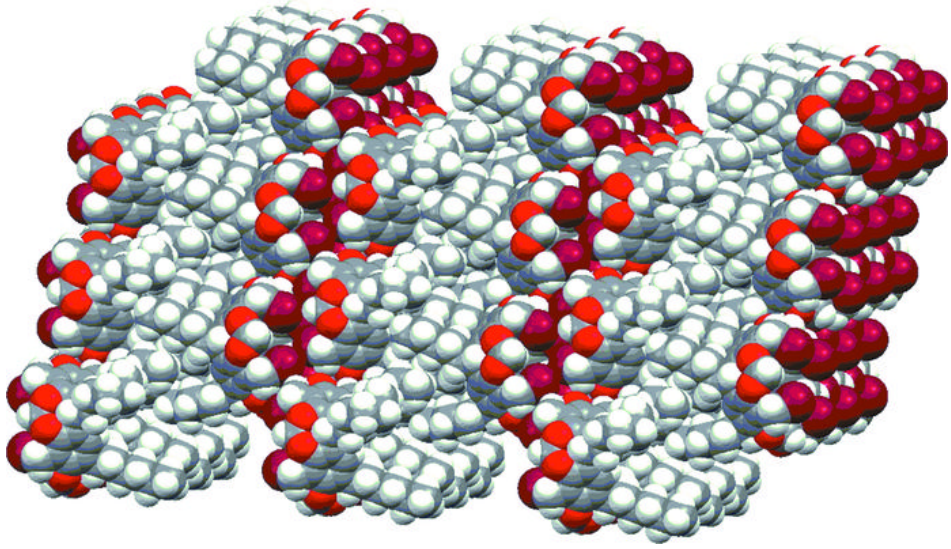


Fig. 4

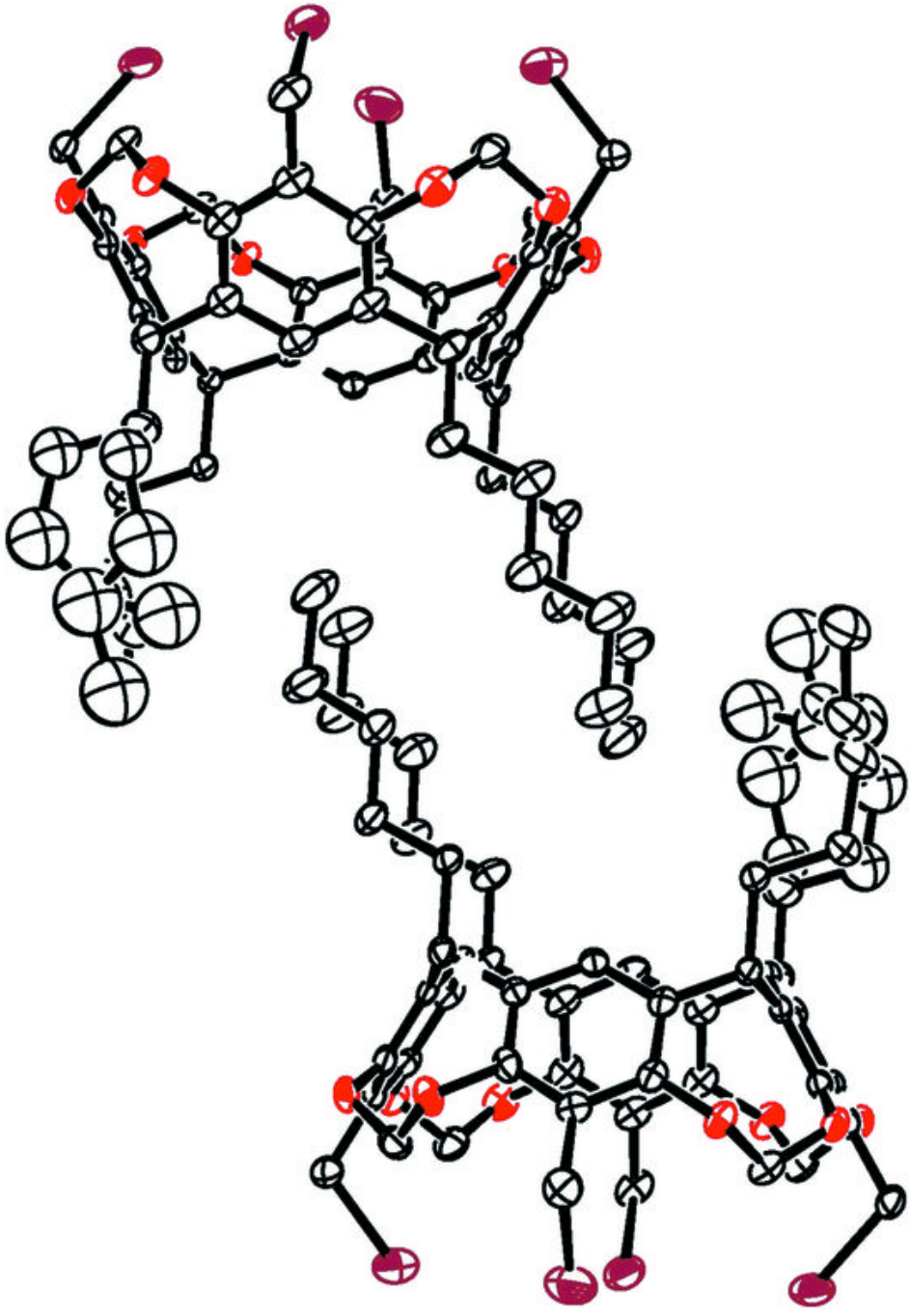
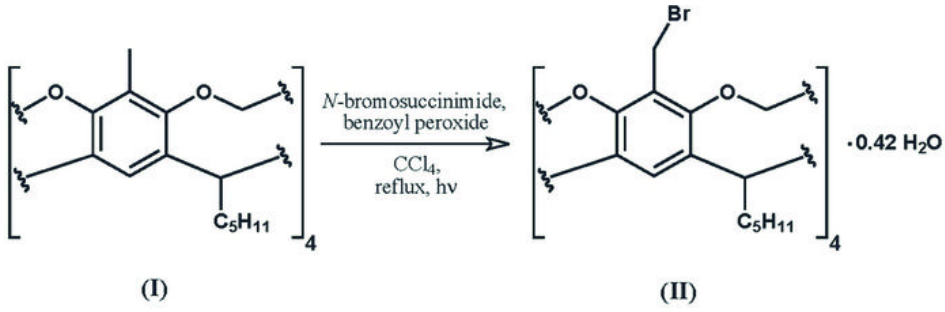


Fig. 5


Br
N-bromosuccinimide,
benzoyl peroxide
CCl4,
reflux, hν
·0.42 H2O
C5H11
4
(I)
(II)