SHORT PAPER

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Synthesis, structure and chiral inclusion crystallisation of tetrakis(4-ethynylphenyl)ethylene derivatives

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Achiral host molecules, tetrakis(4-ethynylphenyl)ethylene **3** and tetrakis(4-bromoethynylphenyl)ethylene **4**, formed chiral host–guest inclusion crystals with achiral guest molecules via weak intermolecular interactions.

Keywords: achiral host molecules, chiral crystallisation, host–guest inclusion crystals

Chiral crystallisation of achiral molecules has attracted increasing interest not only for absolute asymmetric synthesis but also for the development of new chiral materials for applications such as nonlinear optics.[1] Recently, we have found that tetrakis(4-bromophenyl)ethylene **1** forms chiral inclusion crystals with various achiral guest molecules via halogen-halogen interactions.[2] Here we report the synthesis and chiral inclusion crystallisation of tetrakis(4-ethynylphenyl)ethylene **3** and tetrakis(4-bromoethynylphenyl)ethylene **4** with achiral guest compounds. The X-ray structures of **3** and its inclusion complex with dioxane are also reported.

When a mixture of tetrakis(4-bromophenyl)ethylene **1**[2] and 2-methylbut-3-yn-2-ol was heated in the presence of $Pd(PPh_3)_2$, CuI, and PPh_3 in Et_3N under reflux for 7 h, the alcohol **2** was obtained in 49% yield. Treatment of **2** with KOH in MeOH–toluene under reflux for 6 h gave tetrakis(4-ethynylphenyl)ethylene **3** as yellow prisms in 73% yield. Further treatment of **3** with NaOBr in dioxane-H_2O for 3 h afforded tetrakis(4-bromoethynylphenyl)ethylene **4** as yellow prisms in 95% yield.

Interestingly, host compound **3** was found to form a chiral crystals both as its own crystals and as inclusion crystals with achiral guest compounds. For example, **3** formed chiral crystals by recrystallisation from toluene. The chirality of the crystal was easily determined by CD spectra in Nujol mulls. (Fig. 1) Host compound **3** formed chiral inclusion crystals with acetone (1:2), tetrahydropyrane (1:2), dioxane (1:2), morphorine (1:2) and pyridine (1:1) and these inclusion crystals showed similar CD spectra in Nujol mulls. (Table 1) Host compound **4** also formed chiral inclusion crystals with tetrahydropyran (1:1), toluene (1:1) and pyridine (1:3), although **4** formed achiral inclusion crystals with acetone (1:1), cyclopentanone (1:1), dioxane (1:1), morpholine (1:4), DMSO (1:3) and DMF (1:1).

X-ray analysis of **3** showed that a crystallographic two-fold axis exists in the centre of the C1–C1′ bond of the molecule (space group: C2). (Fig. 2) The molecule **3** has a chiral propeller-shaped structure (molecular symmetry C2), and the dihedral angles of the phenyl planes are 86.65(7)°(phenyl A:C2~C7 and phenyl B:C10~C15) and 50.03(9)°(phenyl A and phenyl B':C10′~C15′). (Fig. 3) (prime means a symmetry-related phenyl group or atoms, symmetry operation: -*x*, *y*, -*z*).

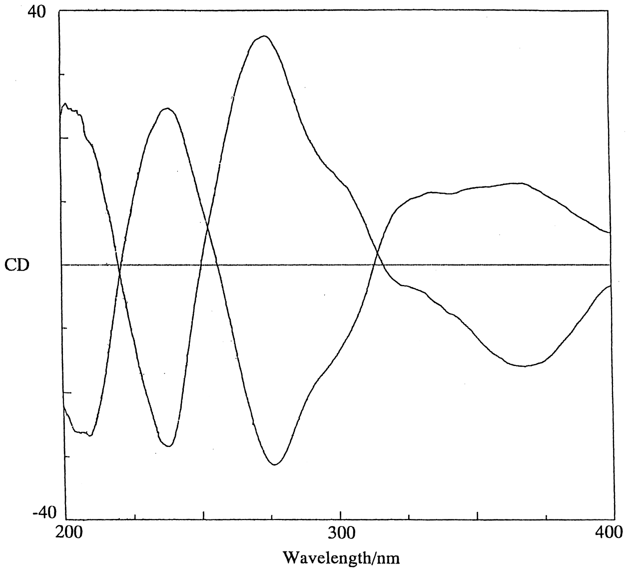

Fig. 1 CD spectra of the enantiomeric crystals of **3** as Nujol mulls showing right- and left-handed chiral propeller of **3**.

Table 1 Host: guest molar ratio of inclusion complexes of **3** and **4**[a]

Guest	3	4
Acetone	1:2[c]	1:1
Cyclopentanone	—[b]	1:1
Tetrahydropyrane	1:2[c]	1:1[c]
Dioxane	1:2[c]	1:1
Morphorine	1:2[c]	1:4
DMSO	—	1:3
DMF	—	1:1
Toluene	—	1:1[c]
Pyridine	1:1[c]	1:3[c]

[a]The host:guest ratio was determined by TG and NMR.

[b]no inclusion occurred.

[c]Chiral crystal.

In the crystal structure of a 1:2 complex of **3** with dioxane, the molecule of **3** also has a chiral conformation (same molecular symmetry C_2) (space group:$P2_12_12_1$). Two crystallographic independent dioxane molecules are included in chiral cavities formed by weak hydrogen bonding between the H atoms of the alkynyl and phenyl groups of **3** and the O atoms of dioxane molecules. (Fig. 4) The intermolecular distances

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

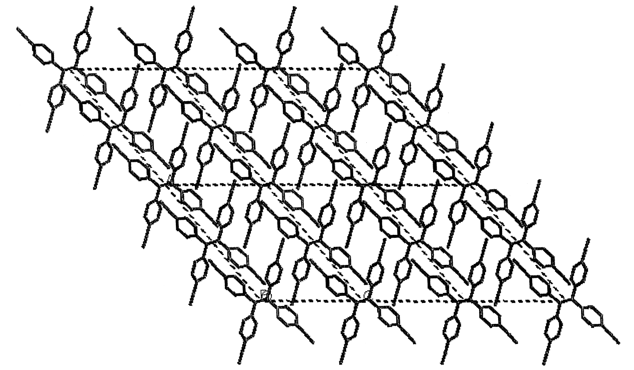


Fig. 2 Packing diagram of **3** viewed down the *b* axis.

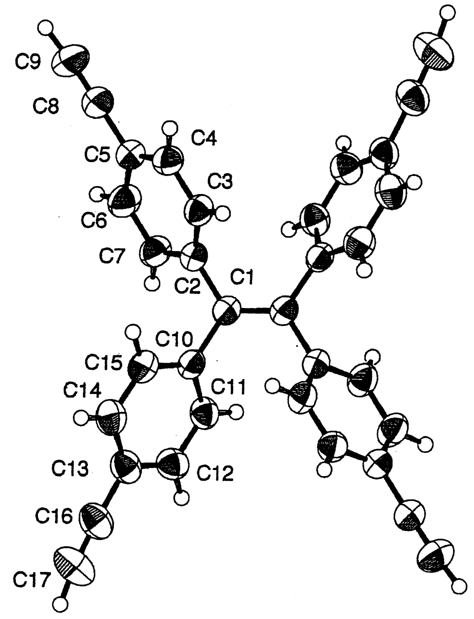


Fig. 3 Ortep drawing of **3**.

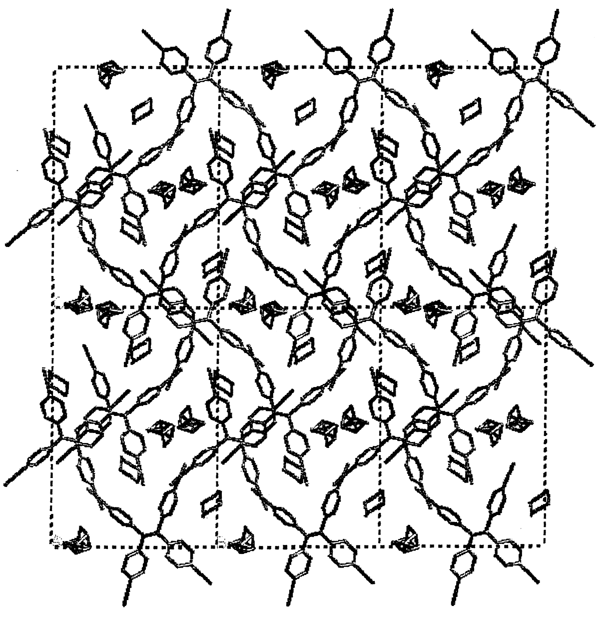


Fig. 4 Packing diagram of the 1:2 inclusion complex of **3** with dioxane viewed down the *a* axis.

Table 2 Bond lengths (Å) and angles (deg) for **3**.

C(1)–C(1)[a]	1.351(3	C(7)–C(2)–C(3)	118.36(16)
C(1)–C(10)	1.492(2)	C(7)–C(2)–C(1)	120.31(17)
C(1)–C(2)	1.494(2)	C(3)–C(2)–C(1)	121.32(17)
C(2)–C(7)	1.388(3)	C(4)–C(3)–C(2)	120.75(18)
C(2)–C(3)	1.398(3)	C(3)–C(4)–C(5)	120.68(19)
C(3)–C(4)	1.376(3)	C(4)–C(5)–C(6)	118.95(17)
C(4)–C(5)	1.389(3)	C(4)–C(5)–C(8)	120.6(2)
C(5)–C(6)	1.394(3)	C(6)–C(5)–C(8)	120.5(2)
C(5)–C(8)	1.441(3)	C(7)–C(6)–C(5)	120.2(2)
C(6)–C(7)	1.383(3)	C(6)–C(7)–C(2)	121.04(19)
C(8)–C(9)	1.162(3)	C(9)–C(8)–C(5)	178.3(3)
C(10)–C(11)	1.391(3)	C(11)–C(10)–C(15)	118.15(16)
C(10)–C(15)	1.396(3)	C(11)–C(10)–C(1)	121.93(17)
C(11)–C(12)	1.388(3)	C(15)–C(10)–C(1)	119.92(17)
C(12)–C(13)	1.387(3)	C(12)–C(11)–C(10)	120.74(19)
C(13)–C(14)	1.389(3)	C(13)–C(12)–C(11)	120.5(2)
C(13)–C(16)	1.443(3)	C(12)–C(13)–C(14)	119.22(17)
C(14)–C(15)	1.385(3)	C(12)–C(13)–C(16)	119.6(2)
C(16)–C(17)	1.168(3)	C(14)–C(13)–C(16)	121.1(2)
C(1)[a]–C(1)–C(10)	122.60(18)	C(15)–C(14)–C(13)	120.0(2)
C(1)[a]–C(1)–C(2)	122.88(18)	C(14)–C(15)–C(10)	121.2(2)
C(10)–C(1)–C(2)	114.49(13)	C(17)–C(16)–C(13)	177.0(2)

Symmetry transformations used to generate equivalent atoms.[a] –x,y,-z

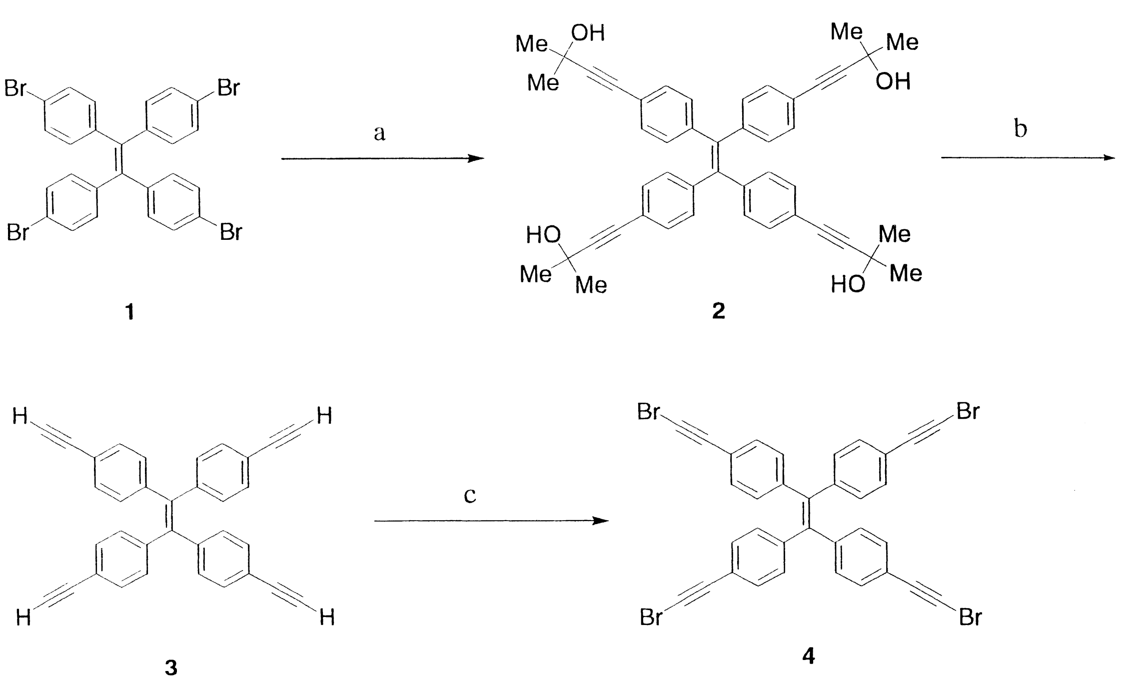
Table 3 Bond lengths [Å] for 1:2 inclusion complex of **3** with dioxane

C(1)–C(18)	1.346(5)	C(23)–C(24)	1.399(6)
C(1)–C(10)	1.488(5)	C(25)–C(26)	1.177(6)
C(1)–C(2)	1.501(5)	C(27)–C(28)	1.384(5)
C(2)–C(3)	1.390(5)	C(27)–C(32)	1.385(5)
C(2)–C(7)	1.399(5)	C(28)–C(29)	1.378(5)
C(3)–C(4)	1.383(5)	C(29)–C(30)	1.403(5)
C(4)–C(5)	1.389(6)	C(30)–C(31)	1.391(5)
C(5)–C(6)	1.395(5)	C(30)–C(33)	1.437(6)
C(5)–C(8)	1.449(5)	C(31)–C(32)	1.387(5)
C(6)–C(7)	1.383(5)	C(33)–C(34)	1.179(6)
C(8)–C(9)	1.168(6)	O(41)–C(42)	1.412(6)
C(10)–C(11)	1.394(5)	O(41)–C(46)	1.414(6)
C(10)–C(15)	1.402(5)	C(42)–C(43)	1.480(7)
C(11)–C(12)	1.383(5)	C(43)–O(44)	1.425(6)
C(12)–C(13)	1.409(5)	O(44)–C(45)	1.419(6)
C(13)–C(14)	1.399(5)	C(45)–C(46)	1.498(7)
C(13)–C(16)	1.437(5)	O(35)–C(36A)	1.439(7)
C(14)–C(15)	1.376(5)	O(35)–C(40)	1.456(7)
C(16)–C(17)	1.183(5)	O(35)–C(36B)	1.61(2)
C(18)–C(19)	1.492(5)	C(36A)–C(37A	1.505(9)
C(18)–C(27)	1.505(5)	C(37A)–O(38A)	1.425(7)
C(19)–C(24)	1.382(5)	O(38A)–C(39)	1.431(7)
C(19)–C(20)	1.400(5)	C(36B)–C(37B)	1.52(3)
C(20)–C(21)	1.388(5)	C(37B)–O(38B)	1.53(3)
C(21)–C(22)	1.390(6)	O(38B)–C(39)	1.38(2)
C(22)–C(23)	1.390(6)	C(39)–C(40)	1.553(8)
C(22)–C(25)	1.436(5)		

between dioxane O atoms and H atoms of the alkynyl and phenyl groups of compound **3**, are 2.35(9) Å (O38A and H9: symmetry operation for H: $-x+1.5$, $-y+1$, $z-0.5$) and 2.55(4) Å (O41 and H11, symmetry operation for H: $x+1$, y, z), respectively.

Experimental

Preparation of **3**: A mixture of tetrakis(4-bromophenyl)ethylene **1** (28.3 g, 44.61 mmol) and 2-methylbut-3-yn-2-ol (15.0 g, 178.45 mmol) was heated in the presence of $Pd(PPh_3)_2$ (0.5 g), CuI (0.1 g), and PPh_3 (0.8 g) in Et_3N (300 ml) under reflux for 7 h. Et_3N was evaporated under reduced pressure and the resultant oil was extracted with ether, washed with water and dried over $MgSO_4$. Removal of solvent gave the alcohol **2** as yellow prisms (14.4 g, 49% yield) after recrystallisation from MeOH. **2**: m.p. 275–287°C; ν_{max} (Nujol)/cm^{-1} 3308 (OH); λ_{max}/nm ($CHCl_3$) 207 (ε 89000), 242 (48000), 275 (83000), 339 (32000); δH (300 MHz, $CDCl_3$) 1.60 (s, 24H), 1.97 (s, 4H), 6.91 (d, J = 8.6 Hz, 8H), 7.16 (d, J = 8.6 Hz, 8H) (Found: C,



Scheme 1 Reagents and conditions: (a) 2-methyl-3-butyn-2-ol, $PdC_{12}(PPh_3)_2$, CuI, PPh_3, Et_3N, reflux for 7 h, 49%; (b) KOH, MeOH-toluene, reflux for 6 h, 73%; (c) NaOBr, dioxane-H_2O, r.t., 3 h, 95%.

79.02; H, 6.59. Calc. For $C_{46}H_{44}O_4$: C, 83.60; H, 6.71). A mixture of **2** (14.0 g, 21 mmol) and KOH (7.1 g) in MeOH-toluene (5:1, 100 ml) was heated under reflux for 6 h. The reaction mixture was washed with water and dried over $MgSO_4$. Removal of solvent gave tetrakis(4-ethynylphenyl)ethylene **3** as yellow prisms (6.63 g, 73% yield) after recrystallisation from toluene. **3**: polymerisation occurred upon heating at 250°C without melting; nmax (Nujol)/cm^{-1} 3270, 3290 (C∫CH); λ_{max}/nm (CHC13) 243 (ε 34000), 271 (50000), 343 (23000); δH (300 MHz, $CDCl_3$) 3.07 (s, 4H), 6.94 (d, *J* = 8.0 Hz, 8H), 7.25 (d, *J* = 8.0 Hz, 8H) (Found: C, 95.48; H, 4.95. Calc. For $C_{34}H_{20}$: C, 95.30; H, 4.70).

Preparation of **4:** Bromine (22.4 g, 140 mmol) was added to aq. NaOH (14.0 g, 350 mmol in 300 ml) stirred at 0–5°C. **3** (3.0 g, 7 mmol) in dioxane (50 ml) was added dropwise to the above mixture over a period of 15 min. The reaction mixture was stirred for another 3 h without further cooling and poured into 50 ml of ice-cold water. The product was extracted with ether. Upon drying over $MgSO_4$ and removal of solvent, tetrakis(4-bromoethynylphenyl)ethylene **4** was obtained as yellow prisms (4.9 g, 95% yield). **4:** m.p. 153°C (decomp.); ν_{max} (Nujol)/cm^{-1} 2196 (C≡C); λ_{max}/nm ($CHCl_3$) 249 (ε 32000), 283 (55000), 351 (24000); δH (300 MHz, $CDCl_3$) 6.90 (d, *J* = 8.4 Hz, 8H), 7.19 (d, *J* = 8.4 Hz, 8H) (Found: C, 54.61; H, 1.95. Calc. For $C_{34}H_{16}Br_4$: C, 54.88; H, 2.17).

Preparation of inclusion crystals: Inclusion crystals of **3** and **4** were prepared by recrystallisation in the neat guest compounds. The host–guest ratios were determined by NMR and TG. The data are summarised in Table 1.

Measurement of CD spectra: CD spectra were recorded on a JASCO J-720 spectropolarimeter in Nujol mulls.

Crystallographic studies: The X-ray data for the crystal of **3** and the 1:2 inclusion crystal of **3** with dioxane were collected on a Bruker SMART 1000 diffractometer, using ω/2θ scan mode. The structures were solved by direct methods (SHELXS-97)[3] and refined by full-matrix least-squares refinement (SHELXL-97)[4].

Crystal data for **3**: C34H20, *M* = 428.50, monoclinic, space group *C*2, *Z* = 2, *a* = 16.546(3), *b* = 8.842(2), *c* = 11.178(2) Å, *V* = 1270.9(4) Å^3, *T* = 298(2) K, μ(Mo-Kα) = 0.63 cm^{-1}, 4078 reflections measured, 2263 unique (R_{int} = 0.0131), 2263 reflections with $I_0 > 2\sigma(I_0)$ used in refinement, *R* = 0.0484, *R*w = 0.0533. CCDC 163147.

Crystal data for 1:2 inclusion complex of **3** *with dioxane*: $C_{42}H_{36}O_4$, M = 604.71, orthorhombic, space group $P2_12_12_1$, *Z* = 4, *a* = 9.4415(10), *b* = 15.6602(17), *c* = 22.682(2) Å, *V* = 3353.7(6) Å^3, *T* = 198(2) K, μ(Mo-Kα) = 0.76 cm^{-1}, 14249 reflections measured, 5699 unique (R_{int} = 0.0335), 5699 reflections with $I_0 > 2\sigma(I_0)$ used in refinement, *R* = 0.0603, *R*w = 0.0871. CCDC 163148.

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Table 4 Bond angles [deg] for 1:2 inclusion complex of **3** with dioxane

C(1)–C(18)	1.346(5)	C(23)–C(24)	1.399(6)
C(18)–C(1)–C(10)	123.1(3)	C(23)–C(22)–C(21)	119.1(3)
C(18)–C(1)–C(2)	122.2(3)	C(23)–C(22)–C(25)	120.0(4)
C(10)–C(1)–C(2)	114.6(3)	C(21)–C(22)–C(25)	120.9(4)
C(3)–C(2)–C(7)	118.7(3)	C(22)–C(23)–C(24)	119.8(4)
C(3)–C(2)–C(1)	120.5(3)	C(19)–C(24)–C(23)	121.8(4)
C(7)–C(2)–C(1)	120.6(3)	C(26)–C(25)–C(22)	177.5(5)
C(4)–C(3)–C(2)	120.8(4)	C(28)–C(27)–C(32)	118.6(3)
C(3)–C(4)–C(5)	120.2(4)	C(28)–C(27)–C(18)	121.4(3)
C(4)–C(5)–C(6)	119.6(3)	C(32)–C(27)–C(18)	120.0(3)
C(4)–C(5)–C(8)	119.6(4)	C(29)–C(28)–C(27)	120.5(3)
C(6)–C(5)–C(8)	120.7(4)	C(28)–C(29)–C(30)	121.0(3)
C(7)–C(6)–C(5)	119.9(4)	C(31)–C(30)–C(29)	118.4(3)
C(6)–C(7)–C(2)	120.8(4)	C(31)–C(30)–C(33)	120.4(4)
C(9)–C(8)–C(5)	176.2(5)	C(29)–C(30)–C(33)	121.2(3)
C(11)–C(10)–C(15)	118.3(3)	C(32)–C(31)–C(30)	119.7(4)
C(11)–C(10)–C(1)	121.8(3)	C(27)–C(32)–C(31)	121.6(3)
C(15)–C(10)–C(1)	119.9(3)	C(34)–C(33)–C(30)	177.6(4)
C(12)–C(11)–C(10)	121.5(3)	C(42)–O(41)–C(46)	110.1(4)
C(11)–C(12)–C(13)	119.9(3)	O(41)–C(42)–C(43)	110.9(4)
C(14)–C(13)–C(12)	118.5(3)	O(44)–C(43)–C(42)	111.1(5)
C(14)–C(13)–C(16)	121.5(3)	C(45)–O(44)–C(43)	109.2(4)
C(12)–C(13)–C(16)	120.1(3)	O(44)–C(45)–C(46)	111.8(4)
C(15)–C(14)–C(13)	121.0(3)	O(41)–C(46)–C(45)	111.1(4)
C(14)–C(15)–C(10)	120.7(3)	C(36A)–O(35)–C(40)	108.1(4)
C(17)–C(16)–C(13)	177.3(4)	C(36A)–O(35)–C(36B)	94.6(10)
C(1)–C(18)–C(19)	122.9(3)	C(40)–O(35)–C(36B)	94.5(10)
C(1)–C(18)–C(27)	122.5(3)	O(35)–C(36A)–C(37A)	110.4(5)
C(19)–C(18)–C(27)	114.6(3)	O(38A)–C(37A)–C(36A)	107.9(5)
C(24)–C(19)–C(20)	117.4(3)	C(37A)–O(38A)–C(39)	111.4(4)
C(24)–C(19)–C(18)	121.0(3)	C(37A)–O(38A)–C(39)	111.4(4)
C(20)–C(19)–C(18)	121.4(3)	C(37B)–C(36B)–O(35)	107(2)
C(21)–C(20)–C(19)	121.5(4)	C(36B)–C(37B)–O(38B)	110(3)
C(20)–C(21)–C(22)	120.3(4)	C(39)–O(38B)–C(37B)	100(2)
O(38B)–C(39)–O(38A)	35.6(15)	O(38A)–C(39)–C(40)	104.3(5)
O(38B)–C(39)–C(40)	129.1(16)	O(35)–C(40)–C(39)	109.6(5)

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