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Cation binding resorcinarene bis-crowns: The effect of lower rim alkyl chain length to crystal packing and solid lipid nanoparticles

Kaisa Helttunen,* Kirsi Salorinne, Tahnie Barboza, Hélène Campos Barbosa, Aku Suhonen and Maija Nissinen*

A group of seven resorcinarene bis-crown ethers (CNBC5) with two polyether bridges at the upper rim and either propyl, butyl, pentyl, heptyl, nonyl, decyl or undecyl groups at the lower rim were synthesized and their binding properties with Cs⁺ were investigated by NMR titration. The bis-crowns form 1:2 complexes with Cs⁺ with binding constants of log K 4–5. Crystal structures of bis-crowns and their Cs⁺ and K⁺ complexes were studied and different packing motifs were found depending on the alkyl chain length. Short ethyl, propyl and butyl alkyl chains gave a layer or pillar packing where the polar and non-polar regions cannot be distinguished, whereas, longer pentyl and decyl chains formed bilayers.

Amphiphilic properties and self-assembly in water was studied by preparing solid lipid nanoparticles (SLN) from the bis-crowns. All investigated compounds formed stable SLNs showing amphiphilic character, which in the case of the short chain bis-crowns probably rises from their locked boat conformation separating the polar face of the molecule from the non-polar face.

Introduction

Combining host-guest chemistry and surfactant properties into a single molecule by structural design of supramolecules, nanoscale materials, i.e. films, particles or gels with host-guest functionality can be obtained. Calixarenes and resorcinarenes are macrocyclic supramolecular hosts well suited for this task since they have a concave binding cavity capable of binding various guest molecules or ions. Resorcinarenes can be easily converted into amphiphilic molecules using long aliphatic aldehydes in their synthesis resulting in hydrophobic chains below the binding site. The upper rim of the resorcinarene bowl has innate hydrophilic character because of the OH-functionalities derived from the resorcinol, and in addition, the upper rim is readily available for further functionalization to improve the binding affinity and selectivity. The self-assembly of amphiphilic calixarenes and resorcinarenes in water and at interfaces into mono/bilayers, thin films, vesicles and micelles, and properties of these assemblies have been studied avidly to extend the use of calixarenes.

Some recent examples of their potential applications include gene delivery, catalytic activity, liquid crystals and VOC sensing. In addition to host-guest properties, environmentally responsive functionalities, which change the organized structures from micelles into larger vesicle according to pH, have been prepared.

Solid lipid nanoparticles (SLN), or particles prepared from solid lipids, are the latest addition to the family of drug carrier structures since the introduction of liposomes and polymeric nanoparticles, which are prepared from liquid lipids. The preparation process of SLNs leads to particles with diameters from tens to few hundred or thousand nanometers, which can be loaded with drugs or other sensitive compounds and used for their protection and transport. Since calixarenes and resorcinarenes are usually solid materials at room temperature, they can be used for preparation of solid lipid nanoparticles and studies of their potential in encapsulation of biologically important guests, DNA and cell transfection and surface modification for drug targeting have been published.

Calixarenes and resorcinarenes with crown ether bridges connecting the hydroxyl groups are very selective cation receptors called calixcrowns. Depending on the number of oxygen donors and thus the length and geometry of the crown bridge, calixcrowns have very good affinity towards alkali and alkaline earth metal cations and ammonium ions. Resorcinarene bis-crowns and their K⁺, Cs⁺, Rb⁺ and Ag⁺ complexes have shown very interesting structural properties such as formation of layers, capsules and nanorods. Therefore, we have been interested in studying the effect of alkyl chain length in the crystal packing of the resorcinarene bis-crowns and their metal complexes, where it can (a) influence the twisting of the resorcinarene framework and (b) induce a layer or bilayer packing when the hydrophobic effect of the alkyl chains becomes strong enough. The alkyl chain length also affects the amphiphilic properties and self-assembly in water, which was studied by...
preparing SLNs out of series of resorcinarene bis-crowns with short, medium and long alkyl chains.

**Results**

**Synthesis and complexation studies**

A group of seven resorcinarene bis-crown ethers or CNBC5, where N denotes to the number of carbons at the lower rim alkyl group and 5 to the number of oxygen donors in each polyether bridge, were prepared by O-alkylation of the free hydroxyl groups of various tetramethoxy resorcinarenes† (Fig. 1). Propyl, butyl, pentyl, heptyl, nonyl, decyl and undecyl groups at the resorcinarene lower rim were chosen for structural comparison with the previously synthesized C2BC5,21,22 and to create amphiphilic bis-crowns. Synthesis was carried out in dry dimethyl formamide (DMF) using Cs₂CO₃ and ditosylated tetra(ethylene glycol) yielding tetramethoxy resorcinarene bis-crown ethers after purification as 15–30 % yields.

Complexation of the bis-crowns with an alkali metal cation, cesium hexafluorophosphate, was carried out using NMR titration in order to investigate if the lower rim alkyl chain length has an effect on the binding affinity. C3BC5, C5BC5, C9BC5 and C11BC5 bind Cs⁺ with the affinity of log K₁₂ 1.0–2.2 and total binding constant of log K₁₂ 4.0–5.0 (Table 1). C2BC5 has binding constant of log K₁₂ 1.75 for 1:1 complex,23 which falls at the same magnitude of order as now determined log K₁₁ values.

The second binding constant log K₁₂ is larger than the first binding constant for all investigated complexes. In case of C2BC5, K₁₂ was not determined because Job plot showed that intrinsic water concentration over 1 molar equivalent relative to the host leads to 1:1 complexation. For C3BC5–C11BC5 such a strong trend was not observed, water content being 1–2.5 molar equivalents except for the 13 mol. eq. for C11BC5. In all cases a 1:2 binding model gave better fits than the 1:1 model.

**Crystal structures**

**Resorcinarene bis-crowns**

Single crystals of resorcinarene bis-crowns were grown by slow evaporation from alcohol solutions. C4BC5 (structure C4) and C5BC5 (C5) crystallized in a triclinic P-1 without any solvent in their binding cavity or in the crystal lattice. Analysis of the conformational properties of individual molecules (Table 2) revealed that the bis-crowns are in a boat or slightly twisted boat conformation and upright aryl rings (A and C) are tilted towards the cavity with -8.3–10.7 deviational angels. Crown ether bridges are folded on top of the binding cavities closing the space inside.

<table>
<thead>
<tr>
<th>C3BC5</th>
<th>C5BC5</th>
<th>C9BC5</th>
<th>C11BC5</th>
</tr>
</thead>
<tbody>
<tr>
<td>log K₁₁</td>
<td>1.04 ± 0.18</td>
<td>1.59 ± 0.41</td>
<td>1.49 ± 0.60</td>
</tr>
<tr>
<td>log K₁₂</td>
<td>4.43 ± 0.03</td>
<td>4.62 ± 0.10</td>
<td>4.06 ± 0.19</td>
</tr>
</tbody>
</table>

Table 1. Binding constants for Cs⁺ complexes in acetone-D6.

The crystal packing of C5 can be described as “squeezed bilayer” where the upper rim interface of two opposing rows appears as if compressed into one layer (Fig. 2). However, the polar and non-polar layers can still be distinguished. Rows are aligned parallel to A/C aryl plane direction (later A/C direction, Fig. 1). The clockwise (cw) counterclockwise (ccw) enantiomers of the bis-crowns are related by inversion symmetry. In C5, cw and ccw enantiomers alternate in each bilayer in such a way that each cw is facing up and is surrounded by a ccw facing down on both sides. C4 has two molecules in the asymmetric unit, I and II, which could be assigned either to a boat or a slightly twisted boat conformation. Molecules pack in a pillar assembly with alternating I and II molecules (Fig. 3). Each pillar consists of either cw enantiomers or ccw enantiomers, which in turn form layers of cw and ccw enantiomers, but separation into polar and non-polar regions does not occur. Long chain bis-crowns C9BC5, C10BC5 and C11BC5 crystallized readily from ethanol in a monoclinic lattice (Z=8).

Interestingly, most of these structures showed straight alignment of the alkyl groups in the bilayer assembly without disorder but had unresolvable disorder at the crown ether bridges and therefore these structures can only be considered as preliminary structures.

**Alkali metal complexes**

Alkali metal complexes of the bis-crowns were studied by crystallizing CNBC5s with excess of potassium or cesium hexafluorophosphate in alcohols yielding 1:2 (host-guest) complexes. When the binding pockets of the host are filled with

Table 2 Conformational properties of the resorcinarene bis-crowns and their alkal metal complexes.

<table>
<thead>
<tr>
<th>C4¹</th>
<th>C5</th>
<th>C2K2</th>
<th>C3K2</th>
<th>C5K2</th>
<th>C10K2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal packing arrangement</td>
<td>pillar</td>
<td>pillar</td>
<td>squeezed bilayer</td>
<td>layer</td>
<td>layer / shifted capsule</td>
</tr>
<tr>
<td>Conformation</td>
<td>boat</td>
<td>boat</td>
<td>twisted boat</td>
<td>boat</td>
<td>twisted boat</td>
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<tr>
<td>Twi⁵</td>
<td>3.7</td>
<td>5.7</td>
<td>8.9</td>
<td>1.4</td>
<td>7.0</td>
</tr>
<tr>
<td>Distance Å</td>
<td>4.79 / 8.01</td>
<td>4.87 / 8.00</td>
<td>4.80 / 7.98</td>
<td>5.28 / 7.98</td>
<td>5.46 / 7.95</td>
</tr>
<tr>
<td>Dihedral angle between opposite rings</td>
<td>-10.7 / 175.2</td>
<td>-8.3 / 173.3</td>
<td>-10.3 / 176.3</td>
<td>14.4 / 151.4</td>
<td>22.2 / 148.8</td>
</tr>
<tr>
<td>Dihedral angle against methine plane</td>
<td>80.0 / 89.1</td>
<td>88.9 / 82.9</td>
<td>86.4 / 83.2</td>
<td>96.5 / 97.9</td>
<td>100.3 / 101.5</td>
</tr>
<tr>
<td>Cavity diameter Å</td>
<td>5.17 / 5.11</td>
<td>5.26 / 5.21</td>
<td>4.59 / 4.79</td>
<td>4.80 / 5.15</td>
<td>5.42 / 5.28</td>
</tr>
<tr>
<td>Aromatic rings plane A.C.B.D against methine plane C7-C14-C21-C28.</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Average cavity diameter measured as O–O distance.</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

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cations the dihedral angles of A/C aryl rings are 11.8–22.2° and cavity diameters between 4.69–5.23 Å. The binding pocket of the bis-crowns is flexible and able to adjust its size slightly according to the size of the guest cation giving smaller cavity diameters for K+ than Cs+ complexes. Cations bind to the host with cation–π (nπ) interaction with a centroid-cation distance of 3.0–3.1 Å for K+ and 3.2–3.3 for Cs+, and with M+–O interactions with methoxy group oxygens and 3–4 coordination bonds to the bridge (O–M+ 2.70–3.54 Å). One of the PF6– anions is coordinated between the two cations inside the binding pocket, which helps to reduce the charge repulsion between the cations. The other anion is located outside the cavity and creates short contacts between the complexes. Depending on the structure, alkyl chain length and the cation, the complexes pack in shifted capsule, layer or bilayer assemblies.

C2BC5 has been previously crystallized as KPF6 complex in a capsule assembly.25 Now, another packing for C2BC5•2KPF6 complex (C2K2) was obtained, forming layered packing without the capsule formation. When viewed on top, each ccw enantiomer alternates with ccw enantiomers within a layer, and therefore polar and non-polar sides cannot be distinguished. A side view (B/D direction) of the packing reveals that cw and ccw enantiomers are separated on their own stacks in a parallel alignment (Fig. 4).

C3BC5•2CsPF6 (C3C2) crystallized with ethanol as a solvate in the crystal lattice. The conformation of the host is a twisted boat in contrast to the boat conformation of all the other complexes, which can be understood by analyzing the anion/solvent coordination of the cation. One of the PF6– anions is coordinated between the two Cs+ inside the cavity. In addition, a water molecule, not found in the other structures, is coordinated to Cs2 with 3.13 Å Cs–O distance and has a short contact of 2.99 Å to the F10A of the (disordered) second PF6–, which in turn is located close to the crown ether bridge of the opposite enantiomer with F8A–C59 distance of 3.12 Å (Fig. 5). A pair of complexes, cw and ccw enantiomers, form a shifted capsule connected by the solvent-anion contacts. The top view of the complexes shows similar alternating pattern of cw and ccw enantiomers as in C2K2, and side view from the B/D direction shows a layered packing, where shifted capsules form diagonal lines through the crystal. The role of the ethanol solvate is to fill the voids at the B/D edges of the complexes, where they form H-bonded circles of four ethanol molecules without connecting to the host-guest complex.

C5BC5•2KPF6 complex (C5K2) forms layers of single cw or ccw enantiomer which consist of rows aligned in the A/C direction with 2.43 Å shift between the molecules (15 % of complex width) and in the B/D direction with a 3.28 Å (35 %) shift. In contrast to the Cs, all alkyl chains are oriented straight below the methine plane forming a clear bilayer packing. The upper rim interface of C5K2 forms shifted capsules with a 2.80 Å dislocation of the B/D planes accounting for 30 % of the width of a molecule (Fig. 6A). Similar packing was obtained for the C10BC5•2CsPF6 complex (C10C2) despite the difference in cation size and thus larger cavity diameter, but the longer alkyl groups expand the thickness of the bilayer up to 27.39 Å (Fig. 6B).

**Solid lipid nanoparticles**

The ability of CNBC5’s to form solid lipid nanoparticles was tested to assess their self-assembling properties in water. Previously, calixarenes and resorcinarenes bearing long alkyl chains and hydrophilic functionalities at the upper rim have been used to prepare stable SLN’s by solvent diffusion (solvent replacement) method.25, 26 The same method was applied for the CNBC5s, where approximately 5–7 mg of CNBC5 was dissolved in a small amount of THF and water was added to the solution by vigorous stirring, after which a cloudy suspension was formed. The size of the SLN’s was analyzed using dynamic light scattering, which gave hydrodynamic diameters of 220–320 nm for the particles with polydispersity indexes of 0.04–0.34. The particle shape and size was confirmed by SEM images, which revealed spherical particles at a size distribution corresponding to the DLS measurements (Fig. 7). For calixarenes and resorcinarenes, it has been discovered that the size of the SLNs is affected by several parameters: THF/water ratio, stirring speed, pH of the solution, and length of the alkyl chains of the calixarene.25, 26 However, changes on the particle size are mostly affected by the final concentration of the calixarene in the suspension. Therefore in this study, other parameters except the length of the alkyl chains and final concentration of the resorcinarene suspensions were kept constant. In the first series (Fig. 8) the molar concentration of the bis-crowns was constant and the diameters of the particles increase when the amount of carbon atoms at the alkyl chains increase. In the second series SLNs were prepared keeping the mg/L concentration constant to make sure that the increased particle diameter was not originating from the increased amount (in milligrams) of bis-crown in the suspensions. The second series (Fig. 8) has very similar particle sizes than the first one, which indicates that the change in the amount of bis-crowns between the two series has negligible effect. The variation in the particle size, although quite modest, is mostly likely caused by the different alkyl chain length of the bis-crowns, which affects their amphiphilic properties.

**Discussion**

Resorcinarene bis-crowns were shown to bind Cs+ as 1:1 and 1:2 complexes in solution, 1:2 being the dominant species. There is some variation especially between the log K11 values, giving 1.04 for C3BC5 and 3.31 for C11BC5. However, the higher log K12 value for C3BC5 partly compensates this difference when the total binding constants are examined. In contrast to the previously examined C2BC5, all compounds gave 1:2 complexes when more than 1 molar equivalent of water relative to the host was present in the solution. Therefore, what at first glance appears to be the effect of the alkyl chain length, may well be the indirect result of desolvation of the cation. The sensitivity of the measurement towards water may explain some of the observed differences in the binding constants between the experiments.

Since the affinity of C2BC5 towards K+ is very low, log K of 0.23 for the 1:1 complex,21 the binding constant was not determined for the other bis-crown potassium complexes. However, the structural properties of solid state K+ complexes were compared to the Cs+ complexes with the purpose of exploring alternative crystal packing forms due to different cation size. Based on the results it seems that the size of the cation does not have a direct influence on the packing, since similar
structures were obtained for the different cations (C2K2 and C2BC5·CsPF6 complex, C5K2 and C10Cs2). Instead, solvent coordination together with the cation size has more important role in the packing, which is seen by comparing the C2K2 and C3Cs2 and a capsule structure of C2BC5·2KPF6 with a water molecule coordinated inside the cavity. C3Cs2 also contains water, which is involved in the shifted capsule coordination. The larger diameter of Cs+ probably prevents similar coordination of water and the tilted angle of PF6− between the cations inside the binding pocket as in C2BC5·2KPF6 capsules, and now coordination happens outside the binding pocket.

Twisting of the resorcinarene skeleton was observed in C4, C5 and C3Cs2, and is therefore not limited to short alkyl chain bis-crowns. Rather, all interaction in the lattice determine the conformation of the resorcinarene to provide optimal close packing.

The effect of the lower rim alkyl chain length is connected to the amphiphilic nature of the bis-crowns. When alkyl chains are 2–4 carbons long, they have not been found to form bilayer packing with separated polar and non-polar parts. Instead, layers with alternating upper and lower rims in neighboring molecules or complexes are seen, and in addition, C4 formed a pillar type assembly with tilted methine carbon planes. For C5Bc5 a squeezed bilayer in C5 and a bilayer in C5K2 were found, which shows that five carbons is a limiting alkyl chain length for the bilayer type packing. For the long chain bis-crowns increased molecule size made crystallization more difficult and the crystal packing and the amphiphilic properties since C2BC5–C4BC5 form layered packing, whereas, a bilayered packing typical for amphiphilic molecules is observed with C3 and longer alkyl chains. The locked boat conformation of CNBC5 makes also the short chain derivatives behave as amphiphilic molecules, which form stable solid lipid nanoparticles with slight dependence between the SLN size and the alkyl chain length.

Experimental

X-ray crystallography

Single crystal X-ray data were recorded on a Nonius Kappa CCD diffractometer with Apex II detector using graphite monochromatized CuKα (λ = 1.54178 Å) radiation at a temperature of 173 K. The data were processed and absorption correction was made to all structures with Denzo-SMN v.0.97.638 unless otherwise mentioned. The structures were solved by direct methods (SHELXS-97) and refined (SHELXL-97) against F2 by full-matrix least-squares techniques using SHELX-97 software package (Table 3). The hydrogen atoms were calculated to their idealized positions with automatic riding models.

NMR titration

4 mM CNBC5 was titrated with CsPF6 solution in acetone-D6 and the 1H NMR spectra were recorded after each addition at 30 °C. The shift the in aromatic resorcinarene signal at 6.005 ppm for the free host was followed and the binding constants were
Solid lipid nanoparticles were prepared by a solvent replacement method. 5 mg (or 5.27 μmol, 5.2–7.8 mg) of CNBC5 was dissolved in 1.5 ml of THF and 50 ml of purified water (Millipore, resistivity >18 MΩ) was added at a constant flow during 10 s into the organic solution under vigorous stirring at 800 rpm with a magnetic stirrer. A cloudy suspension formed immediately. The suspension was stirred for an additional minute and THF was removed under reduced pressure by a rotary evaporator (44 °C, 60–70 mbar). The volume of the suspension was adjusted to 50 ml giving the final nanoparticle concentration of 100 mg/L (or 0.1 mM). The hydrodynamic diameter of the nanoparticles was measured using dynamic light scattering (Beckman Coulter N5 Submicron Particle Size Analyzer) at 90° angle in water using plastic cuvettes (3 min equilibration, 3 min measurement). Three samples for each SLN were measured. The morphology and size of the SLN’s were analyzed using scanning electron microscopy (Zeiss EVO 50). Sample preparation: a drop of SLN suspension was pipetted on a piece of silicon wafer attached by carbon tape to the sample holder and dried at ambient conditions. Samples were coated with gold (JEOL Fine coat Ion Sputter JFC-1100) prior to imaging.

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Fig. 1 Structure of the resorcinarene bis-crowns CNBC5, R=CsH26, where N= 2,3,4,5,7,9,10,11 with selected crystallographic numbering. cw and ccw enantiomers are shown; A/C plane runs through the upright aryl rings (A and C) and B/D plane through parallel aryl rings (B and D) respective to the methine plane C7-C14-C21-C28.

Fig. 2 Crystal packing of C5, flattened bilayer, in a stick model (A) with cw enantiomers with light and ccw in dark green, respectively, and a CPK representation (B), where the polar and non-polar regions are clearly visible. Disorder not shown for clarity.

Fig. 3 Crystal structure of C4 (disorder not shown). C4 has two molecules, I (A) and II (B) in the asymmetric unit, the twist angle in II indicated. C) Pillar packing of C4: cw (up, purple) and ccw (down, green) enantiomers are separated in pillars with alternating I (dark shade) and II (light shade). Each pillar consists of a single enantiomer with methine plane angle (43.6°) and distances indicated; a top view shows pillars of cw and ccw enantiomers in dark and light color, respectively.
Fig. 4 Side and top views of the crystal packing of $C_2K_2$ layers (A, B) and $C_3Cs_2$ shifted capsules/layers (C, D); side view: $ccw$ enantiomers facing down (green); top view of a layer: outlying anions and ethanol molecules (in D, green) shown as a stick model.

Fig. 5 $C_3Cs_2$ shifted capsule consisting of $cw$ and $ccw$ enantiomers, short contacts to the solvent and anions shown with dashed lines, atoms labelled with an asterisk are generated by a symmetry operation $-x+1, -y+2, -z+1$. Disorder not shown for clarity.

Fig. 6 $C_5K_2$: a front view of an offset capsule and a bilayer packing (A); $C_{10}Cs_2$: a front view of a bilayer (B). $ccw$ enantiomers in green color; outlying anions and disorder not shown.

Fig. 7 SEM image of $C_{11}BC_5$ SLN on $SiO_x$; spherical particles with mean diameter of 300 nm are shown.
Fig. 8 SLN diameters for all CNBC5 (mean of the size distribution from DLS showing standard deviation). SLNs with a constant 0.1 mM concentration (black) and with a constant mass 100 mg/L (grey) show increasing diameter for longer alkyl chains.

Table 3 Crystal structure parameters.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Composition</th>
<th>C4</th>
<th>C5\textsuperscript{b}</th>
<th>C2K2</th>
<th>C3Cs2</th>
<th>C5K2</th>
<th>C10Cs2</th>
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<td>FW</td>
<td>C\textsubscript{6}H\textsubscript{10}O\textsubscript{4}</td>
<td>C\textsubscript{10}H\textsubscript{18}O\textsubscript{4}</td>
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<td><a href="H%5Ctextsubscript%7B2%7DO">C\textsubscript{5}K\textsubscript{2}</a>PF\textsubscript{6}•2C\textsubscript{2}H\textsubscript{5}O</td>
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<td>Crystal system</td>
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<tr>
<td>D\textsubscript{calc}</td>
<td>1.182</td>
<td>1.164</td>
<td>1.423</td>
<td>1.515</td>
<td>1.355</td>
<td>1.377</td>
</tr>
<tr>
<td>F(000)</td>
<td>2352</td>
<td>1240</td>
<td>5600</td>
<td>1732</td>
<td>1592</td>
<td>2056</td>
</tr>
<tr>
<td>μ/μm\textsuperscript{-1}</td>
<td>0.661</td>
<td>0.641</td>
<td>2.676</td>
<td>8.867</td>
<td>2.323</td>
<td>6.958</td>
</tr>
<tr>
<td>Crystal size/mm</td>
<td>0.150×0.100×0.07</td>
<td>0.260×0.200×0.10</td>
<td>0.150×0.100×0.05</td>
<td>0.300×0.200×0.10</td>
<td>0.100×0.100×0.05</td>
<td>0.200×0.200×0.06</td>
</tr>
<tr>
<td>Meas. reflns</td>
<td>29260</td>
<td>15745</td>
<td>17010</td>
<td>45717</td>
<td>16668</td>
<td>19576</td>
</tr>
<tr>
<td>Indep. reflns</td>
<td>20072</td>
<td>10590</td>
<td>10802</td>
<td>12755</td>
<td>11625</td>
<td>13472</td>
</tr>
<tr>
<td>R\textsubscript{int}</td>
<td>0.0909</td>
<td>0.0593</td>
<td>0.0589</td>
<td>0.0587</td>
<td>0.1246</td>
<td>0.0927</td>
</tr>
<tr>
<td>Rw [I&gt;2\sigma(I)]</td>
<td>0.0792</td>
<td>0.0852</td>
<td>0.0788</td>
<td>0.0449</td>
<td>0.0969</td>
<td>0.0826</td>
</tr>
<tr>
<td>Goof on F\textsuperscript{2}</td>
<td>1.0761</td>
<td>0.2338</td>
<td>0.2001</td>
<td>0.1125</td>
<td>0.2355</td>
<td>0.1656</td>
</tr>
<tr>
<td>Largest diff. peak and hole/ e Å\textsuperscript{3}</td>
<td>0.470, -0.378</td>
<td>0.580, -0.335</td>
<td>0.713, -0.646</td>
<td>0.882, -1.338</td>
<td>0.828, -0.457</td>
<td>1.027, -0.634</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Unit cell dimensions for C9BC5, C10BC5 and C11BC5 at the endnotes. \textsuperscript{b} Isomorphous structures obtained from tert-butanol/methanol, iso-butanol/methanol, and ethanol solutions.
Notes and references


