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## Binding properties and self-assembly of $C_{2\nu}$ -symmetrical resorcin[4]arene tetrabenzoates

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interact with ammonium salts in CDCl<sub>3</sub>.

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ABSTRACT

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#### 1. Introduction

# Readily available resorcin[4]arene octaols $\mathbf{1}^1$ and their various derivatives have been used as building blocks for rational design of container molecules,<sup>2</sup> self-assembling capsules,<sup>3</sup> and nanotubes.<sup>4</sup>

Regioselective tetraacylation of compounds  $1^5$  with arylsulfonylchlorides or (het)aroyl-chlorides in MeCN in the presence of Et<sub>3</sub>N gave  $C_{2\nu}$ -symmetrical tetrabenzoates  $2^6$  and tetrasulfonates  $3^7$ (Fig. 1). Compounds **2** and **3** form hydrogen bonded aggregates<sup>8</sup> and molecular capsules<sup>9</sup> in the crystalline state and nonpolar solvents. Chemical modifications of tetraesters **2** and **3** afforded cation receptors,<sup>10</sup> chiral and bridged resorcin[4]arenes<sup>11</sup> (Scheme 1).

Re-crystallization of complexes  $3.2Et_3$ NHCl from MeCN or EtOH resulted in negatively charged, hydrogen bonded dimeric hollow assemblies including two  $Et_3$ NH<sup>+</sup> cations.<sup>12</sup> The structure of the dimeric assemblies was shown to be independent on the type of arylsulfonyl groups and radicals at the methine bridges of **3**. Crystal structures and spectroscopic studies of tetrasulfonates **3** revealed the formation of intermolecular hydrogen bonds S=0...H–O in the

crystalline state and in apolar solutions. Only one example of capsular assemblies of tetraesters **2** with Et<sub>3</sub>NHCl was reported,<sup>12</sup> whereas in other cases the re-crystallization of **2** · 2Et<sub>3</sub>NHCl resulted in crystals of free tetraesters **2**, leaving Et<sub>3</sub>NHCl in the mother liquor.

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The present research was undertaken in order to study complexation of resorcinarene tetrabenzoates **2** with medium size alkylammonium salts both in the crystalline state and in solutions.

#### 2. Results and discussion

In the crystalline state two molecules of resorcin[4]arene tetrabenzoates and four chloride anions form

molecular wraps containing two Et<sub>3</sub>NH<sup>+</sup> cations. The structure and composition of the wraps depend on

the length of the alkyl chains at the narrow rim of the macrocycle. Resorcin[4]arene tetrabenzoates

Tetrabenzoates **2a** and **2b** were synthesized through tetraacylation of the corresponding resorcin[4]arene octaols **1** with benzoyl chloride (MeCN, Et<sub>3</sub>N, rt). Model octabenzoate **4** was obtained through the complete acylation of compound **1b** with benzoyl chloride (THF, Et<sub>3</sub>N, rt). Compounds **2a** and **2b** precipitated from the reaction mixtures together with Et<sub>3</sub>NHCl. Washing the precipitate with water removed the unbound salt and gave crystalline complexes **2a,b**·2Et<sub>3</sub>NHCl the stoichiometry of which was determined by <sup>1</sup>H NMR spectroscopy. Individual compounds **2a** and **2b** were obtained through multiple washings of chloroform solution of the complexes with water. Slow crystallization of tetrabenzoate **2a** from MeCN/H<sub>2</sub>O (95:5) gave transparent colorless





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Fig. 1. (a) Molecular structure of 2a · 5MeCN. One of two crystallographically independent molecules is shown. Non-hydrogen bonded MeCN molecules are omitted for the sake of clarity. (b) Fragment of crystal packing. Hydrogen bonds are shown in broken lines.



crystals, which, although unstable without mother liquor, were suitable for single crystal X-ray diffraction studies.

In the crystalline state a molecule of **2a** adopts a *boat* conformation (Fig. 1) in which the acylated resorcinol rings are quasicoplanar and the unsubstituted resorcinol rings are nearly parallel. As indicated by interatomic distances four OH groups of **2a** are solvated by four ordered hydrogen bonded acetonitrile molecules and no C=0···HO hydrogen bonds are formed. The intramolecular HO–C=O distances (2.9–3.2 Å) indicate four rather strong dipole–dipole interactions. Two ordered MeCN molecules are not hydrogen bonded and fill what otherwise would be voids in the crystal.

Crystallization of octabenzoate **4** from MeCN/H<sub>2</sub>O (95:5) resulted in diffraction quality crystals of solvate  $\mathbf{4} \cdot \mathbf{4}$  MeCN. In the crystalline state molecule **4** adopts a boat conformation (Fig. 2).

The dihedral angles between quasi-parallel and quasi-coplanar resorcinol rings are  $29.7^{\circ}$  and  $1.0^{\circ}$ , respectively. Along the crystal-lographic *a*-axis molecules **4** are stacked to form infinite columns (Fig. 2b and c) stabilized by multiple intermolecular C–H···O





**Fig. 2.** (a) Molecular structure of **4** in **4**·4MeCN; (b) infinite columns of molecules **4** along the crystallographic *a*-axis (side view); (c) top view.

interactions as indicated by d(C-O)=3.28-3.39 Å. The cavities formed by benzoyl groups and *n*-propyl chains of molecules **4** are filled by ordered MeCN molecules. The channels between the columns of molecules **4** are also occupied by MeCN molecules. As indicated by intermolecular distances the MeCN molecules are involved in dipole–dipole interactions between each other and fragments of molecules **4**.

Slow crystallization of  $2a \cdot 2Et_3$ NHCl from MeCN/H<sub>2</sub>O (95:5) resulted in diffraction quality crystals of composition  $2a \cdot 2Et_3$ NHCl·2MeCN·2H<sub>2</sub>O. In the crystalline state the molecule of 2a adopts a *boat* conformation (Fig. 3a and b) similar to that in

![](_page_2_Figure_1.jpeg)

**Fig. 3.** Molecular structure of  $2a \cdot 2Et_3$ NHCl·2MeCN·2H<sub>2</sub>O (top (a) and side (b) views); (c) hydrogen bonded dimeric capsules. Et<sub>3</sub>NH<sup>+</sup> cations are omitted for clarity. Selected distances between hydrogen bonded atoms.

**2a**  $\cdot$  5MeCN. Dihedral angle between the acylated resorcinol units is 70.6° whereas the angle between the resorcinol rings equals to 40.5°.

The H–O···C=O distances (2.96 and 3.25 Å) indicate two intramolecular dipole–dipole attractions as in 2a·5MeCN.

Two molecules of 2a are hydrogen bonded to four chloride anions and four water molecules (Fig. 3c) and form a multicomponent hydrogen bonded wrap having two portals on both sides of the cavity. Hydrogen bonded water molecules bridge the neighboring chloride anions and link them to the carbonyl oxygen atoms of the benzoyl fragments. The molecular wrap is filled with two symmetry-related Et<sub>3</sub>NH<sup>+</sup>, which are separated by 6.6 Å (N–N distance) and hydrogen bonded to water molecules. The shortest distance between the nitrogen of included Et<sub>3</sub>NH<sup>+</sup> and the chloride anion (4.29 Å) is considerably longer than the N–Cl distance in the crystal of Et<sub>3</sub>NHCl (3.08 Å),  $^{13}$  where cations and anions are directly hydrogen bonded. The methylene and methyl protons of the encapsulated Et<sub>3</sub>NHCl form close contacts (d(C-C)=2.99, d(C-O)=2.55 Å) with carbon atoms of the aromatic rings and carbonyl oxygens of molecules **2**, which may be attributed to CH $\cdots\pi$  and CH $\cdots$ O hydrogen bonding. The two non-encapsulated Et<sub>3</sub>NH<sup>+</sup> assume well-defined positions and are hydrogen bonded to chloride anions as in pure Et<sub>3</sub>NHCl. Thus, a crystal of **2a** · 2Et<sub>3</sub>NHCl · 2MeCN · 2H<sub>2</sub>O contains both contact and solvent separated ion pairs of Et<sub>3</sub>NHCl.

The IR spectrum of tetrabenzoate **2a** in the solid state (KBr pellets) contains a broad band with a maximum at  $3455 \text{ cm}^{-1}$ , which indicates groups forming weak hydrogen bonds of the phenolic OH groups. In the IR spectrum of solid **2a**  $\cdot 2Et_3NH$  the OH groups appear as a broad band with maximum at  $3197 \text{ cm}^{-1}$ , which most probably indicates the formation of hydrogen bonds  $O-H\cdots CI^{-}$  as found in the crystal structure described above.

Slow crystallization of  $2b \cdot 2Et_3$ NHCl from MeCN/H<sub>2</sub>O (95:5) gave diffraction quality crystals of compositions  $2a \cdot 2Et_3$ NHCl·MeCN. In the crystalline state a molecule of 2b adopts a *boat* conformation (Fig. 4a) in which the acylated resorcinol rings are quasi-coplanar (dihedral angle 158.8°), whereas the unsubstituted ones are nearly parallel (dihedral angle 24.2°).

Eight OH groups form hydrogen bonds to four chloride anions resulting in the negatively charged dimeric wrap-like assembly (Fig. 4b). Two Et<sub>3</sub>NH<sup>+</sup>-cations hydrogen bonded to chloride anions

![](_page_2_Figure_9.jpeg)

**Fig. 4.** (a) Molecular structure of  $2b \cdot 2Et_3NHCl \cdot MeCN$ . Two pairs of symmetry-related  $Et_3NH^+$  cations are shown; (b, c) dimeric capsule in the crystalline state.

are included in the cavity. The distance between the nitrogen atoms of the encapsulated cations (7.6 Å) is nearly the same as in  $2a \cdot 2Et_3$ NHCl·2MeCN·2H<sub>2</sub>O (Fig. 4) and in previously reported dimeric hollow structures of  $C_{2v}$ -symmetrical resorcinarene tetrasulfonates **3**.<sup>12</sup> Thus, the relatively small differences in structures of **2a** and **2b** cause considerable differences in the crystal structures of their complexes with Et<sub>3</sub>NHCl.

#### 2.1. Solution studies

In the presence of tropylium or tetramethylammonium cations self-complementary resorcin[4]-arenetetraesters **2** form dimeric capsules in CDCl<sub>3</sub> stabilized by eight O–H···O=C hydrogen bonds and four stacking interactions between (het)aroyl fragments.<sup>9</sup> The guest cations form CH··· $\pi$  and  $\pi$ – $\pi$  bonds to the  $\pi$ -basic interiors of the capsules. Molecular mechanics calculations<sup>14</sup> revealed that Et<sub>3</sub>NH<sup>+</sup> is too bulky to be included in the dimeric capsule, which explains the formation of extended solid state capsules in **2a**·2Et<sub>3</sub>NH Cl·2MeCN·2H<sub>2</sub>O and **2b**·2Et<sub>3</sub>NHCl·MeCN.

The fact that the carbonyl groups of resorcinarene tetrabenzoates do not form intramolecular hydrogen bonds suggested that compounds **2** might bind alkylammonium salts through the inclusion of cations into the resorcinarene cavity and hydrogen bonding of anions to the OH groups.<sup>15</sup>

The <sup>1</sup>H NMR spectrum of tetrabenzoate **2a** measured in CDCl<sub>3</sub> contains four singlets for the CH protons of the resorcinol rings, a triplet for the protons of the methine bridges, and one set of signals for the ethyl and phenyl groups (Fig. 5 (top)). The OH groups emerge as a very broad singlet or do not emerge at all most probably due to the rapid exchange with the protons of residual water in CDCl<sub>3</sub>. This can be explained by weakness of hydrogen bonds. The 2D NOESY experiment revealed that the singlets at 6.91 and 6.84 ppm correspond to the protons in positions 5 of the resorcinol rings. Relatively small differences in the chemical shifts of these signals indicate that

![](_page_3_Figure_2.jpeg)

Fig. 5. <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>, 295 K) of 2a (top) and  $2a+2Et_3NHCl$  (bottom).

molecules **2a** assume in solution a somewhat distorted crown (cone) conformation rather than the pinched boat conformation.<sup>16</sup> The addition of 2 M equiv of Et<sub>3</sub>NHCl results in downfield shifts of the proton signals (Fig. 5 bottom) of the resorcinol rings (0.15–0.4 ppm) and benzoyl fragments (0.1–0.15 ppm). The methylene protons of Et<sub>3</sub>NH<sup>+</sup> underwent up-field shift of 0.3 ppm most probably due to shielding effects of aromatic rings of **2a**. The NMR dilution experiment revealed that the complex between **2a** and Et<sub>3</sub>NHCl is not stable on the NMR time scale at ambient temperature.

The model NMR dilution experiments revealed that the addition of 2 M equiv of  $Et_3$ NHCl to the solution of resorcinol in CDCl<sub>3</sub> resulted in a downfield shift (0.2 ppm) of the signal of protons in position 2 while all other signals did not change their shape and position. Thus the change of chemical shifts of protons in positions 5 of the resorcinol rings of **2a** and **2b** may indicate a conformational change of the resorcinarene skeleton.

Decreasing the temperature to 223 K results in broadening and splitting the <sup>1</sup>H NMR signals of **2a**+2Et<sub>3</sub>NHCl. A broad signal at -0.47 ppm indicates the inclusion of Et<sub>3</sub>NH<sup>+</sup> in the basic cavity of **2a** or its hydrogen bonding oligomers.<sup>3c,17</sup> Unfortunately, the poor quality of the <sup>1</sup>H NMR spectra did not allow to establish stoichiometry of complexes between **2a** and Et<sub>3</sub>NHCl at 223 K. It seems likely that OH groups of **2a** form hydrogen bonds to chloride anions of Et<sub>3</sub>NHCl in CDCl<sub>3</sub>.

Sonication of a suspension of  $H_2NCH_2CH_2OH \cdot HCl$  in solution of **2d** in CDCl<sub>3</sub> for 8 h resulted in extraction of equimolar quantity of the salt according to integration of signals in the <sup>1</sup>H NMR spectrum of the solution (Fig. 6b). The presence of  $H_2NCH_2CH_2OH \cdot HCl$  induces considerable changes in positions of protons of the resorcinol rings and methyne bridges of **2b** (Fig. 6a and b) and leads to the splitting of signals of diastereotopic methylene protons H3.

The addition of *t*-BuNH<sub>3</sub>Cl to a solution of **2b** in CDCl<sub>3</sub> results in a considerable change in positions and shape of <sup>1</sup>H NMR signals for **2b** (Fig. 6c), which indicates complexation. Remarkably the methyne protons of the bridges emerge as doublet of doublets due to spin–spin coupling with the diastereotopic protons of the neighboring methylene groups. Dilution experiments revealed that the complex between **2b** and *t*-BuNH<sub>3</sub>Cl was not stable on the NMR time scale at 295 K. It should be noted that Me<sub>4</sub>N<sup>+</sup>, which is comparable in size to *t*-BuNH<sub>3</sub><sup>+</sup> forms highly stable dimeric capsules with **2b** stabilized by hydrogen bonds and stacking interactions.

Solutions of tetrabenzoates **2a** and **2b** in  $CDCl_3$  extract L-proline from solid phase. The <sup>1</sup>H NMR spectroscopic studies of the

![](_page_3_Figure_10.jpeg)

**Fig. 6.** <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>, 295 K) of **2c** (a), **2c**+H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH·2HCl (b), and **2c**+3 *t*-BuNH<sub>3</sub>Cl (c).

saturated solutions revealed a 1:4 molar ratio between resorcinarene tetrabenzoates and L-proline and considerable spectral changes (shifting, broadening, splitting of the signals) for the resorcinarene components. Since L-proline is poorly soluble in CDCl<sub>3</sub> this ratio may indicate the stoichiometry of the lipophilic complex formed. The model experiment with octabenzoate **4** revealed no considerable extraction of L-proline into CDCl<sub>3</sub>. Although the detailed structure of this complex could not be inferred from the NMR data it seems plausible that benzoyl and hydroxyl groups of **2a** and **2b** can bind four L-proline molecules through C(O)  $O^-\cdots$ HO,  $N^+H_2\cdots O$ =C and  $N^+H_2\cdots O$  interactions.

#### 2.2. Calculations

A number of local energy minima are expected for compounds 2. Two major energy minima are different boat conformations of the resorcinarene macrocycle and many local energy minima correspond to a variety of arrangements of benzoyl groups. Molecular mechanics (MM) study of the  $C_{2\nu}$ -symmetrical resorcinarene tetrabenzoates using the MMX force field was performed as follows. The structure of **2** was energy-minimized starting from the two boat conformations with parallel and co-planar unsubstituted resorcinol rings (Fig. 7). The energy barrier between these conformations was sufficiently high to prevent their interconversion during the geometry optimization. In both conformations the arrangement of the benzoyl groups was optimized using the dihedral driver procedure (see Experimental part). The lowest energy corresponds to the boat conformation having parallel diacylated resorcinol rings (structure A, Fig. 7). Despite the presence of four intramolecular hydrogen bonds, the second boat conformation with co-planar diacylated resorcinol rings was found to be

![](_page_4_Figure_1.jpeg)

**Fig. 7.** MMX force field optimized conformations of  $C_{2\nu}$ -symmetrical resorcinarene tetrabenzoates.

energetically less favorable by about 5 kcal/mol. Given the relatively low precision of molecular mechanics calculations of flexible structures, either of the boat conformations could be favored in solution or in the crystalline state depending on experimental conditions. The main factor influencing the preferred boat conformer of **2** seems to be the solvent that can either stabilize or disrupt intramolecular hydrogen bonds.

In optimized conformation C, four hydroxyl groups cannot form intramolecular hydrogen bonds to the neighboring oxygen atoms and can be involved in intermolecular hydrogen bonding like in the crystalline state. Conformation C is predicted to be to be less stable than conformation A by 15 kcal/mol, probably due to the lack of intramolecular hydrogen bonding. Hydrogen bonding between the hydroxyl groups of conformation C and four MeCN molecules results in a complex the energy of which is 5 kcal/mol lower than the sum of energy of conformer A and four nonbonding acetonitrile molecules. Although the MM calculation does not take into account the entropic factors, these results correlate with the observed capacity of compounds **2** to form hydrogen bonds to solvent molecules or/and chloride anions (as described above).

Density functional theory calculations with B3LYP/cc-pvdz basis set confirmed the conclusions of the above MM studies of resorcinarene tetrabenzoate **2a** and its complex with acetonitrile.

#### 3. Conclusions

The disposition of four OH and benzoyl groups on the wide rim of resorcinarene tetrabenzoate 2 does not allow the formation of strong intramolecular C=0···H-O hydrogen bonds. Such a geometry of molecules 2 facilitates the formation of intermolecular hydrogen bonds between the OH groups and hydrogen bond acceptors such as MeCN and H<sub>2</sub>O molecules, or chloride anions. The self-complementarity of molecules 4 is the main reason for the formation of dimeric hydrogen bonded capsules around such complementary guests like tropylium and tetramethylammonium cations. In this case the molecular capsule is stabilized through eight intramolecular hydrogen bonds and four pairs of weaker stacking interactions while the anion is involved predominantly in electrostatic interaction with the nanosized capsular cation. The cocrystallization of tetrabenzoates 2a and 2b with Et<sub>3</sub>NHCl results in the formation of nanosized wrap-like structure encapsulating two Et<sub>3</sub>NH<sup>+</sup> cations. In this case the chloride anions are the components

of the hollow assemblies. Thus, depending on the nature of the guest resorcinarene tetrabenzoates form closed dimeric positively charges molecular capsules, hydrogen bonded solvates or nanosized molecular wraps.

#### 4. Experimental part

#### 4.1. General methods and procedures

All reactions were carried out under open atmosphere with no precautions taken to exclude ambient moisture. Melting points were measured with a Buchi melting points apparatus are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker Avance DRX 500 (500 and 125 MHz, respectively) with TMS as an internal standard. IR spectra were measured on a Vertex 70 spectrometer.

#### 4.2. General procedure for the preparation of tetrabenzoates 2

Triethylamine (20 mmol) was added in one portion to a stirred solution of **2** (5 mmol) in dry MeCN (50 ml) and the suspension formed was stirred for 10 min. Benzoylchloride (20 mmol) was added to the suspension at vigorous shaking. The precipitate was dissolved and in 5 min a white solid started to crystallize from the reaction mixture. The reaction mixture was stirred for 8 h, the precipitated was filtered off, washed with acetonitrile (2×20 ml), and was recrystallized from MeCN/H<sub>2</sub>O to give analytically pure  $2 \cdot 2Et_3$ NCl. A solution of  $2 \cdot 2Et_3$ NCl (1 g) in CHCl<sub>3</sub> (50 ml) was washed with water (5×50 ml), the organic layer was separated, filtered through paper filter, and evaporated in vacuo.

4.2.1. Compound **2a**. Yield 37%. Mp >300 °C (MeCN). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.99 (d, *J*=7.6 Hz, 8H, CH), 7.48 (t, *J*=7.3 Hz, 4H), 7.22 (t, *J*=8.4 Hz, 8H, CH), 6.91 (s, 2H, CH), 6.84 (s, 2H, CH), 6.71 (s, 2H, CH), 6.11 (s, 2H, CH), 4.41 (t, *J*=7.5 Hz, 4H, CH), 2.10–1.91 (m, 8H, CH<sub>2</sub>), 0.91 (t, *J*=7.0 Hz, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 164.59, 154.03, 145.71, 135.98, 134.09, 130.17, 129.31, 127.81, 125.39, 125.39, 120.32, 116.45, 102.63, 95.95, 36.86, 28.70, 13.12. Anal. Found %: C, 75.28; H, 5.74. Anal. Calcd for C<sub>64</sub>H<sub>56</sub>O<sub>12</sub> %: C, 75.59; H, 5.51.

4.2.2. Compound **2b**. Yield 32%. Mp >300 °C (MeCN). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.02 (d, *J*=7.0 Hz, 8H, CH), 7.48 (t, *J*=7.3 Hz, 4H, CH), 7.23 (t, *J*=8.4 Hz, 8H, CH), 6.89 (s, 2H, CH), 6.86 (s, 2H), 6.12 (s, 2H, CH), 4.48 (t, *J*=7.3 Hz, 4H, CH), 2.08–1.84 (m, 8H, CH<sub>2</sub>), 1.45–1.14 (m, 8H, CH<sub>2</sub>), 0.89 (t, *J*=7.3 Hz, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 164.60, 154.08, 145.52, 136.26, 134.09, 130.17, 129.28, 127.96, 125.38, 120.05, 116.43, 102.73, 95.97, 37.30, 34.32, 20.98, 14.34. Anal. Found %: C, 75.93; H, 6.12. Anal. Calcd for C<sub>68</sub>H<sub>64</sub>O<sub>48</sub> %: C, 76.11; H, 5.97.

4.2.3. Compound **4**. Compound **1b** (1 g, 1.67 mmol) and Et<sub>3</sub>N (2.1 g, 20.04 mmol) were dissolved in THF (100 ml). Benzoyl chloride (2.82 g, 20.04 mmol) was slowly added to the solution under vigorous stirring. The mixture was stirred for 12 h at room temperature and the solvent was evaporated. The residue was partitioned between water and CH<sub>2</sub>Cl<sub>2</sub> (50:50 ml). The organic layer was collected, washed with water (3×25 ml), and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the product was recrystallized from MeCN to furnish the product as white crystals. Yield 33% (not optimized). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 7.92 (br s, 8H, CH), 7.81 (br s, 8H, CH), 7.70 (s, 2H, CH), 7.58 (br m, 8H, CH), 7.41 (br m, 10H, CH), 7.34 (br m, 8H, CH), 7.05 (s, 2H, CH), 6.58 (s, 2H, CH), 4.50 (br m, 4H, CH), 2.21 (br m, 4H, CH<sub>2</sub>), 2.03 (br m, 4H, CH<sub>2</sub>), 1.24 (br m, 4H, CH<sub>2</sub>), 1.22

(br m, 4H, CH<sub>2</sub>), 0.99 (br m, 12H, CH<sub>3</sub>). Anal. Found %: C, 76.82; H, 6.00. Anal. Calcd for  $C_{96}H_{88}O_{16}$  %: C, 77.00; H, 5.88.

## **4.3.** X-ray data collection and crystal structure determinations

X-ray diffraction data were collected on the «Xcalibur-3» diffractometer (graphite monochromated MoK $\alpha$  radiation, CCD detector,  $\omega$ -scans,  $2\Theta_{max}=50^{\circ}$ ) at 173 K. The structures were solved by direct methods using the SHELXTL<sup>18</sup> package. Positions of hydrogen atoms were calculated geometrically and refined by riding them on the carrier atom with  $U_{iso}=nU_{eq}$  (n=1.5 for methyl and hydroxyl groups and n=1.2 for other hydrogen atoms). The hydrogen atoms of hydroxyl groups and water molecules in the structure **2a**·2Et<sub>3</sub>NHCl·2MeCN·2H<sub>2</sub>O were refined in isotropic approximation. The crystallographic data and experimental parameters are listed in Table 1. Final atomic coordinates, geometrical parameters, and crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, 11 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). The deposition numbers are given in Table 1.

Table 1	1
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X-ray crystallographic data

	2a · 5MeCN	<b>2a</b> · 5Et <sub>3</sub> NHCl · 2 MeCN · 2H <sub>2</sub> O	<b>4</b> ·5MeCN	<b>2b</b> ·2Et₃NHCl· MeCN
a, Å	19.495(4)	15.359(3)	9.8208(3)	22.362(1)
b, Å	29.830(4)	30.396(6)	35.423(1)	26.420(2)
<i>c</i> , Å	24.615(4)	16.977(3)	25.0371(9)	26.594(1)
α, °	90	90	90	90
β, °	103.24(2)	92.27(1)	91.475(3)	92.191(5)
γ, °	90	90	90	90
<i>V</i> , Å <sup>3</sup>	13,934(4)	7920(2)	8707.2(5)	15,700(2)
F(000)	5196	3096	3488	5936
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	C2/c
Ζ	4	4	4	8
Т, К	100	100	100	100
$\mu$ , mm <sup>-1</sup>	0.080	0.147	0.085	0.143
$D_{\text{calcd}}, \text{g/cm}^3$	1.173	1.217	1.262	1.176
$2\Theta_{\rm max}$ , grad	50	50	60	50
Measured reflections	41,824	20,623	90,464	54,590
Independent reflections	22,159	12,696	25,254	13,643
R <sub>int</sub>	0.133	0.057	0.067	0.071
Reflections with $F > 4\sigma(F)$	3730	6235	14,494	9113
Parameters	1663	981	1144	941
$R_1$	0.047	0.052	0.069	0.081
$wR_2$	0.063	0.123	0.173	0.206
S	0.534	0.813	1.027	1.026
CCDC number	876625	876624	876627	876626

#### 4.4. Calculations

Molecular mechanics calculations were performed using the MMX force field as implemented in PCMODEL 7.5. Energy minimization was accomplished with a conjugate gradient procedure. A root-mean-square (rms) gradient of 0.01 kcal/mol or less was assumed as a condition of energy convergence. A value of 1.5 D was assumed for the dielectric constant. For optimization of the arrangement of the benzoyl groups the dihedral driver procedure was applied in which two torsions for the Ar–OBz and ArO–Bz bonds were changed with the step of 30°. From the 144 conformers, the lowest energy one was minimized with no constraints and taken, in turn, as the starting point for the following rotations of remaining benzoyl groups. B3LYP calculations<sup>19</sup> were carried out using the PCGAMES/Firefly program<sup>20</sup> with cc-pVDZ basis set.<sup>21</sup>

#### **References and notes**

- (a) Timmerman, P.; Verboom, W.; Reinhoudt, D. N. Tetrahedron 1996, 52, 2663–2704; (b) Jain, V. K.; Kanaiya, P. H. Russ. Chem. Rev. 2011, 80, 75–102.
- (a) Cram, D. J.; Cram, J. M. Container Molecules and Their Guests. In Monographs in Supramolecular Chemistry: Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, UK, 1994; (b) Chapman, R. G.; Sherman, J. C. Tetrahedron 1997, 53, 15911–15945; (c) Rudkevich, D. M. Bull. Chem. Soc. Jpn. 2002, 75, 393–413; (d) Atwood, J. L.; Szumna, A. Chem. Commun. 2003, 940–941.
- (a) Mac Gillivray, L. R.; Atwood, J. L. Nature 1997, 389, 469–472; (b) Murayama, K.; Aoki, K. Chem. Commun. 1998, 607–608; (c) Shivanyuk, A.; Rissanen, K.; Kolehmainen, E. Chem. Commun. 2000, 1107–1108; (d) Gerkensmeier, T.; Iwanek, W.; Agena, C.; Frolich, R.; Kotila, S.; Nather, C.; Mattay, J. Eur, J. Org. Chem. 1999, 2257–2262; (e) Kuberski, B.; Szumna, A. Chem. Commun. 2009, 1959–1961; (f) Schröder, T.; Sahu, S. N.; Anselmetti, D.; Mattay, J. Isr. J. Chem. 2011, 51, 725–727; (g) Shivanyuk, A. J. Am. Chem. Soc. 2007, 129, 14196–14199.
- (a) Negin, S.; Daschbach, M. M.; Kulikov, O. V.; Rath, N.; Gokel, G. W. J. Am. Chem. Soc. 2011, 133, 3234–3237; (b) Heaven, M. W.; Cave, G. W. V.; McKinlay, R. M.; Antesberger, J.; Dalgarno, S. J.; Thallapally, P. K.; Atwood, J. L. Angew. Chem., Int. Ed. 2006, 45, 6221–6224.
- 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. J. Org. Chem. **1989**, 54, 1305–1312.
- Shivanyuk, A.; Paulus, E. F.; Böhmer, V.; Vogt, W. J. Org. Chem. 1998, 63, 6448–6449.
- (a) Lukin, O. V.; Pirozhenko, V. V.; Shivanyuk, A. N. *Tetrahedron Lett.* **1995**, *36*, 7725–7728;
  (b) Lukin, O.; Shivanyuk, A.; Pirozhenko, V. V.; Tsymbal, I. F.; Kal'chenko, V. I. J. Org. Chem. **1998**, *63*, 9510–9516.
- 8. Shivanyuk, A. Chem. Commun. 2001, 1472–1473.
- (a) Shivanyuk, A.; Paulus, E. F.; Böhmer, V. Angew. Chem., Int. Ed. 1999, 38, 2906–2909; (b) Shivanyuk, A. Tetrahedron 2005, 61, 349–352.
- (a) Eisler, D. J.; Puddephatt, R. J. Inorg. Chem. 2003, 42, 6352–6365; (b) Eisler, D. J.; Kirby, C. W.; Puddephatt, R. J. Inorg. Chem. 2003, 42, 7626–7634; (d) Eisler, D. J.; Puddephatt, R. J. Inorg. Chem. 2003, 42, 8192–8202.
- (a) Shivanyuk, A.; Schmidt, C.; Böhmer, V.; Paulus, E. F.; Lukin, O. V.; Vogt, W. J. Am. Chem. Soc. 1998, 120, 4319–4326; (b) Shivanyuk, A.; Rafai Far, A.; Rebek, J., Jr. Org. Lett. 2002, 4, 1555–1558; (c) Arnott, G.; Page, P. C.; Heaney, H.; Hunter, R.; Sampler, E. P. Synlett 2001, 412–414.
- 12. Shivanyuk, A.; Paulus, E. F.; Rissanen, K.; Kolehmainen, E.; Böhmer, V. *Chem.* —*Eur. J.* **2001**, *7*, 1944–1951.
- James, M. A.; Cameron, T. S.; Knop, O.; Neuman, M.; Falk, M. Can. J. Chem. 1985, 63, 1750–1758.
- 14. Serena Software, Dr. Kevin E. Gilbert, P.O. 3076, Bloomington, IN 47402.
- 15. See for example: Winstanley, K. J.; Sayer, A. M.; Smith, D. K. Org. Biomol. Chem. **2006**, *4*, 1760–1767.
- Abis, L.; Dalcanale, E.; Du Vosel, A.; Spera, S. J. J. Org. Chem. 1988, 53, 5475–5479.
- For example methyl protons of Et<sub>3</sub>NH<sup>+</sup> encapsulated in hexameric resorcinarene capsules emerge at -0.08 ppm: (a) Palmer, L.; Shivanyuk, A.; Yamanaka, M.; Rebek, J., Jr. *Chem. Commun.* **2005**, 857–858.
- Sheldrick, G. M. SHELXTL PLUS. PC Version A system of computer programs for the determination of crystal structure from X-ray diffraction data; V. 5.1. 1998, 1998.
- (a) Hohenberg, P.; Kohn, W. Phys. Rev. **1964**, 136, B864–B871; (b) Kohn, W.; Sham, L. J. Phys. Rev. **1965**, 140, A1133–A1138; (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Chem. Phys. Lett. **1989**, 157, 200–206.
- Granovsky, A. A. PC GAMES Version 7.0. http://classic.chem.msu.su/gran/ gamess/index.html.
- (a) Dunning, T. H., Jr. J. Chem. Phys. **1989**, 90, 1007–1024; (b) Woon, D. E.; Dunning, T. H., Jr. J. Chem. Phys. **1994**, 100, 2975–2989; (c) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. J. Chem. Phys. **1992**, 96, 6796–6807; (d) Woon, D. E.; Dunning, T. H., Jr. J. Chem. Phys. **1993**, 98, 1358–1372; (e) Wilson, A. K.; Woon, D. E.; Peterson, K. A.; Dunning, T. H., Jr. J. Chem. Phys. **1999**, 110, 7667–7677.