Supplementary Data

Design, synthesis and structure determination of new inherently chiral *para*-bromoalkoxycalix[4]arenes

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X-Ray description

General

X-Ray diffraction studies were performed on an automatic “X-calibur-3” diffractometer (graphite monochromated MoK α radiation, CCD-detector, ω -scanning). The structures were solved by direct method using SHELXTL package. The restrictions on the bond lengths in the disordered fragments (Car-Car 1.38 Å) were applied for the compound **8a**. The absolute structure of **8a** was determined using the Flack parameter (-0.02(1)). Positions of the hydrogen atoms were located from electron density difference maps and refined by “riding” model with Uiso = nUeq of the carrier atom (n = 1.5 for methyl groups and n = 1.2 for other hydrogen atoms). The hydrogen atoms of the hydroxyl groups in **2**, **5**, **6**, **7** and all hydrogens in **3** are refined using isotropic approximation. The crystallographic data, experimental parameters and deposition numbers are listed in Table 1 in the article.

5-Bromo-25-propoxy-26,27-dibenzoyloxycalix[4]arene **2** (see the Figure 1 in the article):

The molecule of *para*-bromocalixarene **2** has *partial cone* conformation. In the crystal, molecules with opposite orientation of substituents (**A** and **B**) are alternated presented in the unit cell. The molecules **A** and **B** also differ from each other by the conformation of the propyl substituent (*ap* - *ap* conformation in molecule **A** and *ap* - *-sc* conformation in molecule **B**). The C15...C20 benzene ring of calixarene **2** is inverted. However the phenylaclyic substituent at it does not participate in the formation of stacking interactions with benzene rings of the macrocycle. It can be caused by insufficient entry of phenylaclyic substituent into the macrocyclic cavity as compared to the compound **1** (the distance between centroids of the C1...C2 aromatic ring of the macrocycle and aromatic ring of the phenylaclyic substituent at the inverted ring is 6.1 Å (molecule **A**) or 5.8 Å (molecule **B**) in **2** as compared to 4.9 Å in **1**. The hydroxyl group forms the intramolecular hydrogen bond with propoxy group: the O1a-H...O4a (H...O 2.00 Å O-H...O 165°) in molecule **A** and O1b-H...O2b (H...O 1.87 Å O-H...O 169°) in molecule **B**.

In the crystal phase molecules **2** are bonded by a lot of C-H... π intermolecular hydrogen bonds: C23b-H...C1a' (π) (1-x, 2-y, 1-z) H...C 2.86 Å C-H...C 171°; C23b-H...C2a' (π) (1-x, 2-y, 1-z) H...C 2.84 Å C-H...C 143°; C7b-H7bb...C37a' (π) (-x, 1-y, 1-z) H...C 2.84 Å C-H...C 140°; C7b-H7bb...C38a' (π) (-x, 1-y, 1-z) H...C 2.57 Å C-H...C 160°; C24b-H...C23a' (π) (-x, 2-y, 1-z) H...2.82 Å C-H...C 114°; C17b-H...C17b' (π) (2-x, 2-y, 2-z) H...C 2.81 Å C-H...C 141°; C11a-H...C5b' (π) (-x, 1-y, 1-z) H...C 2.69 Å C-H...C 177°. Presence of the bromine substituent creates conditions for forming of the halogen bonding. However the bromine atom forms only one hydrogen bond as proton cceptor in molecule **A** and molecule **B**: C11b-

H...Br1b' (1+x, y, z) H...Br 2.96 Å C-H...Br 149° and C9b-H...Br1a' H...Br 2.98 Å C-H...Br 139°.

5-Bromo-25-propoxy-26-benzoyloxycalix[4]arene 3 (see the Figure 2 in the article):

The X-ray analysis of calixarene **3** confirmed the *partial cone* conformation for the molecule in the crystal and showed that benzoyl group from distal position is removed. Similar to *para*-bromocalixarene **2** the C15...C20 benzene ring of compound **3** is inverted and phenylaclyic substituent is located in the macrocycle cavity. At that the entry of the aromatic ring of substitent into the cavity is insufficient for formation of stacking interactions (the distance between centroids of the C1...C6 and C30...C35 rings is about 5.6 Å). Two hydroxyl groups at the lower rim form the O1-H...O4 (H...O 1.86 Å O-H...O 171°) and O2-H...O1 (H...O 2.03 Å O-H...O 160°) intramolecular hydrogen bonds.

In the crystal phase molecules **3** form only two C-H... π intermolecular hydrogen bonds (C10-H...C23' (π) (x, y-1, z) H...C 2.82 Å C-H...C 122° and C11-H...C1' (π) (1+x, y, z) H...C 2.69 Å C-H...C 164°) and two C-H...Br hydrogen bonds (C25-H...Br1' (-x, -y, -z) H...Br 3.00 Å C-H...Br 134° and C23-H...Br1' (1+x, 1+y, z) H...Br 2.96 Å C-H...Br 143°).

5-Bromo-25-propoxycalix[4]arene 4 (see the Figure 3 in the article):

Three unsubstituted hydroxyl groups at lower rim of compound **4** form intramolecular hydrogen bonds at lower rim of the macrocycle: O1-H...O4 (H...O 1.94 Å, O-H...O 165°); O2-H...O1 (H...O 1.82 Å, O-H...O 168°); O3-H...O2 (H...O 1.90 Å, O-H...O 164°). Stabilizing by hydrogen bonds and absence of the substituent with π -system cause a cone conformation of the macrocycle. The propyl substituent has ap-ap conformation (the C27-O4-C29-C30 and O4-C29-C30-C31 torsion angles are 172.7(3)° and 175.4(3)°, respectively).

In the crystal phase molecules **4** form intermolecular interactions only with the participation of the bromine substituent. The halogen atom takes part in these interactions as donor as acceptor of an electron density: C2-H...Br1a' (1-x, 1-y, 1-z) H...Br 2.89 Å C-H...Br 169°; C14-H14b...Br1a' (0.5-x, 0.5-y, 1-z) H...Br 2.88 Å, C-H...Br 124°; Br1a...C5' (π) and Br1a...C6' (π) (x, y-1, z) Br...C 3.41 Å and 3.11 Å, respectively, and C-Br...C 151° and 161°, respectively.

5-Bromo-25,28-dipropoxy-26-benzoyloxycalix[4]arene 5 and 5-Bromo-25,27-dipropoxy-26-benzoyloxycalix[4]arene 6 (see the Figure 5 in the article):

Molecules **5** and **6** have a *partial cone* conformation of the macrocycle. However these conformations are slightly different. In the case of proximal position of two propyl substituents in **5** the ring neighboring relatively the brominated one is inverted while in compound **6** with distal position of propyl groups the opposite ring is inverted. At that the formation of the host-guest complex in **5** competes with the self-inclusion process in **6**. The complex of acetonitrile with molecule **5** is stabilized by a lot of C-H... π hydrogen bonds: C2s-H2s3...C4' H...C 2.86 Å C-H...C 171°; C2s-H2s3...C5' H...C 2.77 Å C-H...C 151°; C2s-H2s3...C6' H...C 2.84 Å C-H...C 136°; C2s-H2s1...C24' H...C 2.74 Å C-H...C 173°; C2s-H2s1...C25' H...C 2.84 Å C-H...C 145°. The self-inclusion of the phenylacylic substituent was expected to be stabilized by stacking interactions between the C33...C38 aromatic ring and aromatic rings of the macrocycle. However the overlapping degree and angles between planes of the corresponding aromatic rings do not allow to confirm this assumption in spite of the distance between centroids of the brominated and C33...C38 rings (5.0 Å) that is very close to corresponding value in compound **1**. The propyl substituents have *ap--sc* conformation in **5** and *ap+sc* conformation in **6** (the C20-O3-C32-C33 and O3-C32-C33-C34 torsion angles are -174.0(3)° and -71.0(4)°, respectively, for one propyl group in **5** and the C13-O2-C29-C30 and O2-C29-C30-C31 torsion angles are 174.0(3)° and -66.0(4)°, respectively, for another propyl group in **5**; the C27-O4-C39-C40 and O4-C39-C40-C41 torsion angles are 177.9(2)° and 60.9(4)°, respectively, in **6** and the C13-O2-C29-C30 and O2-C29-C30-C31 torsion angles are 173.4(2)° and 64.8(3)°, respectively, in **6**). The hydroxyl group takes part in the intramolecular hydrogen bonding: the O1-H...O2 (H...O 1.89 Å, O-H...O 174°) in **5** and O1-H...O2 (H...O 1.88 Å, O-H...O 170°) in **6**.

It can be noted the difference in the intermolecular interactions for structures **5** and **6**. The molecules **5** are bonded by a lot of C-H... π and C-H...Br intermolecular hydrogen bonds: C24-H...C18' (π) (x, -y, -0.5+z) H...C 2.79 Å C-H...C 151°; C24-H...C19' (π) (x, -y, -0.5+z) H...C 2.67 Å C-H...C 161°; C21-H21b...C21' (π) (1-x, -y, 1-z) H...C 2.86 Å C-H...C 117°; C21-H21b...C23' (π) (1-x, -y, 1-z) H...C 2.75 Å C-H...C 147°; C31-H31b...Br1' (0.5-x, 0.5+y, 0.5-z) H...Br 3.05 Å C-H...Br 151°; C40-H...Br1' (0.5+x, 0.5-y, 0.5+z) H...Br 2.89 Å C-H...Br 144°. The self-inclusion of the phenylacylic substituent in the macrocycle cavity is supposed to be the reason of the formation of only one C-H... π and only one C-H...Br intermolecular hydrogen bonds: C23-H...C3' (π) (x-1, y, z) H...C 2.78 Å C-H...C 172° and C23-H...Br1' (x-1, y, z) H...Br 2.94 Å C-H...Br 148°.

5-Bromo-25,28-dipropoxycalix[4]arene 7 (see the Figure 6 in the article):

According to X-ray diffraction data of molecule **7** the brominated benzene ring of the macrocycle is inverted. Two hydroxyl groups at lower rim form the O2-H...O1 (H...O 2.13 Å, O-H...O 165°) and O1-H...O4 (H...O 1.78 Å, O-H...O 178°) intramolecular hydrogen bonds. The propyl groups have slightly different conformations where *ap*–*+sc* conformation is for propyl group of the substituent at the C22...C27 benzene ring (the C27-O4-C32-C33 and O4-C32-C33-C34 torsion angles are 162.8(2)° and 63.9(3)°, respectively) and *–sc*–*ap* conformation is for propyl group of the substituent at the inverted ring (the C20-O3-C29-C30 and O3-C29-C30-C31 torsion angles are -81.8(3)° and -173.3(2)°, respectively).

In the crystal phase the molecules **7** are bonded by the C3-H...Br1' (x, 1+y, z) (H...Br 2.90 Å C-H...Br 137°) intermolecular hydrogen bond and a lot of C-H... π hydrogen bonds: C28-H28b...C2' (π) (2-x, 2-y, -z) H...C 2.78 Å C-H...C 126°; C28-H28b...C3' (π) (2-x, 2-y, -z) H...C 2.87 Å C-H...C 137°; C14-H14a...C26' (π) (x, 1.5-y, 0.5+z) H...C 2.85 Å C-H...C 133°.

5-Bromo-26-benzoyloxy-27-N-(1'-phenylethyl)aminocarbonylmethoxy-25-propoxycalix[4]arene 8a (see the Figure 7 in the article):

The macrocycle of compound **8a** has a *partial cone* conformation where the phenylacylic substituted ring is inverted. The distance between centroids of the brominated ring and the C40...C45 ring is about 5.6 Å and does not allow to allege the existence of stacking interactions between ones. The carbamide fragment of the substituent at the C8-C13 ring is located in *–ac* position relatively the C13-O2 bond and is coplanar to the O2-C29 bond (the C13-O2-C29-C30 and O2-C29-C30-N1 torsion angles are -133.3(2)° and -0.6(3)°, respectively). Such location of this fragment is stabilized by the N1-H...O1 (H...O 2.26 Å N-H...O 163°) and C7-H7a...N1 (H...N 2.56 Å C-H...N 164°) hydrogen bonds. The aromatic ring of this substituent is orthogonal to the carbamide fragment and is slightly turned relatively it (the C30-N1-C31-C33 and N1-C31-C33-C38 torsion angles are 90.1(3)° and 13.3(3)°, respectively). The propyl group has *ap*–*ap* conformation (the C27-O4-C46-C47 and O4-C46-C47-C48 torsion angles are 174.6(2)° and -176.7(2)°, respectively).

In the crystal phase molecules **8a** are bonded by the C-H...Br and C-H... π intermolecular hydrogen bonds: C29-H29b...Br1' (0.5+x, 1.5-y, 1-z) H...Br 2.88 Å C-H...Br 134°; C37-H...Br1' (0.5-x, 1-y, -0.5+z) H...Br 3.02 Å C-H...Br 166°; C11-H...C1' (π) (1+x, y, z) H...C 2.72 Å C-H...C 151°; C28-H28b...C45' (π) (x-1, y, z) H...C 2.69 Å C-H...C 166°; C16-H...C36' (π) (1+x, y, z) H...C 2.78 Å C-H...C 161°; C25-H...C36' (π) (0.5-x, 1-y, 0.5-z) H...C 2.77 Å C-H...C 142°; C7-H7b...C10' (π) (-0.5+x, 1.5-y, 1-z) H...C 2.83 Å C-H...C 153°.

^1H NMR spectrum (CDCl_3) of 5-bromo-25-propoxy-26,27-dibenzoyloxycalix[4]arene **2**

^1H NMR spectrum (CDCl₃) of 5-bromo-25-propoxy-26-benzoyloxycalix[4]arene **3**

¹H NMR spectrum (CDCl₃) of 5-bromo-25-propoxycalix[4]arene **4**

¹H NMR spectrum (CDCl₃) of 5-bromo-25,28-dipropoxy-26-benzoyloxycalix[4]arene **5**

^1H NMR spectrum (CDCl_3) of 5-bromo-25,27-dipropoxy-26-benzoyloxycalix[4]arene **6**

¹H NMR spectrum (CDCl₃) of 5-bromo-25,28-dipropoxycalix[4]arene **7**

¹H NMR spectrum (CDCl₃) of 5-bromo-27-aminocarbonylmethoxy-26-benzoyloxy-25-propoxy-calix[4]arene **9a** or **9b**

^1H NMR spectrum (CDCl_3) of 5-bromo-27-aminocarbonylmethoxy-25-propoxycalix[4]arene **10a** or **10b**