Quantitative method for analysis of mixtures of homologues and stereoisomers of hemicucurbiturils allows to follow their formation and stability.

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Supplementary Material

Table of Contents

1. HPLC chromatogram of oligomeric mixture and structures of isolated oligomers ........................................... S2
2. HRMS results for isolated oligomers and for cycHC\([10, 11, 12]\) ................................................................. S2
3. UV-measurements ...................................................................................................................................................... S3
   3.1 \((all-R,R)\)-cyclohexanohemicucurbit[8]uril .................................................................................. S3
   3.2 \((all-R,R)\)-cyclohexanohemicucurbit[6]uril .................................................................................. S3
   3.3 \((all-R,S)\)-cyclohexanohemicucurbit[6]uril .................................................................................. S4 3.4
       \((R,R)\)-cyclohex-1,2-diylurea .................................................................................................................. S4
   3.5 \((R,S)\)-cyclohex-1,2-diylurea.................................................................................................................. S5 3.6
       4-membered oligomer .............................................................................................................................. S5
   3.7 6-membered oligomer ............................................................................................................................. S6
   3.8 7-membered oligomer ............................................................................................................................. S6
4. HPLC and structures of cyclohex-1,2-diylurea diasteromers modelled by MM .............................................. S7
1  HPLC chromatogram of oligomeric mixture and structures of isolated oligomers

Figure S1. HPLC chromatogram of oligomeric mixture. Peaks and structures of isolated 4-, 6- and 7-membered oligomers are pointed out.

2  HRMS results for isolated oligomers and for cycHC[10,11,12]

Table S1. HRMS data of oligomers and (all-R,R)-cyclohexanohemicucurbituril homologues

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Calculated m/z [M+Na]^+</th>
<th>Experimental m/z [M+Na]^+</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-membered oligomer</td>
<td>C32H48N8O5</td>
<td>647.3645</td>
<td>647.3654</td>
</tr>
<tr>
<td>6-membered oligomer</td>
<td>C47H72N12O6</td>
<td>923.5590</td>
<td>923.5562</td>
</tr>
<tr>
<td>7-membered oligomer</td>
<td>C58H84N14O8</td>
<td>1105.6678</td>
<td>1105.6666</td>
</tr>
<tr>
<td>(all-R,R)-cycHC[10]</td>
<td>C80H120N20O10</td>
<td>1534.9389</td>
<td>1543.9409</td>
</tr>
<tr>
<td>(all-R,R)-cycHC[12]</td>
<td>C96H144N24O12</td>
<td>1848.1288</td>
<td>1848.1288</td>
</tr>
</tbody>
</table>
3  UV-measurements

3.1  (all-R,R)-cyclohexanohemicucurbit[8]uril

(all-R,R)-cycHC[8] with purity of 95 % was used for preparation of stock solution 9.51 · 10⁻⁵ M. Into 2 ml of CH₃CN 20 μl of stock solution was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S2.

Figure S2. A) UV-spectra and B) molar extinction coefficient of (all-R,R)-cycHC[8] in acetonitrile.

3.2  (all-R,R)-cyclohexanohemicucurbit[6]uril

(all-R,R)-cycHC[6] with purity of 86 % was used for preparation of stock solution 6.95 · 10⁻⁴ M. Into 2 ml of CH₃CN 20 μl of stock solution was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S3.
Figure S3. A) UV-spectra and B) molar extinction coefficient of (all-\(R,R\))-cycHC[6] in acetonitrile.

3.3 (all-\(R,S\))-cyclohexanohemicucurbit[6]uril

(all-\(R,S\))-cycHC[6] with purity of 96% was used for preparation of stock solution 8.90 \(\cdot\) 10\(^{-6}\) M. Into 2 ml of CH\(_3\)CN 20 \(\mu\)l of stock solution was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S4.

Figure S4. A) UV-spectra and B) molar extinction coefficient of (all-\(R,S\))-cycHC[6] in acetonitrile.

3.4 (\(R,R\))-cyclohex-1,2-diylurea

Into 2 ml of CH\(_3\)CN 20 \(\mu\)l of (\(R,R\))-cyclohex-1,2-diylurea stock solution (6.98\(*10^{-3}\) M) was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S5.
3.5 (R,S)-cyclohex-1,2-diylurea
Into 2 ml of CH$_3$CN 20 µl of (R,S)-cyclohex-1,2-diylurea stock solution (7.40*10$^{-3}$ M) was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S6.

3.6 4-membered oligomer
Into 2 ml of CH$_3$CN 10 µl of 4-memebered oligomer stock solution (1.5*10$^{-3}$ M) was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S7.
3.7 6-membered oligomer

Into 2 ml of CH$_3$CN 10 µl of 6-membered oligomer stock solution (1.5*10$^{-3}$ M) was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S8.

3.8 7-membered oligomer

Into 2 ml of CH$_3$CN 10 µl of 7-membered oligomer stock solution (2.1*10$^{-3}$ M) was added repeatedly 5 times resulting in solutions with concentrations shown on the Figure S9.
Figure S9. A) UV-spectra and B) molar extinction coefficient of 7-membered oligomer in acetonitrile.

4 HPLC and structures of cyclohex-1,2-diylurea diasteromers modelled by molecular mechanics

Figure S10. RP-HPLC chromatogram of (R,S)- and (R,R)-cyclohex-1,2-diylurea (46 and 62 µg/ml, respectively) in chloroform:methanol (1:9).

Figure S11. RP-HPLC analysis of degradation of a homogenous solution of HC[6] in 0.1 M HCl at 65 °C. *solvent peak contains hydrochloric acid aqueous and methanol solution.

Figure S12. $^1$H-NMR analysis of saturated solution of unsubstituted hemicucurbiturils in 0.1 M HCl in D$_2$O at room temperature and at elevated temperature on a Bruker Avance III 400 MHz spectrometer. Experimental conditions: 16 scans for HC[6] and 256 scans for HC[12], 30 degree flip angle, 1 second relaxation delay.