

Synthesis of complementary hydrogen bonding cyclotrimeratrylenes

Magali Darzac, Stéphanie Montésinos, André Collet[†]
and Jean-Pierre Dutasta*

*Stéréochimie et Interactions Moléculaires, École Normale Supérieure de Lyon, UMR-CNRS
No. 5532, 46 allée d'Italie, F-69364 Lyon Cedex 07, France*

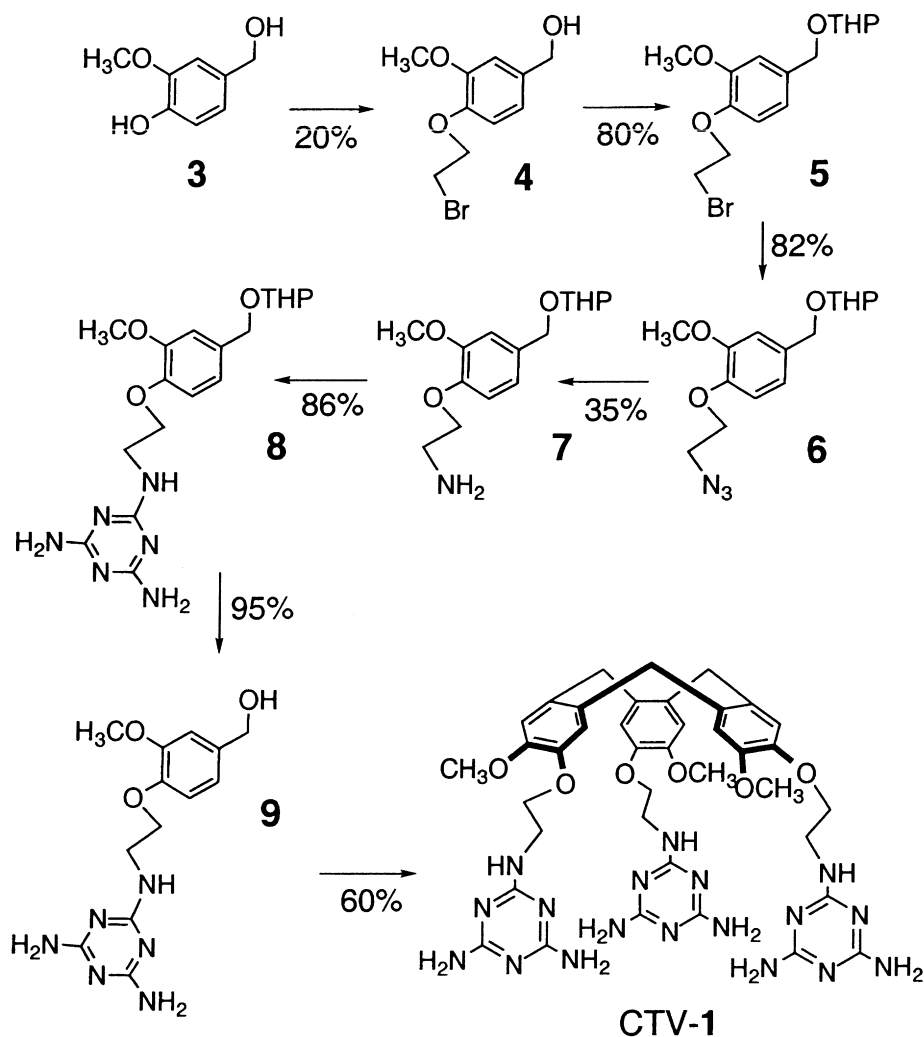
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Two new cyclotrimeratrylenes CTV-1 and CTV-2 bearing complementary H-bond donor-acceptor substituents were prepared from 4-hydroxy-3-methoxybenzyl alcohol following a multistep strategy to introduce melamine or cyanuric acid substituents.

Keywords: cyclotrimeratrylenes, complementary hydrogen bonding

Supramolecular assemblies can be obtained by self-association of molecular precursors to generate new host molecules, which are able to encapsulate reversibly one large guest or several guests within the confined space of molecular cavity. For this purpose, hydrogen bonding is probably the most significant intermolecular interaction, because of its directionality, specificity, reversibility and important role in biological processes.^{1,2} The cone shape cyclotrimeratrylenes¹³ (CTV) are

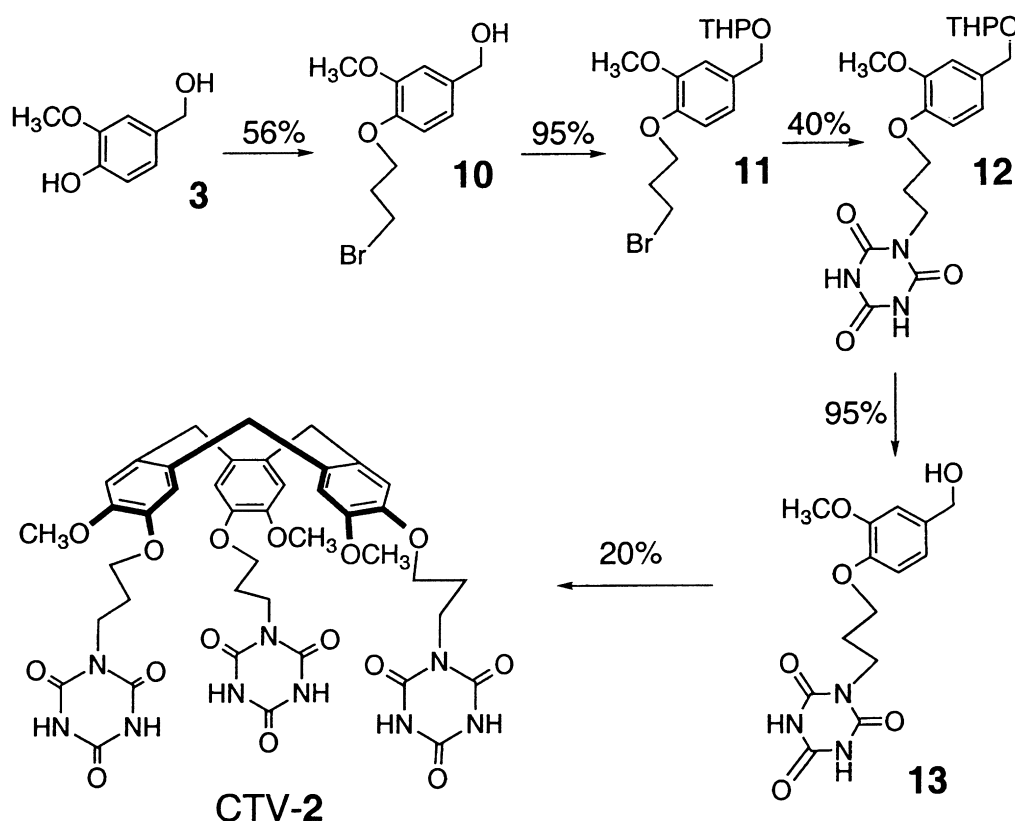
particularly attractive building blocks for the contribution of molecular cavities. Their assembly can be achieved by the rim-to-rim association through H-bond formation.¹⁰ We have developed a method for the synthesis of suitably substituted cyclotrimeratrylenes, and we report herein the synthesis of two complementary hydrogen bonded cyclotrimeratrylenes, CTV-1 and CTV-2, substituted by three melamine groups (CTV-1) and three cyanuric acid groups (CTV-2) respectively.



Scheme 1

[†] This work is dedicated to the memory of Professor A. Collet

* To receive any correspondence. E-mail: dutasta@ens-lyon.fr



Scheme 2

Cyclotrimeratrylenes CTV-1 and CTV-2 were synthesised from the corresponding precursors **9** and **13** using 65% perchloric acid in methanol in respectively 60% and 20% yield.

Compounds **9** and **13** were obtained by a stepwise synthesis starting from vanillyl alcohol **3** (Schemes 1 and 2 respectively). O-alkylation of vanillyl alcohol **3** with dibromoethane gave the brominated derivative **4**, which was then protected with DHP to give **5**. Reaction of **5** with sodium azide in the presence of sodium iodide produced **6**, which was then reduced to give the amine **7**. N-alkylation of **7** with 2-chloro-4,6-diamino-1,3,5-triazine afforded compound **8**, which led to the benzylic alcohol **9** after deprotection (3.7% overall yield from **3**).

A similar pathway was used to prepare the precursor **13**. The O-alkylation of **3** with dibromopropane gave compound **10**, which was protected with DHP to give **11**. The precursor **12** was then obtained by reaction of **11** with cyanuric acid and DBU. Deprotection of **12** provided the benzylic alcohol **13** (20% overall yield from **3**).

The very low solubility of CTV-1 and CTV-2 did not allow further investigations in solution. However, the reaction path-

ways described above are an interesting alternative to produce new CTVs with specific functionalities.

Techniques used: ^1H and ^{13}C NMR, MS

References: 20

Schemes: 2

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References cited in this synopsis

- 1 L.J. Prins, P. Timmerman and D.N. Reinhoudt, *Angew. Chem. Int. Ed.*, 2001, **40**, 2382–2426.
- 2 G.A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer-Verlag, Berlin, 1991
- 10 S.B. Lee and J. Hong, *Tetrahedron Lett.*, 1996, **37**, 8501–8504.
- 13 A. Collet in *Comprehensive Supramolecular Chemistry*, J.L. Atwood, J.E.D. Davies, D.D. Macnicol, F. Vögtle, Eds., Elsevier Science, 1996, vol. 6, pp. 281–303.