



Synthesis of new resorcinarene-based molecular clips

Miroslav Kvasnica^{a*}, Byron W. Purse^b

^aIOCB AS CR, Flemingovo nám. 2, 166 10 Praha 6, Czech Republic; ^bDepartment of Chemistry and Biochemistry, University of Denver, 2199 S. University Blvd., Denver, Colorado 80208, USA

*e-mail corresponding author: kvasnica@uochb.cas.cz

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INTRODUCTION

Molecular clips or tweezers are curved compounds with properties of self-assembly and host-guest recognition.¹ These clips are capable of binding guests using various supramolecular interactions. They are designed with two 'arms' chosen for their inclination to "sandwich" a given guest. Most examples of resorcinarene-derived cavitand synthesis are symmetrical: the resorcinarene-derived deep cavitands either belong to the point groups C_4 or C_{4v} (four identical walls) or have one of their walls differentiated by a more elaborate synthesis (C_s symmetry). To date there exists no efficient synthetic methods to control the placement of two different cavitand walls A and B to generate all five possible combinations— A_4 , A_3B , *cis* A_2B_2 , *trans* A_2B_2 , AB_3 , and B_4 —because the problem of synthesizing *cis* A_2B_2 and *trans* A_2B_2 in more than trace amounts has not been solved.^{2,3} We now present a new regioselective synthesis of the *cis* A_2B_2 isomer, which will complete the solution to this problem, and in so doing provide a new class of molecular clip or tweezer that is effectively a two-walled deep cavitand.

RESULTS AND DISCUSSION

Synthesis of resorcinarene cavitand is based mostly on two main sequential steps - preparation of resorcin[4]arene and bridging of phenols with (het)aryls (e.g. 1,2-difluoro-4,5-dinitrobenzene - DFDNB). Deeper cavitands can be prepared by incorporation of additional walls on upper rim. *Cis* A_2B_2 cavitands cannot be prepared in high amount by such bridging reactions. If only two equivalents of aryl reagents is used mostly the *trans* bis-substituted isomers are formed with high amount of tri-substituted and tetra-substituted products. However possible way was found using procedure published by Dalcanale's group⁴. Partial hydrolysis of tetraphosphonate of resorcinarene led to high amount of *cis* bis-substituted isomer. Free phenolic groups were then easily bridged with DFDNB followed with spontaneous hydrolysis of remaining phosphonates. Reduction of nitro groups to amines and their reactions with benzyl amide or propionyl chloride led to two precursor for *cis* A_2B_2 cavitand

(Fig. 1). These compounds, that can be used as molecular clips for specific guests, were further substituted to form *cis* A_2B_2 cavitands.

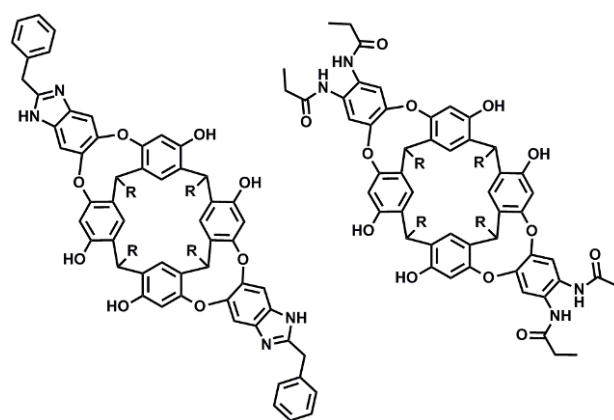


Figure 1. Structure of two molecular clips and precursors for *cis* A_2B_2 cavitand (R = alkyl chain).

CONCLUSION

Our current research on methods for the synthesis of cavitands of reduced symmetry has now provided a new avenue to prepare resorcin[4]arene-based molecular clips and *cis* A_2B_2 deeper cavitand.

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