



Synthesis of four new carboxylic derivatives based on the [1.1.1.1] metacyclophane backbone blocked in 1,3-Alternate conformation

Ekaterina F. Chernova^{a,b}, Alexander S. Ovsyannikov^{b,c}, Sylvie Ferlay^{a,*}, Svetlana E. Solovieva^{b,c}, Igor S. Antipin^{b,c}, Alexander I. Konovalov^{b,c}, Nathalie Kyritsakas^a, Mir Wais Hosseini^{a,*}

^a Molecular Tectonics Laboratory, University of Strasbourg, UMR UDS–CNRS 7140, Institut le Bel, 4, Rue Blaise Pascal, F-67000 Strasbourg, France

^b Kazan Federal University, Kremlevskaya Str.18, 420008 Kazan, Russian Federation

^c A.E. Arbusov Institut of Organic and Physical Chemistry of Kazan Scientific Center of Russian Academy of Science, Arbuzov Str. 8., 420008 Kazan, Russian Federation

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ABSTRACT

Four new tetrasubstituted [1.1.1.1]metacyclophanes (**4–7**), that are inherently adopting a 1,3-Alternate conformation, bearing four or eight peripheral carboxylic binding sites, and appended with spacers group (alkyl or phenyl) differing by the flexibility, have been synthesised in high yields. The structures of the obtained compounds have been investigated in solution as well as in the solid state, for three of them, by using single-crystal X-ray analysis.

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Calix[*n*]arenes¹ and especially calix[4]arenes and thiacalix[4]arenes,² are macrocyclic units presenting large cavities and flexible conformations. These compounds, as well as calix[4]resorcinarenes,³ composed of four phenolic or resorcinolic units and connected through bridging CH₂ or S groups, have been intensively exploited as molecular receptors in supramolecular chemistry⁴ for binding substrates, for the recognition of different substances and for the transport of neutral molecules or ions.⁵ This class of preorganized backbones offers unlimited possibilities for molecular design through functionalization of the lower and/or upper rims of the macrocyclic backbones. They seem also effective organic ligands for coordination of metallic cations, leading to the formation of clusters⁶ and also extended coordination networks⁷ or well-known MOFs, obtained by bridging inorganic and organic molecular building units through coordination bonds, where the organic units (linkers/bridging-ligands) are often rigid carboxylates, or other organic anions.⁸

In order to restrict the flexibility of calixarene based ligands and enhance their propensity to form extended supramolecular architectures via coordination bonds, one of a possible strategy is based on the appending of methyl groups to the macrocyclic backbone, thus blocking the spontaneous rotation of the aryl units around

the C–C single bonds in solution, as well as in the solid state. This can be observed while using the mesitylene based [1.1.1.1]metacyclophane (**1**, Fig. 1), as a conformationally preorganized macrocycle, that was synthesized decades ago by condensation of mesitylene in the presence of hard Lewis bases with CH₂Cl₂.⁹ When substituted or not, these compounds, presenting a rigid concave surface, are blocked in the 1,3-Alternate conformation over a wide range of temperature (60 °C to 150 °C).¹⁰ It is important to note that, for a macrocycle, this blocked conformation is especially well suited for the formation of extended coordination networks of high dimensionalities, through combination with metals, because of the tetrahedral orientation of the terminal binding sites.

An improved synthetic procedure of metacyclophane derivatives based on the condensation of mesitylene or its functional derivatives (bromomesitylene or hydroxymesitylene¹¹), in the presence of SnCl₄, with an electrophilic agent like chloromethyl methyl ether, allowed to obtain compound **1** without any functional groups on the macrocyclic backbone (R₁ = R₂ = R₃ = R₄ = H, Fig. 1 A), tetrachloromethylated compound **2**¹¹ (R₁ = R₂ = R₃ = R₄ = CH₂Cl, Fig. 1 A) and tetrabromo derivative **3**¹² (R₁ = R₂ = R₃ = R₄ = Br, Fig. 1 A). The synthesis of all these reported metacyclophanes prompted us to study further modifications of this appealing rigid macrocyclic platform in order to obtain new coordination compounds based on the metacyclophane platform.

* Corresponding authors.

E-mail address: ferlay@unistra.fr (S. Ferlay).

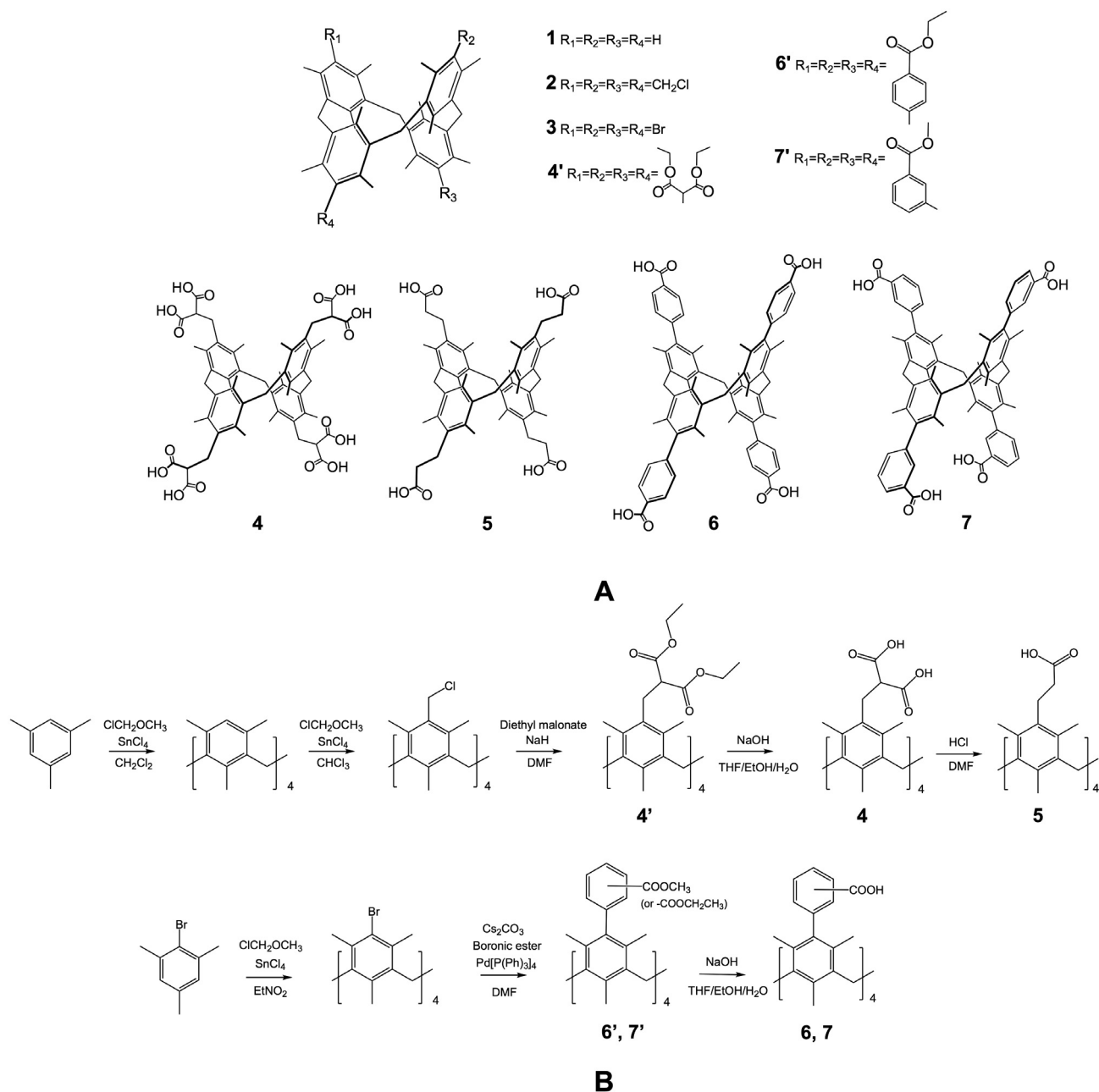


Fig. 1. A: Macrocyclic compounds derived from [1.1.1.1]metacyclophane blocked in 1,3-Alternate conformation; the mesitylene [1.1.1.1]metacyclophane **1**, the tetrachloromethylene **2** and the tetrabromo **3** precursors, together with the targeted ligands **4–7** based on [1.1.1.1]metacyclophane and their corresponding ester intermediates **4'**, **6'** and **7'**. B: The synthetic strategy used for preparation of targeted ligands **4–7**.

The formation of new coordinating ligands towards transition metals based on [1.1.1.1]metacyclophane derivatives possessing two or four coordinating sites located in an alternate fashion above and below the mean plane of the cyclophane ring, was undertaken essentially by Hosseini *et al.* Disubstituted compounds, with coordinating sites located in *syn* fashion ($R_1 = R_2, R_3 = R_4$, Fig. 1 A) containing phenol, thiophenol, methylthio, *p*-methylthiophenyl, *p*-methoxyphenyl groups have been synthesised and characterized in solution as well as in the solid state by X-ray diffraction.¹³ Other disubstituted compounds with N donor coordinating groups like cyano¹³ or pyridyl,^{13,14} imidazolyl or pyrazolyl¹⁵ have also been obtained leading to V-shaped preorganized ligands which have been involved in 1D or 2D coordination networks or metallomacrocycles in the crystalline phase.¹⁶ Furthermore, the synthesis of tetrasubstituted [1.1.1.1]metacyclophane bearing mercapto,¹⁷

thiomethyl,¹⁸ aldehyde,¹³ acid,¹⁴ nitro,¹⁴ amino,¹⁴ diphenylphosphanyl¹³ or diphenylphosphoryl,¹⁸ bipyridyl and bisquinolyl¹⁹-groups has also been achieved but no related coordination compounds have been reported. In contrast, the tetrasubstituted [1.1.1.1]metacyclophane appended with N donor coordinating groups such as cyano,²⁰ pyridyl^{18,21} imidazolyl²² and pyrazolyl²³ have been prepared and different coordination compounds (0D–3D) have been generated when the ligands were combined with different metal salts.¹⁶ A less symmetrical tetrasubstituted ligand bearing two sets of coordinating sites, *i.e.*, pyridyl and imidazolyl, has also been synthesised together with its corresponding 2D coordination networks.¹⁵

Among the O donor coordinating groups, carboxylate moieties attract lots of interest, because of their high ability to form stable coordination compounds with d and f metal cations. For example,

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