

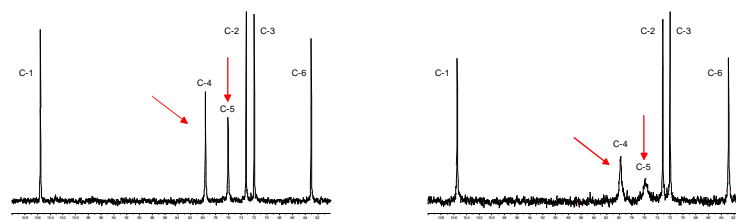
# $\alpha$ -CYCLOALTRIN: MOLECULAR SHAPE AND HYDRATION PROPERTIES

**Stefan Immel, Guido E. Schmitt, and Frieder W. Lichtenthaler\***

*Institute of Organic Chemistry, Darmstadt University of Technology,  
D-64287 Darmstadt, Germany*

$\alpha$ -Cycloaltrin (**1**)<sup>[1]</sup> adopts in the solid state<sup>[2]</sup> a unique  $C_3$  symmetrical conformation with nearly perfect  ${}^4C_1$  and  ${}^1C_4$  chairs in an alternating sequence (**1a**).  ${}^1H$  and  ${}^{13}C$  NMR data in  $D_2O$  at  $30^\circ C$  and  $4^\circ C$  (cf. Fig. 1) indicate a dynamic conformational equilibrium of at least two different altrose geometries with almost equal energies in the macrocycle.

Fig. 1:  ${}^{13}C$  NMR (75 MHz) spectra of  $\alpha$ -CA (**1**) in  $D_2O$  at  $30^\circ C$  (left) and  $4^\circ C$  (right) indicate a pronounced low-temperature broadening of the C-4 and C-5 signals, and hence, a dynamic equilibrium between at least two different altrose conformations.



Unlike the conformation **1a** (Fig. 2) which features side-on indentations only, the intermediate all- ${}^0S_2$  structure **1b** in the  ${}^4C_1 \rightleftharpoons {}^0S_2 \rightleftharpoons {}^1C_4$  equilibrium features a "through-going" central cavity (Fig. 2). We have investigated the dynamic processes in **1** by means of molecular dynamics (MD) simulations in aqueous solution, focusing in particular on the hydration properties and water exchange phenomena of **1a** and **1b**, defining the first hydration shells of both geometries (Fig. 2).

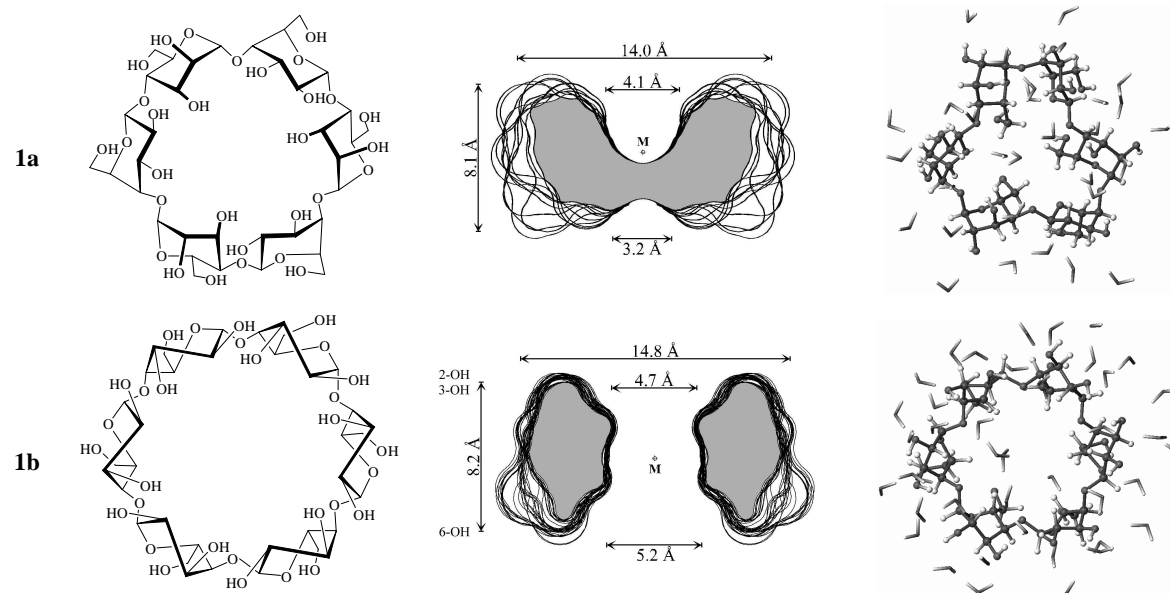


Fig. 2: Superimposed surface cross section cuts (center) of the alternating  ${}^4C_1 / {}^1C_4$  (**1a**) and all- ${}^0S_2$  conformation (**1b**) of  $\alpha$ -cycloaltrin with approximate molecular dimensions in Å. On the right, typical MD derived snap-shot geometries of the first hydration shell of both geometries with 31 and 41 water molecules hydrogen bonded to **1a** and **1b** are displayed.

[1] Y. Nogami, K. Fujita, K. Ohta, K. Nasu, H. Shimada, C. Shinohara, and T. Koga, *J. Incl. Phenom. Mol. Recogn. Chem.* **1996**, 25, 57-60.

[2] Y. Nogami, K. Nasu, T. Koga, K. Ohta, K. Fujita, S. Immel, H. J. Lindner, G. E. Schmitt, and F. W. Lichtenthaler, *Angew. Chem.* **1997**, 109, 1987-1991; *Angew. Chem., Int. Ed. Engl.* **1997**, 35, 1899-1902.