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Hexabromocyclododecanes: From Smart Molecules to Persistent Pollutants

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In the seventies, about 70% of the world's bromine production of 400 000 t/y was used for 1,2-dibromoethane synthesis, a fuel additive for leaded gasolines. The implementation of three-way catalysts stopped these activities. Nowadays, brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A, and hexabromocyclododecanes (HBCDs) are the major bromine products. BFRs are added to polymers used in electronic devices, textiles, and insulation materials to lower their flammability. The EU has banned the use of penta- and octa-BDEs, but HBCDs, currently produced at >20 000 t/y, are still allowed.

Persistence, bioaccumulation potential, and toxicity are important aspects to decide which BFRs have to be regulated as persistent organic pollutants under the Stockholm convention. It is our interest to elucidate the fate of such chemicals, to study their transformation processes and to develop safer alternatives.

When the EU started a risk assessment on HBCDs, we realized that neither HBCD stereochemistry nor selective analytical methods were known. We isolated eight of the 16 HBCD stereoisomers and assigned the absolute configurations of three pairs of enantiomers (**6a/b**, **7a/b**, **8a/b**). Lately, the two *meso* forms could be assigned to structures **9** and **10**. In parallel, we developed LC-MS methods to distinguish different stereoisomers.

A conformational analysis revealed that HBCDs are remarkably similar. We identified a structural motive consisting of three pairs of equally oriented synclinal and two antiperiplanar torsion angles. We found increased reactivity in the flexible part, whereas the conserved motive was less reactive. The understanding of such structure–activity relations is a key element to model environmental transport and transformation.

Some HBCDs accumulate in the environment. Most striking is the fact that γ-HBCDs (8a/b) are abundant in technical products, but α-HBCDs (6a/b) dominate in biological samples. The left-handed form of both α-HBCD enantiomers (6a) is enriched in human breast milk.

A comprehensive risk assessment for chemicals of such high-production volume requires detailed structural information and selective analytical methods to study the fate and toxicity of the individual isomers. In this respect our odyssey on HBCDs might be considered as an analytical highlight but further challenges are ahead of us to assess benefits and risks of HBCDs.

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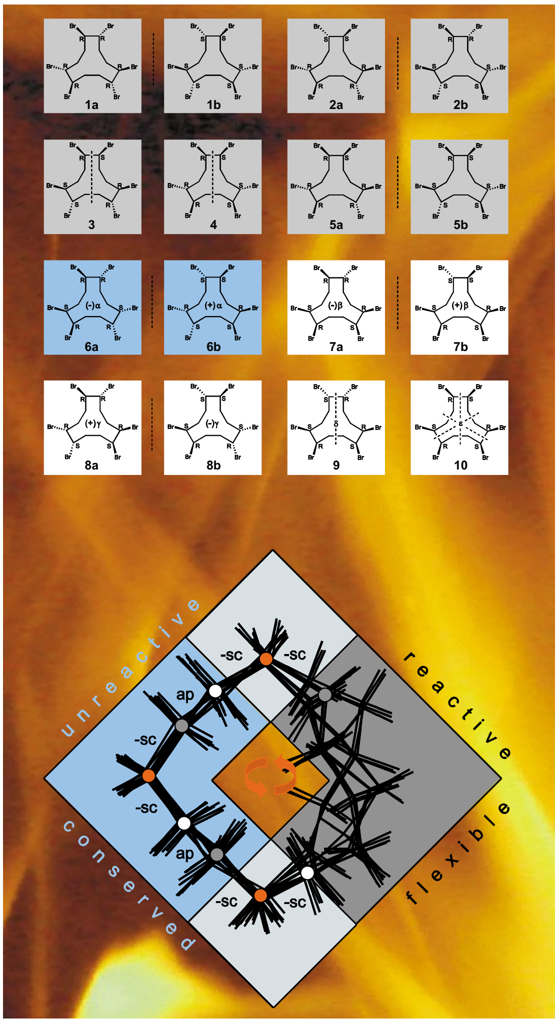

Structure elucidation of eight of the 16 possible 1,2,5,6,9,10-HBCDs was achieved by XRD and NMR analyses. Compounds **6a/b** are more persistent and bioaccumulative than the others. A structural motive consisting of three pairs of synclinal and two antiperiplanar torsion angles was found to be conserved and less reactive.

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