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Synthesis and physicochemical studies of novel resorc[4]arene derivatives with diverse molecular architecture, conformational equilibria and chirality

Abstract

Resorc[4]arenes, despite many years since their discovery, are still important elements of supramolecular chemistry, on the basis of which it is possible to design new supramolecules, including chiral ones. My scientific work is focused on studies on the synthesis and physicochemical properties of new resorc[4]arene derivatives. For this purpose, I have used thermally generated *o-quinomethine* derivatives of resorc[4]arene and their reactions with selected dienophiles (Diels-Alder reaction) and CH-acids (Michael reaction), obtaining new derivatives with enlarged cavity, diverse conformational structure and chirality, and interesting spectroscopic properties. The examples of cycloaddition reaction involving o-quinomethine resorc[4] arene derivatives described in the literature are single examples, therefore it seemed appropriate to study this reaction on a broader group of compounds, which are styrenes substituted at position 4. I have described the conditions of synthesis and yield of cycloaddition reaction involving them. I have determined the crystal structure of one of the derivatives. I have assigned the diastereoselectivity of the cycloaddition reaction depending on the resorc[4] arene derivative used to generate the *o-quinomethine* intermediate as well as on the size of the substituent in the styrene moiety. Furthermore, I separated the diastereoisomeric mixture on a chiral column and compared the experimental ECD spectra with quantum mechanical calculations. In spite of the dipolarophilic nature of CH-acids such as substituted coumarins and enaminones, their reactions with o-quinomethine resorc[4]arene derivatives occur through the interaction of the electrophilic agent, which is the carbon atom of the methine group of the *o-quinomethine* resorc[4]arene derivative with the electronenriched C₃ carbon atom of the coumarin derivative or the C₂ carbon atom of the enaminone. I have shown that in the case of coumarin derivatives, depending on the proton-donor properties of the substituent at position 4 and the solvent, cyclochiral crown conformers of the "in" or "out" type are selectively formed. In contrast, the crystal structure of the obtained enaminone derivative of resorc[4]arene indicates that in the solid state all enaminone units participate in the formation of 12 unidirectional intramolecular hydrogen bonds with the formation of a conformer with C₂ symmetry of "in-out" type. In solution, the enaminone derivative of resorc[4]arene exists as a mixture of conformers with distribution controlled by temperature and the nature of the solvent.