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Phenylurea-equipped *p-tert*-butylthiacalix[4]arenes as the synthetic receptors for monocharged anions

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New *p-tert*-butylthiacalix[4]arenes linked with phenylurea fragments can serve as synthetic receptors for fluoride, acetate or dihydrogen phosphate anions depending on the conformation of the macrocycle (*cone*, *1,3-alternate*) and the number of substituents.

Molecular design of selective complexing agents for anionic substrates is one of the most rapidly developing areas in supramolecular chemistry.[1] Calixarenes and thiacalixarenes are widely used as molecular building platforms for creating hosts for specific types of guests.[2–9] It is well known that compounds containing amide, urea and thiourea moieties interact with anions through hydrogen bonding between the NH protons and the corresponding anion.[10–15] The effectiveness of such interactions, *i.e.*, the binding of receptor to a substrate, can be enhanced by increasing the number of specific spatial binding sites, as it is in dendrimer-like compounds.[16] Thus, we have proposed to combine the prospects of a thiacalixarene platform (existence in several configurations, the spatial orientation of substituents and the macrocyclic structure) and the ability of the urea moieties to interact with some anions.

Previously, we have shown that the variation of the length of the bridge connecting the phthalimide and macrocyclic fragments made it possible to synthesize thiacalix[4]arene derivatives containing from one to four phthalimide groups.[17] In this study, new phenylurea-linked thiacalix[4]arenes were synthesized (Scheme 1, Table 1) and their complexing properties towards some single charged anions were studied.

According to ^{1}H-^{1}H NOESY NMR data, the presence of cross peaks between the protons of the spatially close *tert*-butyl groups and the propylidene fragment of compound **2** and their absence in the case of compound **3** confirm the *1,3-alternate* and *cone* conformation for the macrocycles **2** and **3**, respectively.

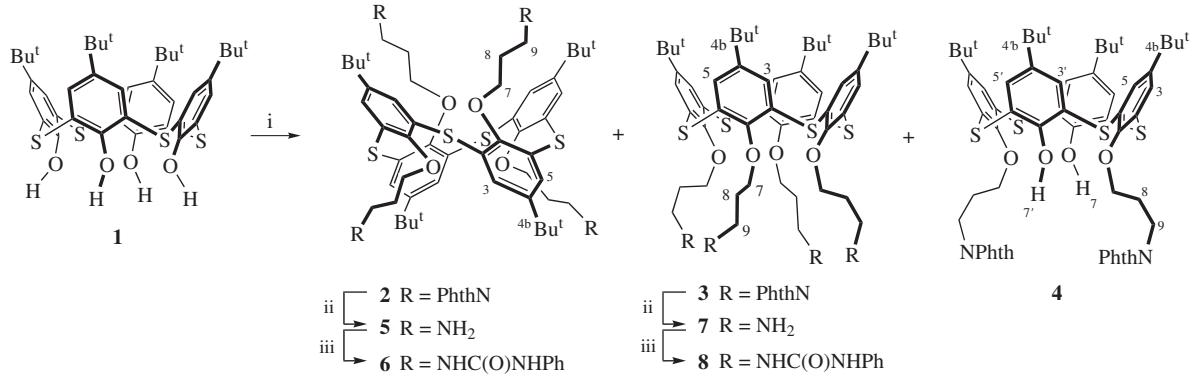
Note that the formation of the *cone* stereoisomer **3** herein observed is not typical of thiacalix[4]arene chemistry. More commonly, *1,3-alternate* stereoisomers do form and no template effect of alkali metal cations is observed.[18–20] In this study, template effect of sodium cation occurred in MeCN and the *cone* stereoisomer **3** was isolated in 53% yield, with the reaction passing through the partially alkylated intermediate **4**. In acetone which is a poorer solvent towards Na_2CO_3,[21] the reaction did not proceed.

Table 1 Yields of compounds **2**–**4**.

Base	Solvent					
	Acetone			Acetonitrile		
	Product	*t*/h	Yield (%)	Product	*t*/h	Yield (%)
Na_2CO_3	no reaction			**3**	100	53
				4	60	72
K_2CO_3	**2**	20	51	**2**	20	50
Cs_2CO_3	**2**	20	70	**2**	20	72

Hydrazinolysis of the phthalimido derivatives **2** and **3** gave amines **5** and **7**, respectively. Subsequent interaction of compounds **5** and **7** with phenyl isocyanate led to corresponding phenylurea derivatives **6** and **8**. According to 2D ^{1}H-^{1}H NOESY NMR data, these transformations did not affect the conformation of the thiacalix[4]arene core.

Treatment of compound **4** with 1-bromodecane in acetone in the presence of cesium carbonate (Scheme 2) afforded tetrasubstituted thiacalix[4]arene derivative **9** in the *1,3-alternate* conformation. Its hydrazinolysis led to diamine **10**, which was then used in the synthesis of the first generation dendrimer-like compound **12** and corresponding phenylurea derivative **11**. The macro-



Scheme 1 *Reagents and conditions*: i, *N*-(3-bromopropyl)phthalimide, M_2CO_3, acetone or acetonitrile; ii, hydrazine hydrate, THF–EtOH; iii, PhNCO, THF.

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