The Characterization and Properties of Calixarenes

- the one-step syntheses of p-tert-butylcalix[4]-, -[ti]-, and -[8]arenes, simple recrystallization suffices
  - Flash chromatography and HPLC

Melting Points of Calixarenes

For the melting points of the parent calixarenes

Dipole Moments of Calixarenes

dipole moment is cone > partial cone > 1,2-alternate > 1,3-alternate

X-Ray Crystallography: The Ultimate Proof of Structure

By 1989, when the previous volume was published, all doubts concerning the structures of the three major and two minor p-tert-butylcalixarenes had been dispelled

pKa Values of Calixarenes

The calixarenes are considerably stronger acids than their monomeric phenolic counterparts, but the accurate measurement of their pK, values has posed some difficuties.

Table 3.1 pK, values of calix[4)arenes and their linear trimer and monomer counterparts

Compound	pK_1	pK_2	pK_3	pK_4
$\mathbf{4}^{SO_2N(CH_2CH_2OH)_2}$	0.8 ± 0.3	9.7 ± 0.1	*ca.* 12.5	> 14
Linear trimer	4.71 ± 0.05	8.27 ± 0.05	11.61 ± 0.1	
Monomer	8.25 ± 0.03			
$\mathbf{4}^{NO_2}$	2.9 ± 0.3	10.9 ± 0.1	12.3 ± 0.2	> 14
Linear trimer	3.6 ± 0.1	10.6 ± 0.1	*ca.* 12.5	
Monomer	8.67 ± 0.03			

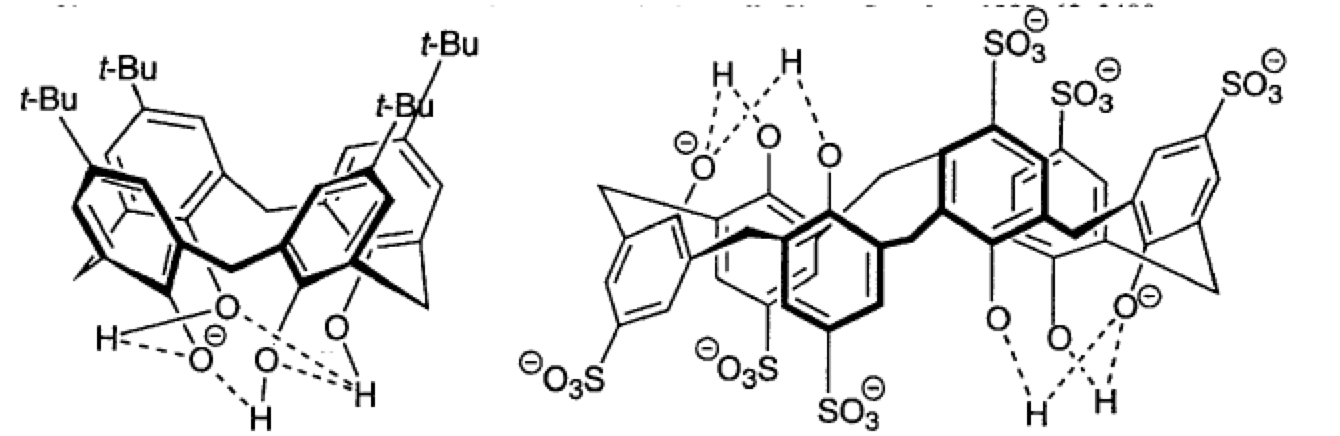

Figure 3.2 *Stabilization of calixarene anions*

Spectral Characteristics of Calixarenes

Infrared Spectra

IR spectra of p-tert-butylcalix[4]- to -[9]arenes

OH stretching band in the 3 100-3500 cm^{-1} region

Ultraviolet Spectra

The UV spectra of the calix[4]- to -[8]arenes

The trend of increasingly large extinction coefficients for the absorptions at 280 and 288 nm, however, reaches a plateau at the calix[8]arene, the larger calixarenes showing little, if any, further escalation in absorptivity.

NMR Spectra

Table 3.3 *Melting points, IR stretching frequences and NMR resonances for the O–H bond in calixarenes*

Compound	*Mp, °C*	ν_{OH}, cm^{-1}	δ_{OH}	*Ref.*
4$^{t\text{-Bu}}$	342–344	3179[a]	10.34	94
4^{SO_3H}		3232, 3411	8.36[b]	97
5$^{t\text{-Bu}}$	310–312		9.64	24
6$^{t\text{-Bu}}$	372–374	3120	10.53	94
6^{SO_3H}		3393[c]	5.13[b]	97
7$^{t\text{-Bu}}$	249 (dec 290)		10.34	24
8$^{t\text{-Bu}}$	418–420	3190	9.60	94
8^{SO_3H}		3242, 3426	4.78[b]	97
p-tert-Butylcalix[9]arene	317–318		9.78	24
p-tert-Butylcalix[10]arene	308–310		9.24	24
p-tert-Butylcalix[11]arene	200–250		9.50	24
p-tert-Butylcalix[12]arene	294–295		9.53	24
p-tert-Butylcalix[13]arene	313–314		9.45	24
p-tert-Butylcalix[14]arene	317–320		9.32	24
p-tert-Butylcalix[15]arene	227–295		9.13	24
p-tert-Butylcalix[16]arene	310–312		9.02	24
p-tert-Butylcalix[17]arene			9.02	24
p-tert-Butylcalix[18]arene			8.98	24
p-tert-Butylcalix[19]arene			9.06	24
p-tert-Butylcalix[20]arene	290–292		8–10	24
Monodeoxy-*p-tert*-butylcalix[4]arene			7.5[d]	108
p-tert-Butylhexahomotrioxacalix[3]arene		3369	8.57	71a

Mass Spectra

primarily for the determination of the molecular weights of compounds

have measured the [dimer]/[monomer] and [trimer]/[monomer] ratios

the calix[7]arenes and calix[8]arenes aggregate as dimers and trimers