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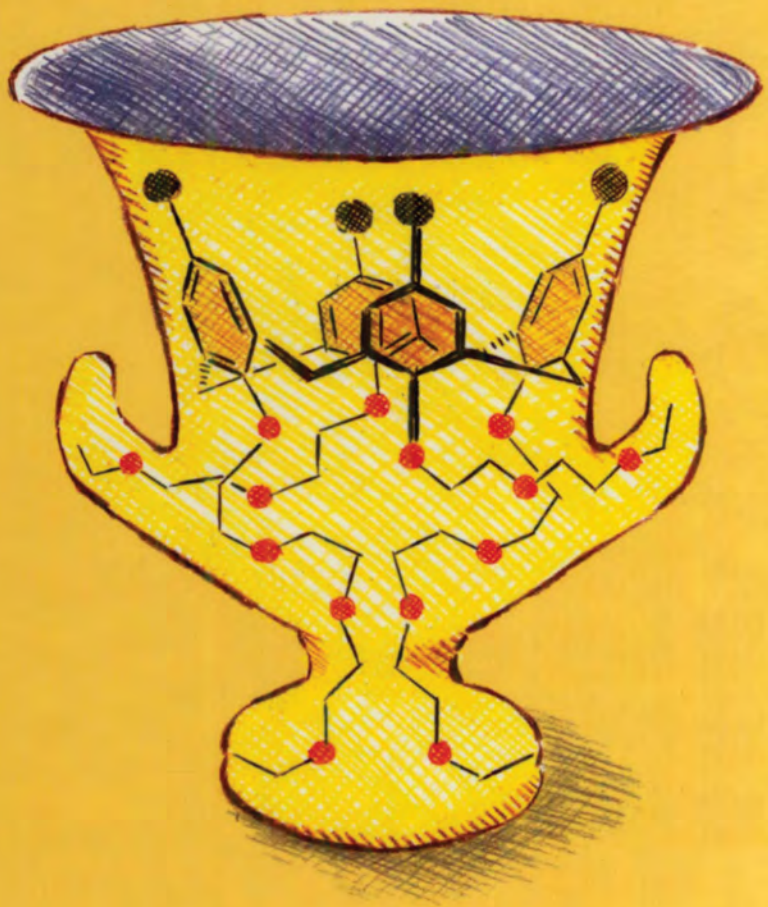
Calixarenes Revisited

by C. David Gutsche



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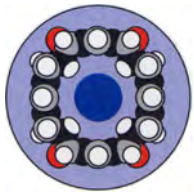

Calixarenes Revisited

C. David Gutsche
Texas Christian University, Fort Worth, USA

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Preface

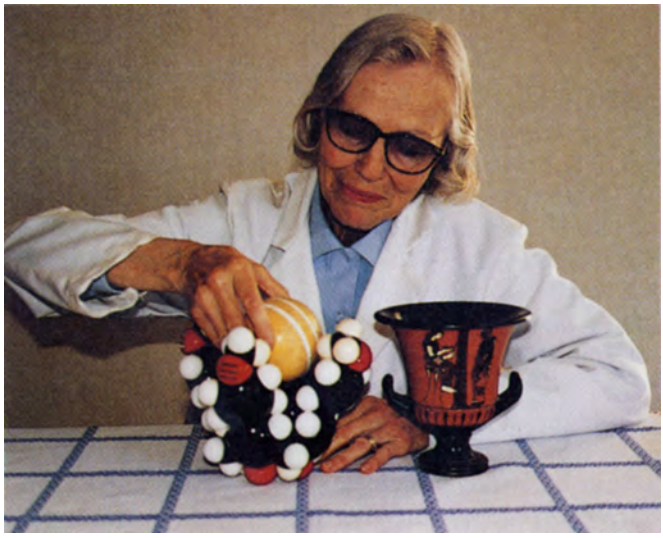
Calixarenes, the predecessor to this book, was published in 1989, at which time slightly more than 200 papers relating to the topic had appeared in the chemical literature. These publications were sufficient to establish the calixarenes as a small but viable subfield of chemistry yet few enough in number to allow easy assimilation into a slim book of 222 pages. The aim of the first volume was to present a comprehensive view of the calixarenes in a relaxed and accessible fashion in the hope of providing a useful summary for those already in the field and an enticement to others to enter the field. In the years that have followed, some of the researchers already committed in 1989 have greatly expanded their efforts while many other researchers not committed in 1989 have entered the field. The result has been an explosive growth of this chemical family which remains still viable but no longer small, well over 1700 papers now populating the literature of calixarenes. Covering the progress of the last seven years with the same leisurely approach used in the previous volume is, unhappily, no longer feasible if *Calixarenes Revisited* is to remain a slim book; a more matter-of-fact account devoid of biographical vignettes has been the result. Nevertheless, *Calixarenes Revisited* builds directly on the framework of the first volume and is intended to stand on its own merits for readers already familiar with the field but to be used in tandem with *Calixarenes* by those with a less detailed background. It covers the literature through the end of 1996, concentrating on the papers published 1989–1996 but also including an occasional paper published before 1989 or after 1996.

In the preface to *Calixarenes* I alluded to my pleasure at seeing the seeds planted in the 1970s sprout and grow in the 1980s. Now, in the 1990s they approach full maturity. This pleasure comes as a mixed blessing, however. Whereas in the early days the likelihood of duplication of effort was rather small, today it is a significant concern as the number of workers has expanded and the level of competition has heightened. As the literature has proliferated, the frequency of the failure of authors to make appropriate attribution to prior work has multiplied. I hope that *Calixarenes Revisited* will help to alleviate this small, but often annoying, problem to which a number of us have unwittingly contributed.

Calixarenes Revisited contains almost 1000 reference citations, which represent about half of those in the literature. Thus, it is not a truly comprehensive survey of the field but, instead, a significant sampling of the literature of the various topics of calixarene chemistry. I hope that it provides a reasonably complete detailing of all of the important topics as well as a useful starting point

for authors wanting to compile a complete bibliography of their particular niche of the field. Of course, arbitrary decisions had to be made whether or not to include particular publications, the general rule being not to include those containing material already well represented by citations in the book. Inevitably, some papers that should have been included were not, either by mistaken judgment on my part or from simple oversight, and for these omissions I express my sincere apologies.

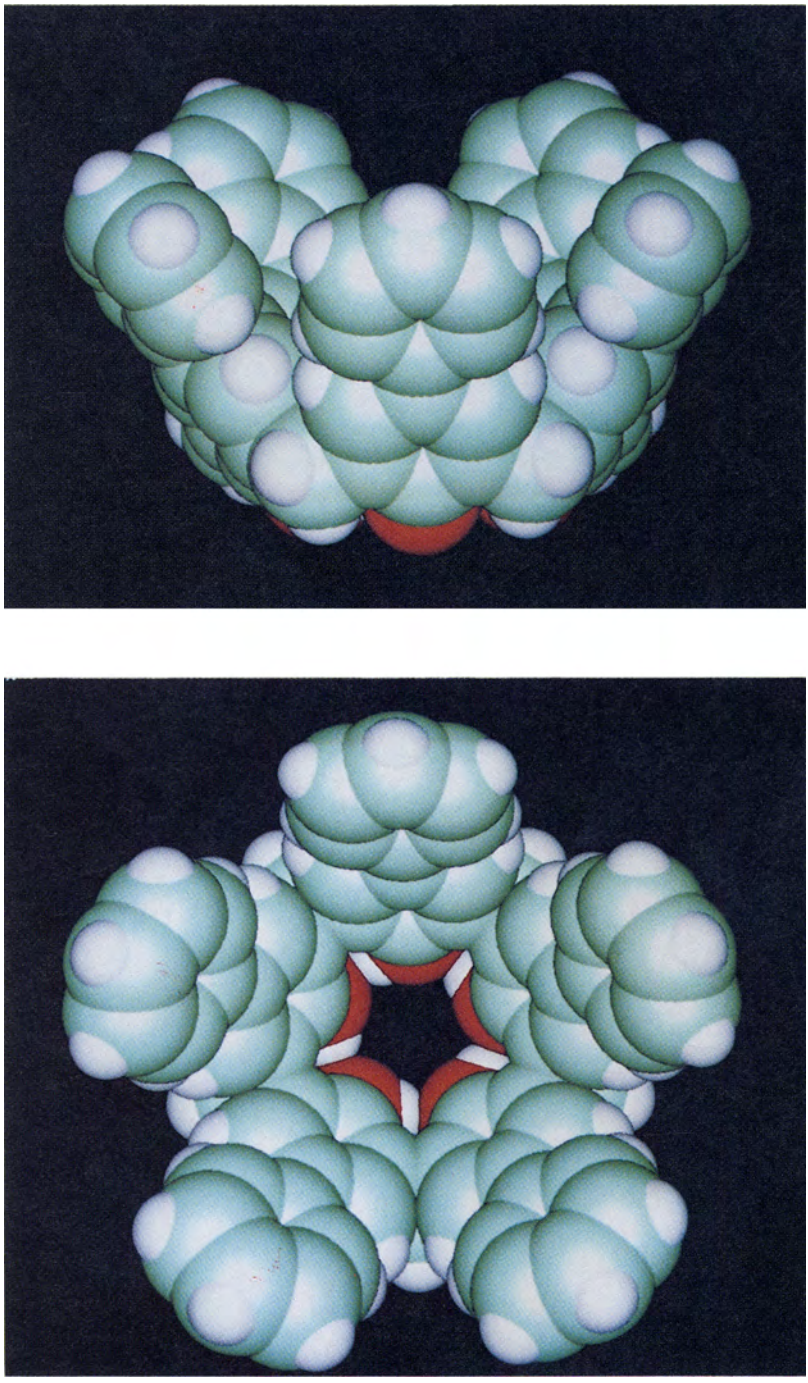
The progress that has been made in modern calixarene chemistry, starting about 25 years ago, can be attributed to the conscientious and often inspired work of many scientists. In Tolstoy's *War and Peace* an incident is described in which the generals have given up the battle and the regiment is facing defeat when a young soldier seizes the fallen flag and rushes toward the enemy, inspiring the others of his regiment to follow suit and turn defeat into victory. In like fashion, members of my own research group have often seized the calixarene flag and carried it forward as, certainly, have the members of the many other research groups around the world. It is to this army of coworkers that the chemical community owes a great debt of gratitude, for without them we generals would have nothing to show for our clever ideas and glorious schemes. The particular members of this army to whom I express special gratitude for their very careful reading of the manuscript in its final phases are Drs. Charles Gibbs, Shiv Kumar Sharma, Donald Stewart, Jian-she Wang, and Dejian Xie. Sharing in this encomium to my coworkers is my wife Alice, whose tireless efforts in collecting literature citations, ceaseless attention to editorial detail, and unerring abilities as homemaker and spouse have contributed inestimably to this second volume of the calixarene series. Finally, appreciation is expressed to the National Science Foundation and the Robert A. Welch Foundation for the research support they have provided during the preparation of this book.



Alice Gutsche with molecular model and calix crater

C. David Gutsche

Fort Worth, Texas
August 1997



Computer-generated structure of *p*-phenylcalix[5]arene showing side and top views

Contents

CHAPTER 1

From Resinous Tar to Molecular Baskets

'The world of books is the most remarkable creation of man . . . Even the books that do not last long, penetrate their own times at least, sailing farther than Ulysses even dreamed of, like ships on the seas. It is the author's part to call into being their cargoes and passengers—living thoughts and rich bales of study and jeweled ideas. And as for the publishers, it is they who build the fleet, plan the voyage, and sail on, facing wreck, till they find every possible harbor that will value their burden'

Clarence S. Day, *The Story of the Yale University Press Told by a Friend*

1.1 Introduction

The world of organic chemistry is populated by several million compounds distributed among hundreds of families. Some of these families have commanded the attention of chemists for many decades and have reached a venerable patrician status. Many others are more recently arrived and have yet to establish their place in the hierarchy of chemical importance. Among the latter is the family of compounds called the calixarenes which, although more than 50 years old, has gained widespread attention from the chemical community only during the last decade.

Calixarenes are [1_n]metacyclophanes (**1**) that acquired their name because of the resemblance of the shape of one of the conformers of the smallest member of their family to a type of Greek vase called a calix crater (Figure 1.1). The name was initially chosen to apply specifically to the phenol-derived cyclic oligomers, but it has subsequently taken on a more generic aspect and is now applied to a wide variety of structurally related types of compounds. The calixarenes were first discussed in comprehensive fashion in 1989 in the first volume of *Monographs in Supramolecular Chemistry*,[1] where the literature on the subject that had been published up to that time was covered in reasonably complete detail in 222 pages. Since 1989, however, there has been such a rapid expansion of the field that a somewhat less comprehensive coverage of topics is now necessary if this

[1] Gutsche, C. D. *Calixarenes* in 'Monographs in Supramolecular Chemistry'; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge; **1989**.

second volume is to be anywhere near as slim as the first. It is our endeavor in this second volume to include a significant portion of the pertinent literature citations in the field through 1996, but to do so in a somewhat selective fashion. The chapter headings used in the first volume are repeated in the present volume and include synthesis, characterization and physical properties, conformations, functionalization, complexation, and practical applications. For readers already familiar with calixarene chemistry this second volume should stand as an independent work. For readers new to the field, however, reference to the first volume should be made to provide the background on which the present volume builds.

1.2 Phenol-derived and Resorcinol-derived Calixarenes

The calixarene family can be subdivided into two major branches, the phenol-derived cyclooligomers (**2**) and the resorcinol-derived cyclooligomers (**3**), as shown in Figure 1.2. Both are discussed in the previous volume.[1] The present monograph, however, will deal almost exclusively with the phenol-derived compounds, the resorcinol-derived compounds having been the subject of a 1994 publication in *Monographs in Supramolecular Chemistry*[2] and a long review article.[3]

1.3 Historical Perspective

The story of the 'resinous tar[4] to molecular baskets' now called calixarenes is described in detail on pages 1–25 of the first volume,[1] where particular emphasis is given to the work by Zinke and coworkers. Zinke's investigations,[5] starting in the early 1940s and extending into the 1950s, dealt with what were thought to be cyclotetramers obtained from the base-induced reactions of *p*-alkylphenols with formaldehyde.[6] Experiments carried out by Cornforth and coworkers[7] in the 1950s indicated that the Zinke products were actually mixtures, and the investigations by Gutsche and coworkers starting in the mid-1970s established the identity of three of the components of the mixtures as cyclic tetramer, cyclic hexamer, and cyclic octamer.[8] It was in these early papers of Gutsche that the

[2] Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests* in 'Monographs in Supramolecular Chemistry'; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge; **1994**.

[3] Timmerman, P.; Verboom, W.; Reinhoudt, D. N. *Tetrahedron* **1996**, 52, 2663–2704.

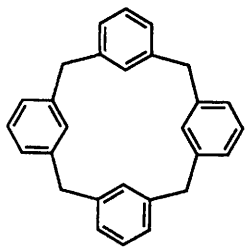
[4] Baeyer, A. *Ber.* **1872**, 5, 25, 280, 1094.

[5] Further insight into life in the Zinke laboratory at that time is provided in a delightful essay by Kappe, T. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, 19, 3–15.

[6] Zinke, A.; Ziegler, E. *Ber.* **1941**, *B*74, 1729; *idem. ibid.* **1944**, 77, 264; Zinke, A.; Zigeuner, G.; Hössinger, K.; Hoffmann, G. *Monatsh.* **1948**, 79, 438; Zinke, A.; Kretz, R.; Leggewie, E.; Hössinger, K. *ibid.* **1952**, 83, 1213.

[7] Cornforth, J. W.; D'Arcy Hart, P.; Nicholls, G. A.; Rees, R. J. W.; Stock, J. A. *Br. J. Pharmacol.* **1955**, 10, 73. Also see Cornforth, J. W.; Morgan, E. D.; Potts, K.T.; Rees, R. J. W. *Tetrahedron* **1973**, 29, 1659.

[8] (a) Gutsche, C. D.; Kung, T. C.; Hsu, M.-L. Abstracts of 11th Midwest Regional Mtg. of Am. Chem. Soc., Carbondale, IL, **1975**, no. 517; (b) Muthukrishnan, R.; Gutsche, C. D. *J. Org. Chem.* **1979**, 44, 3962; (c) Gutsche, C. D.; Dhawan, B.; No, K. H.; Muthukrishnan, R. *J. Am. Chem. Soc.* **1981**, 103, 3782.



1

[1$_4$]metacyclophane

Calix crater

CPK model carrying a guest

Figure 1.1 [1$_4$]*Metacyclophane, calix crater, and CPK model*

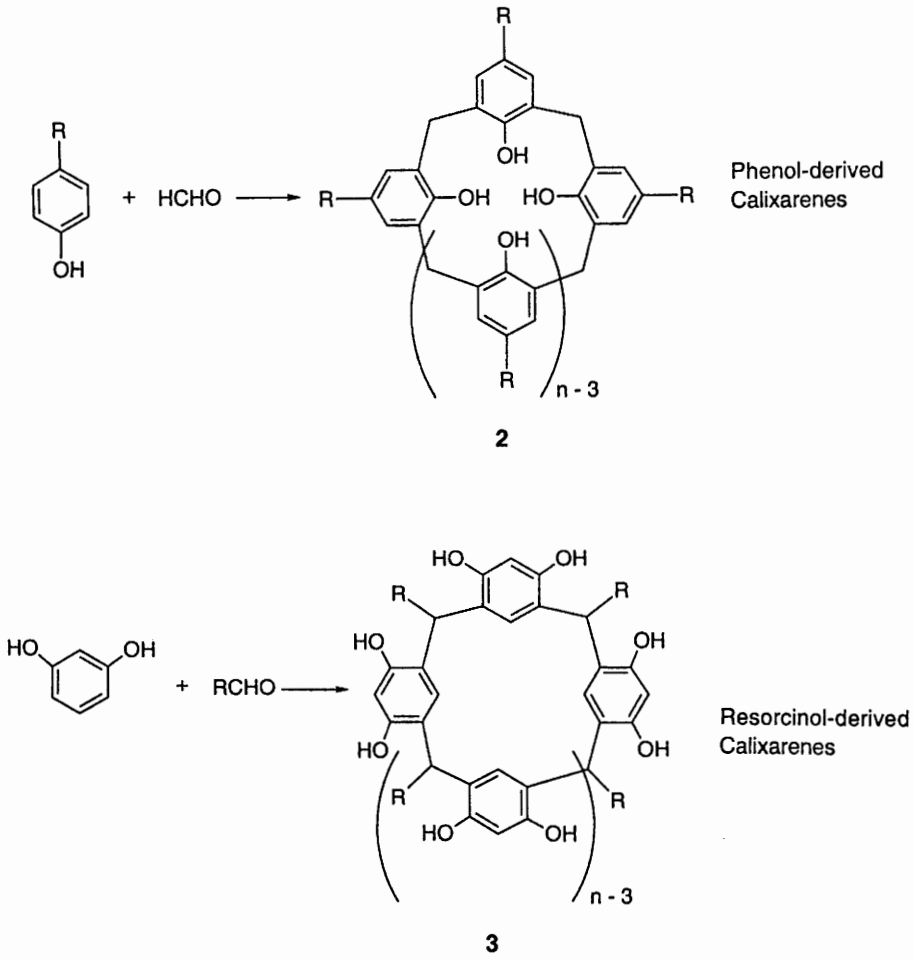


Figure 1.2 *Phenol-derived and resorcinol-derived calixarenes*

Zinke compounds acquired the name 'calixarene'.[9] During the 1980s this group devised simple and easily reproduced procedures for synthesizing *p-tert*-butylcalix[4]arene (**4**; R = *t*-Bu), *p-tert*-butylcalix[6]arene (**6**; R = *t*-Bu), and *p-tert*-butylcalix[8]arene (**8**; R = *t*-Bu) (see Figure 1.3) in good to excellent yield on any scale, from a gram or less to many kilograms.[10] The ready availability of these three calixarenes from cheap starting materials has been an important factor in the rapid escalation of research in this field during the last decade, the magnitude of which can be judged from the two books,[1,11] and the many reviews

[9] Gutsche, C. D.; Muthukrishnan, R. *J. Org. Chem.* **1978**, 43, 4905.

[10] (a) Gutsche, C. D.; Iqbal, M. *Org. Synth.* **1990**, 68, 234; (b) Gutsche, C. D.; Dhawan, B.; Leonis, M.; Stewart, D. *ibid.* **1990**, 68, 238; (c) Munch, J. H.; Gutsche, C.D. *ibid.* **1990**, 68, 243.

[11] 'Calixarenes, A Versatile Class of Macrocyclic Compounds', Vicens, J.; Böhmer, V. Eds.; Kluwer: Dordrecht; **1991**.

(short,[12] medium length,[13] and long[14]) that have been written on the calixarenes.

It is interesting to plot the growth of interest in the calixarenes, as depicted in Figure 1.4. Beginning with the 19th century experiments of Adolf von Baeyer, continuing through the early part of the 20th century with the introduction of Bakelite by Leo Baekeland, and extending to the early 1940s with the experi-

[12] Short reviews: (a) Vocanson, F.; Lamartine, R. 'The Chemistry of *p-tert*-Butyldihomooxacalix[4]arene', *Acros Org. Acta* **1996**, 2, 1, 6–7; (b) Asfari, Z.; Vicens, J. 'Calix[4]-bis-crowns', *Acros Org. Acta* **1996**, 2, 8–9; (c) Gutsche, C. D. 'Calixarenes', *Aldrichim. Acta* **1995**, 28, 3–9; (d) O'Conner, K. M.; Arrigan, D. W. M.; Svehla, G. 'Calixarenes in Electroanalysis', *Electroanalysis* **1995**, 7, 205–215; (e) Takeshita, M.; Shinkai, S. 'Recent Topics on Functionalization and Recognition Ability of Calixarenes', *Bull. Chem. Soc. Jpn.* **1995**, 68, 1088–1097; (f) Asfari, Z.; Wenger, S.; Vicens, J. 'Calixcrowns and Related Molecules', *Pure Appl. Chem.* **1995**, 67, 1037–1043; (g) Asfari, Z.; Vicens, J. 'The Chemistry of the Calix[5]arenes', *Acros Org. Acta* **1995**, 1, 18–21; (h) Danil de Namor, A. F.; Blackett, P. M.; Garrido Pardo, M. T.; Pacheco Tanaka, D. A.; Sueros Velarde, F. J.; Cabaleiro, M. C. 'From Molecules to Electrolytes. Electrochemical and Thermodynamic Aspects of the Interaction of Phenol and Resorcinol Based Calixarenes with Amines', *Pure Appl. Chem.* **1993**, 65, 415–422; (i) Roundhill, D. M.; Georgiev, E.; Yordanov, A. 'Calixarenes with Nitrogen or Phosphorus Substituents on the Lower Rim', *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, 19, 101–109; (j) Linnane, P.; Shinkai, S. 'Calixarenes: Adaptable Hosts Par Excellence', *Chem. Ind. (London)* **1994**, 811–814; (k) Asfari, Z.; Wenger, S.; Vicens, J. 'New Complexing Macrocycles: The Calixcrowns', *Supramol. Sci.* **1994**, 1, 103–110; (l) Swager, T. M.; Xu, B. 'Liquid Crystalline Calixarenes', *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, 19, 389–398; (m) Asfari, Z.; Weiss, J.; Vicens, J. 'Double-Calixarene Design, Synthesis, and Properties', *Synlett* **1993**, 719–725; (n) van Dienst, E.; Iwema Bakker, W. I.; Engbersen, J. F. J.; Verboom, W.; Reinhoudt, D. N. 'Calixarenes, Chemical Chameleons', *Pure Appl. Chem.* **1993**, 65, 387–392; (o) Schwing-Weill, M.-J.; Arnaud-Neu, F.; McKervey, M. A. 'Modulation of the Cation Complexing Properties in the Lower Rim of Chemically Modified Calixarene Series', *J. Phys. Org. Chem.* **1992**, 5, 496–501; (p) Asfari, Z.; Vicens, J. 'Calixarenes' *Janssen Chim. Acta* **1992**, 10, 3–10; (q) McKervey, M. A.; Böhmer, V. 'Calixarenes – Supramolecular Pursuits', *Chem. Br.* **1992**, 28, 724–727; (r) Gutsche, C. D.; Rogers, J. S.; Stewart, D.; See, K. A. 'Calixarenes: Paradoxes and Paradigms in Molecular Baskets', *Pure Appl. Chem.* **1990**, 62, 485–491; (s) Böhmer, V. 'Special Calixarenes, Synthesis and Properties', New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications; Elsevier Applied Science: London; **1991**, pp. 133–141.

[13] Medium length reviews: (a) Ikeda, A.; Shinkai, S. 'Novel Design Using Calix[4]arene Skeletons: Toward Molecular Recognition and Metal Binding', *Chem. Rev.* **1997**, 97, 1712–1734; (b) Otsuka, H.; Shinkai, S. 'Stereochemical Control of Calixarenes Useful as Rigid and Conformationally Diversiform Platforms for Molecular Design', *Supramol. Sci.* **1996**, 3, 189–205; (c) Brouwer, E. B.; Ripmeester, J. A.; Enright, G. D. '*t*-Butylcalix[4]arene Host–Guest Compounds: Structure and Dynamics', *J. Inclusion Phenom. Mol. Recognit. Chem.* **1996**, 24, 1–17; (d) Neri, P.; Consoli, G. M. L.; Cunsolo, F.; Geraci, C.; Piattelli, M. 'Selective Functionalization and Preorganization of Calix[8]arenes', *New J. Chem.* **1996**, 20, 433–446; (e) Taskeshita, M.; Shinkai, S. 'Recent Topics in Functionalization and Recognition Ability of Calixarenes: The Third Host Molecule', *Bull.Chem. Soc. Jpn.* **1995**, 68, 1088–1097; (f) Asfari, Z.; Wenger, S.; Vicens, J. 'Calixcrowns and Related Molecules', *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, 19, 137–148; (g) Bottino, F.; Pappalardo, S. 'Synthesis and Properties of Pyridinocalixarenes', *ibid.* **1994**, 19, 85–100; (h) Diamond, D. 'Calixarene-Based Sensing Agents', *ibid.* **1994**, 19, 149–166; (i) Mnuk, P.; Feltl, L. 'Calixarenes – Selective Molecular Receptors', *Chem. Listy* **1993**, 87, 613–626; (j) Perrin, R.; Lamartine, R.; Perrin, M. 'The Potential Industrial Applications of Calixarenes', *Pure Appl. Chem.* **1993**, 65, 1549–1559; (k) Groenen, L. C.; Reinhoudt, D. N. 'Calix[4]arenes, Molecular Platforms for Supramolecular Structures', in *Supramolecular Chemistry*; Balzani, V.; De Cola, L., Eds.; Kluwer: Amsterdam; **1992**, pp. 51–70; (l) Arduini, A.; Casnati, A.; Fabbi, M.; Minari, P.; Pochini, A.; Sicuri, A. R.; Ungaro, R. 'New Shapes for Selective Molecular Recognition from Calixarenes', in *Supramolecular Chemistry*; Balzani, V.; De Cola, L., Eds.; Kluwer: Amsterdam; **1992**, pp. 31– 50; (m) Gutsche, C. D.; Alam, I.; Iqbal, M.; Mangiafico, T.; Nam, K. C.; Rogers, J. S.; See, K. A. 'Topics in Calixarene Chemistry', *J. Inclusion Phenom. Mol. Recognit. Chem.* **1989**, 7, 61–72; (n) Gutsche, C. D. 'Calixarenes', *Acc. Chem. Res.* **1983**, 16, 161–170.

[14] Long Reviews: (a) Pochini, A.; Ungaro, R. 'Calixarenes and Related Hosts,' in *Comprehensive Supramolecular Chemistry*; Vögtle, F., Ed.; Pergamon Press: Oxford; **1996**, Vol. 2, pp. 103–142; (b) McKervey, M. A.; Schwing-Weill, M.-J.; Arnaud-Neu, F. 'Cation Binding by Calixarenes', in

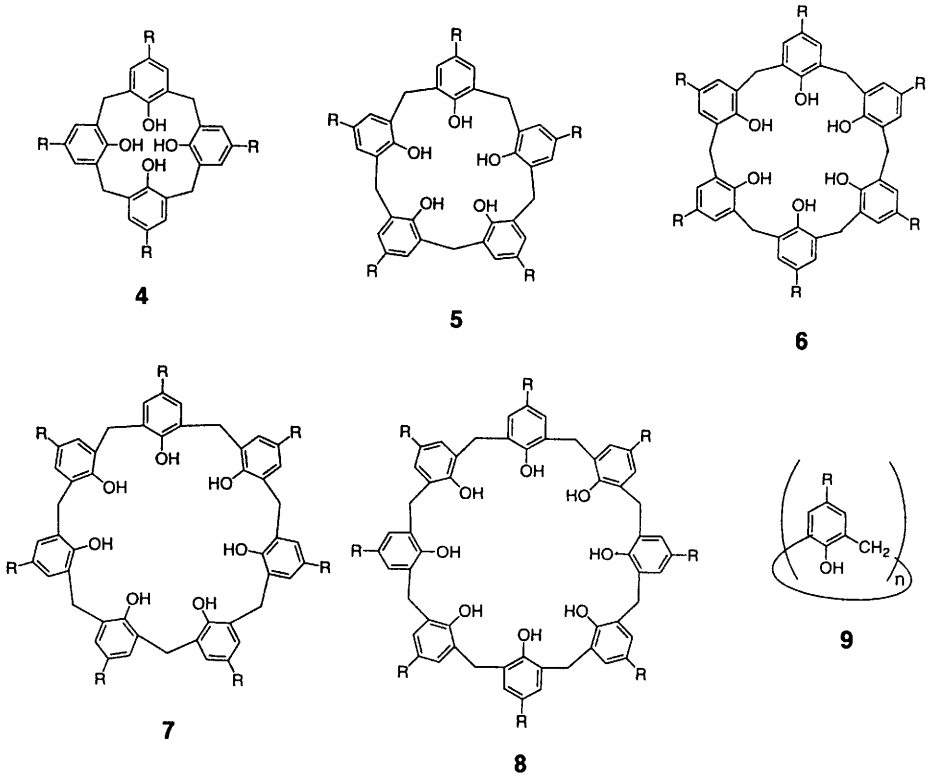


Figure 1.3 *Family of* p-tert-*butylcalix*[n]*arenes*

ments of Zinke and Niederl,[15] the growth curve is almost flat. A minor flurry of activity occurred in the 1950s in the laboratories of Cornforth and Hayes and Hunter, adding a slight positive lift. However, not until the 1970s with the entry of the Mainz group of Kämmerer (and then Böhmer), the Parma group of Andreetti, Pochini, and Ungaro, and the St Louis group of Gutsche (along with

Comprehensive Supramolecular Chemistry; Gokel, G., Ed.; Pergamon Press: Oxford; **1996**, Vol. 1, pp. 537–603; (c) Böhmer, V. 'Calixarenes, Macrocycles with (Almost) Unlimited Possibilties', *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 713–745; (d) Roundhill, D. M. 'Metal Complexes of Calixarenes', *Progr. Inorg. Chem.* **1995**, 533–592; (e) Böhmer, V.; Kraft, D.; Tabatabai, M. 'Inherently Chiral Calixarenes', *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, 19, 17–39; Brodesser, G.; Vögtle, F. 'Homocalixarenes and Homocalixpyridines', *ibid.* **1994**, 19, 111–135; (f) Shinkai, S. 'Calixarenes – The Third Generation of Supramolecules', *Tetrahedron* **1993**, 49, 8933–8968; (g) van Loon, J.-D.; Verboom, W.; Reinhoudt, D. N. 'Selective Functionalization and Conformational Properties of Calix[4]arenes: A Review', *Org. Prep. Proced. Int.* **1992**, 24, 437–462; (h) Gutsche, C. D. 'Calixarenes: An Overview', *Inclusion Compounds*; Atwood, J. L.; Davies, J. E. D.; MacNicol, D., Eds.; Oxford University Press: Oxford; **1991**, Vol. 4, pp. 27–63; (i) Böhmer, V.; Kämmerer, H. 'Oligonuclear Phenolic Compounds to Calixarenes', in *Chemistry and Physics of Macromolecules*; Fischer, E. W., Schulz, R. C.; Sillescu, H., Eds.; VCH: Weinheim; **1991**, pp. 13–38; (j) Gutsche, C. D. 'Calixarenes and the Art of Molecular Basketmaking', in *Synthesis of Macrocyclics: The Design of Selective Complexing Agents*; Izatt, R.M.; Christensen, J. J., Eds.; Wiley: New York; **1987**, pp. 93–165; (k) Gutsche, C. D. 'The Calixarenes', *Top. Curr. Chem.* **1984**, 123, 1–47.

[15] Niederl, J. B.; McCoy, J. S. *J. Am. Chem. Soc.* **1943**, 65, 629.

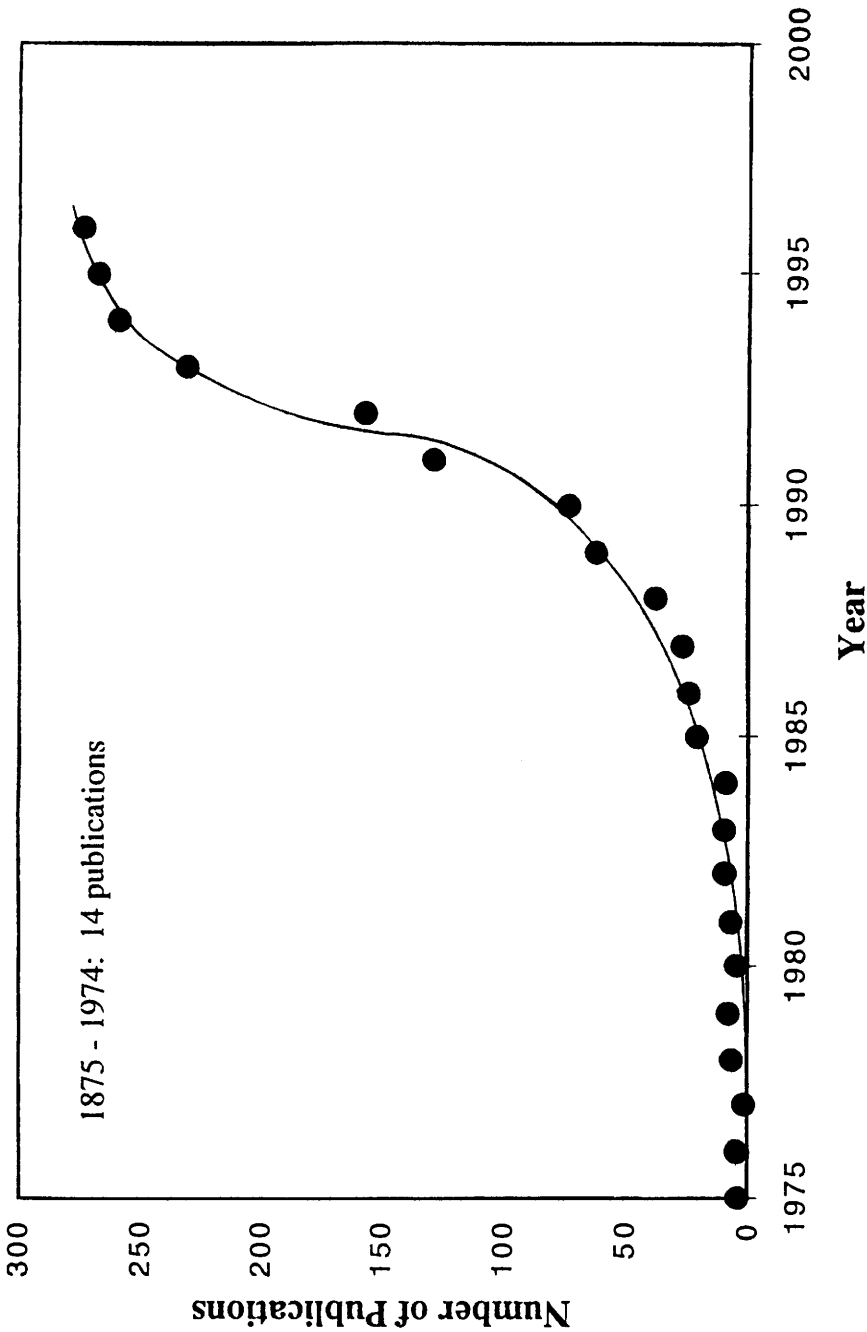
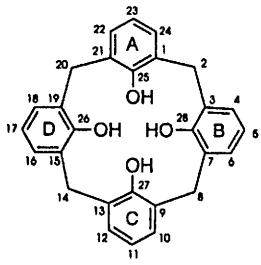


Figure 1.4 *Growth curve of interest in calixarene chemistry*

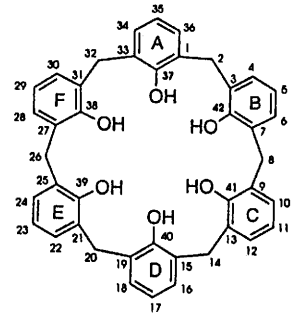
the Petrolite group of Buriks *et al.*) does the curve begin to move inexorably upward. Then, starting in the mid-1980s and continuing to the mid-1990s the curve becomes ever more steeply ascending, now reaching a plateau with the publication of five or more papers/week. The items of fascination that have led to this explosive growth are the subject of the remainder of this book.

1.4 Nomenclature and Representation

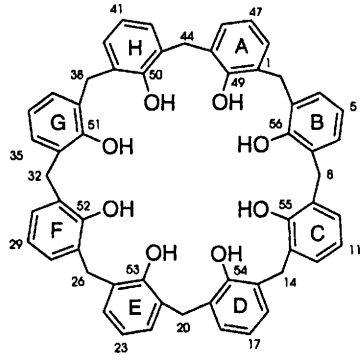
The original calixarene nomenclature implicitly included the OH groups as part of the structure being named. As the field has matured and proliferated, however, this presumption no longer seems warranted, and the term 'calixarene' is better applied only to the basic structures devoid of substituents, as illustrated in Figure 1.5 for the cyclic tetramer, dihomooxatetramer, cyclic hexamer, and cyclic octamer derived from a *p*-substituted phenol and formaldehyde. The phenol-derived and resorcinol-derived cyclooligomers can be differentiated by referring to the former as *endo*-OH calixarenes (*i.e.* the OH groups oriented toward the



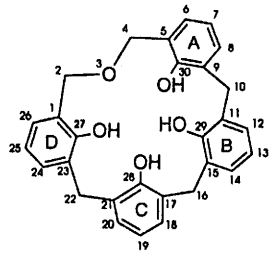
calix[4]arene-25,26,27,28-tetrol



calix[6]arene-36,37,38,39,40,41,42-hexol



calix[8]arene-49,50,51,52,53,54,55,56-octol



2,3-dihomo-3-oxacalix[4]arene-27,28,29,20-tetrol

Figure 1.5 *Nomenclature of calixarenes*

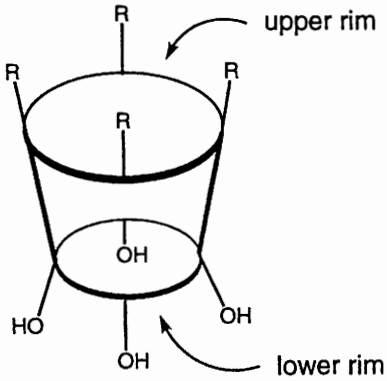


Figure 1.6 *Representation of the calixarenes and designation of the faces*

annulus) and the latter as *exo*-OH calixarenes (*i.e.* the OH groups oriented away from the annulus). As illustrated in the next chapter, calixarenes are now known that contain both *endo*- and *exo*-OH groups. Clearly, both the phenol-derived and the resorcinol-derived cyclooligomers are members of the calixarene family, as was recognized by the earlier assignment of the name 'calixresorcarene' to the latter.[1] Unhappily, it is becoming increasingly the custom to shorten this to 'resorcarene', belying its cyclic array. By analogy, the phenol-derived cyclooligomers should be called 'phenarenes', clearly a less felicitious and descriptive name than 'calixarenes'. It is hoped, therefore, that the 'calixresorcarene' name will be retained even though it flies in the face of the power of brevity.

Since vases ordinarily stand upright on their bases and since calixarenes derive their name from a Greek vase, calixarene structures should generally be depicted with the aryl carbon between the methylene groups (*i.e.* usually carrying an oxygen function) pointing downward and the aryl *para* carbon pointing upward. Accordingly, the face bearing the *endo* hydroxyl groups is designated as the 'lower rim', and the face bearing the *para* substituents is designated as the 'upper rim' (Figure 1.6). 'Upside-down' representations of the calixarenes frequently appear in the literature, and Böhmer has suggested the designations 'narrow rim' and 'wide rim' to avoid the orientation-dependency. All such designations, however, become vague when applied to larger calixarenes in which there may be no well-defined 'upper, wide rim' or 'lower, narrow rim'. Still another designation that might be useful is based on the cyclic structure *per se*, without recourse to either its orientation or its shape. It names the lower, narrow rim as the '*endo* rim' and the upper, wide rim as the '*exo* rim'. In this book, however, the 'upper rim/lower rim' nomenclature will be retained.

As already indicated, the term 'calixarene' is variously employed in different contexts. In colloquial usage (*e.g.* as often employed in the discussion section of a paper) the name implies the presence of hydroxyl groups as, for instance, in '*p-tert*-butylcalix[4]arene' as applied to **4** (R = *t*-Bu). More precisely, in keeping with the suggestion above, the accurate specification of a compound (*e.g.* as used in the experimental section of a paper) implies only the basic skeleton to which

the substituents, including the OH groups, are attached at positions designated by appropriate numbers. Thus, **4** (R = *t*-Bu) becomes 5,11,17,23-tetra-*tert*-butylcalix[4]arene-25,26,27,28-tetrol. The abbreviated names will be frequently used when it is clear that all of the *p*-positions (*exo* positions) are occupied by the same group (*e.g.* four *tert*-butyl groups in *p-tert*-butylcalix[4]arene; eight *tert*-butyl groups in *p-tert*-butylcalix[8]arene, *etc.*). In cases where it might be ambiguous, however, the name will be made more explicit by indicating the number of *p*-substituents (*e.g.* tetra-*p-tert*-butylcalix[4]arene, mono-*p-tert*-butylcalix[6]arene, *etc.*).

The calixarenes represented by the numbers **4**–**8** appear many times throughout this book, so to designate these structures they will be represented by a number (*i.e.* **4**–**8**) which specifies the number of aryl residues in the cyclic array) and a superscript which specifies the *p*-substituent (*i.e.* *t*-Bu, H, SO_3H, *etc.*) Thus, *p-tert*-butylcalix[4]arene is represented as $\mathbf{4}^{t\text{-Bu}}$; *p*-H-calix[6]arene (more correctly named simply as calix[6]arene) is represented as $\mathbf{6}^{\mathbf{H}}$, *etc.* To avoid any confusion with the other numbers in the text the numbers **4**–**8** when used in this fashion appear in a characteristic font. In many instances when the generalized identity and position of attachment of substituents are made more specific, the following conventions are used: (a) the same group (*i.e.* R or Y) appearing on the carbon or oxygen of two or more aryl residues is specified as $R^{1,2}$, $R^{1,3,4}$, R^{1-4}, $Y^{2,4,6}$, *etc.*; (b) a group bridging two positons is specified as R^1R^2, R^1R^3, Y^1Y^4, *etc.*

Another nomenclature device that is used throughout the book as an easy way to indicate the arrangement of substituents on the upper or lower rims of a calixarene is to label the rings A, B, C, *etc.*, and to specify the rings to which the substituents are attached. Thus, a di-*p-tert*-butylcalix[4]arene can be designated as an 'A,B-' or an 'A,C-di-*p-tert*-butylcalix[4]arene'; the symmetrical trimethyl ether of a calix[6]arene can be designated as an A,C,E-trimethyl ether, *etc.* The ways for naming and representing the conformational isomers of calixarenes are discussed in Section 4.1.