

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713649759>

Ab Initio Equilibrium Geometry and Vibrational Spectroscopic Study of 25,26,27,28-tetrahydroxycalix[4]arene

Ferenc Billes^a; Ildikó Mohammed-Ziegler^a

^a Department of Physical Chemistry, Budapest University of Technology and Economics, Budapest, Hungary

Online publication date: 29 October 2010

To cite this Article Billes, Ferenc and Mohammed-Ziegler, Ildikó(2010) 'Ab Initio Equilibrium Geometry and Vibrational Spectroscopic Study of 25,26,27,28-tetrahydroxycalix[4]arene', *Supramolecular Chemistry*, 18: 5, 451 – 459

To link to this Article: DOI: 10.1080/10610270212491

URL: <http://dx.doi.org/10.1080/10610270212491>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Ab Initio Equilibrium Geometry and Vibrational Spectroscopic Study of 25,26,27,28-tetrahydroxycalix[4]arene

FERENC BILLES* and ILDIKÓ MOHAMMED-ZIEGLER†

Department of Physical Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Budafoki út 8., Hungary

The aim of this work was to present a comprehensive vibrational spectroscopic study of 25,26,27,28-tetrahydroxycalix[4]arene. For this purpose, quantum chemical calculations were carried out at the *ab initio* HF/4-31G* level, as a consequence of the great size of the molecule. In the frame of these calculations, the symmetry of the molecule was investigated. Trying C_{4v} , C_{2v} and C_s symmetries as input, the geometry optimization, however, pointed to the C_2 configuration. In the latter case, all the calculated vibrational frequencies were greater than zero, and therefore the equilibrium geometry could be identified. Medium and far infrared as well as Raman spectra of the compound were measured. On the basis of the calculated force constants and geometric parameters, normal coordinate analysis was applied for the interpretation of the experimental vibrational spectra. Problems arose with the choice of the internal coordinates of the molecule, which are important from the point of view of the internal macrocycle ("lower rim") of the molecule. On the basis of the theory of redundant coordinates, a program was written for choosing the coordinates of this 16-membered cycle. Full interpretation of the vibrational fundamentals of the compound is presented. Several force constant matrix elements have surprisingly high values. As a result of the normal coordinate analysis, the relative rigidity of the lower rim was concluded. *Ab initio* calculations and assignment of the vibrational spectra of 25,26,27,28-tetrahydroxycalix[4]arene based on the calculations are presented.

Keywords: Calix[4]arene; *Ab initio*; Geometry; Vibrational spectra; Normal coordinate analysis

INTRODUCTION

The compound 25,26,27,28-tetrahydroxycalix[4]arene (CAL, Fig. 1) has been widely investigated and applied since CAL and its derivatives are used as sensing components in ionic sensors [1–3] or for

extraction [4,5], both due to their complex forming properties [6–8]. They have also been studied as artificial ion channels [9,10]. Therefore it is reasonable to study the structure of the basic compound for the understanding of the properties and the mechanism of the aforementioned phenomena.

This work deals with the interpretation of the vibrational spectra of 25,26,27,28-tetrahydroxycalix[4]arene, and with this knowledge, to provide insight into the properties of this compound.

So far, theoretical studies concerning the CAL molecule and/or its derivatives have mostly been restricted to host–guest interaction calculations applying molecular mechanics [11,12], quantum chemical methods [13–17], or hybrid approaches [18]. The calculation of the equilibrium geometries of the four thiacalix[4]arene conformers was reported recently [19].

Molecular dynamics were frequently used for the simulation of complexes with CAL and its derivatives [20–25], and simulation of the conformational transitions [26,27]. Vibrational spectra of some host–guest structures based on alkyl substituted CAL derivatives were presented recently [28].

To the best of our knowledge, articles concerning the vibrational spectroscopy of CAL (experiment and quantum chemical calculations) have not been published yet.

MATERIALS AND METHODS

Compound

25,26,27,28-tetrahydroxycalix[4]arene was prepared at the Department of the Organic Chemical Technol-

*Corresponding author. E-mail: billes.fkt@chem.bme.hu

†Present address: Chemical Research Center, Hungarian Academy of Sciences, H-1025 Budapest, Pusztaszeri út 59–67, Hungary.

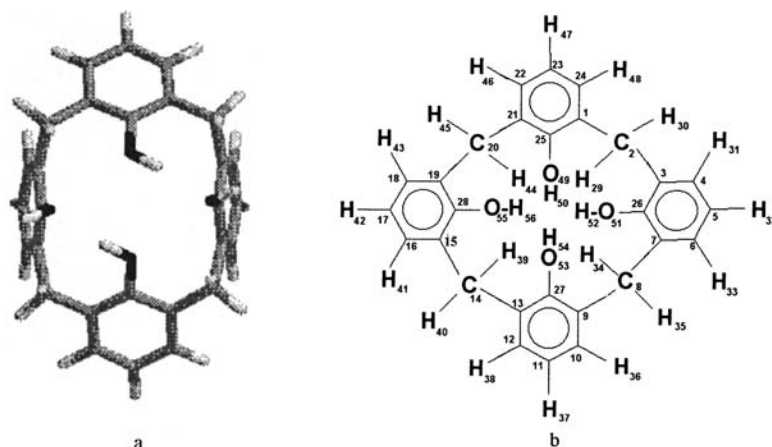


FIGURE 1 The structure of the 25,26,27,28-tetrahydroxycalix[4]arene molecule, a: steric structure (oxygen: black, carbon: gray, hydrogen: white), b: numbering of the atoms.

ogy of the Budapest University of Technology and Economics [29]. Its purity was controlled by thin layer and column chromatography and by measuring the melting point.

Spectra

Spectra were recorded in the *medium infrared* region on a Perkin–Elmer 2000 type spectrometer, using the diffuse reflectance (DRIFT) technique (dried KBr powder was mixed simply with 4 weight% of sample) between 6000 and 400 cm^{-1} , with 1 cm^{-1} resolution and the accumulation of 512 scans. *Far infrared spectra* were measured on a Bio-Rad Digilab FTS 40 type instrument (transmittance, sample in nujol matrix) in the 660–60 cm^{-1} region, with 2 cm^{-1} resolution and the accumulation of 1024 scans.

Raman spectra were obtained on a Perkin–Elmer 1760 FT-IR type spectrometer equipped with a 1700X FT-Raman supplement being excited with 0.8 W of the intensity-stabilized 1064 nm line of a Spectron SL 301 Series Nd:YAG laser. The solid state spectrum was measured between 4000 and 200 cm^{-1} with a resolution of 1 cm^{-1} , and 850 scans were accumulated.

CALCULATION

Quantum Chemical Calculations

Quantum chemical calculations (QCC) were carried out applying the GAUSSIAN 98 program package [30]. The applied method and basis set were chosen taking into account the size and the number of orbitals in the molecule ($\text{C}_{28}\text{O}_4\text{H}_{24}$). It was found that the HF method with 4-31G* basis set was suitable for the calculations in accordance with the size of the molecule and the necessary computing time.

The first step of the calculations was the geometry optimization, which resulted in the optimized

equilibrium geometry (r_e) and the atomic net charges. During the second step, the molecular energy was differentiated twice to the Cartesian coordinates. This facilitated calculation of the Cartesian vibrational force constants, the vibrational frequencies, the infrared and Raman intensities and the depolarization factors of the normal modes.

Normal Coordinate Analysis

Normal coordinate analysis (NCA) was based on the results of the quantum chemical calculations (optimized equilibrium geometry and force constants) and the evaluation of the experimental spectra (positions and intensities of the spectral bands). A home-made program was applied for these calculations. Since the molecule has 56 atoms, the number of independent internal coordinates is 162, i.e. the matrixes used in these calculations have 162×162 elements. According to the C_2 symmetry of the molecule its irreducible representation is

$$\Gamma = 82A + 80B$$

First, the internal coordinates were chosen. It must be considered that, from the point of view of the spectroscopy, the lower rim of the molecular cone can be regarded as a macrocycle. This requirement was fulfilled with the determination of the redundancy conditions of this ring [31]. The six conditions for molecular rings (loops) can be summarized in two theorems:

1. Regarding the chemical bonds as vectors directed in the same sense their vector sum is zero (three conditions). They comprise the bond lengths (l), valence angles (φ) and torsional angles (τ) of the ring.
2. For every ring atom, (r), a coordinate system in the same manner and a unit vector in one of these systems were defined. If this vector is transformed from system to system systematically

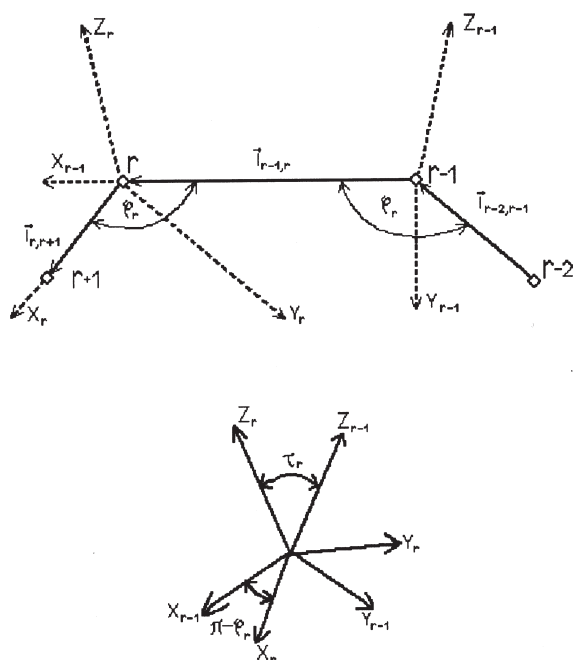


FIGURE 2 Definition of local Cartesian coordinate systems around the ring atoms.

around the ring, the initial one can be derived. This also implies three conditions, since the result is a vector equation containing valence angles and torsional angles of the ring.

Figure 2 presents a part of a ring with two atoms. According to theorem 1

$$\sum_{r=1}^n \mathbf{l}_{r-1,r} = 0 \quad (1)$$

$$\mathbf{l}_{r-1,r} = l_{r-1,r} \mathbf{i}_r \quad (2)$$

where n is the number of ring atoms and \mathbf{i}_r is the unit vector in the direction of $l_{r,r-1}$. The matrix of transformation, from the coordinate system defined around atom r to the same at atom $r - 1$ has the form

$$\mathbf{T}_r = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(\tau_r) & \sin(\tau_r) \\ 0 & -\sin(\tau_r) & \cos(\tau_r) \end{bmatrix} \times \begin{bmatrix} -\cos(\varphi_r) & \sin(\varphi_r) & 0 \\ -\sin(\varphi_r) & -\cos(\varphi_r) & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (3)$$

It is possible to transform all vectors $\mathbf{l}_{r-1,r}$ into the same coordinate system with the help of Eqs. (2) and (3):

$$\sum_{\alpha=r}^{n+r-1} l_{\alpha-1,\alpha} \left(\prod_{\beta=\alpha+1}^{n+r} \mathbf{T}_\beta \right) \mathbf{i}_\alpha = 0 \quad (4)$$

taking into account the ring condition for the indices

$$r = r + kn, \quad k = 1, 2, 3, \dots \quad (5)$$

This equation contains bond lengths, valence angles and dihedral angles, and, being in vector form, gives three scalar redundancy conditions.

According to the second theorem

$$\left[\prod_{\beta=r}^{n+r} \mathbf{T}_\beta \right] \mathbf{i}_r = 0 \quad (6)$$

This vector equation also results in three scalar redundancy conditions. A home-made program, based on this theory, automatically gave these

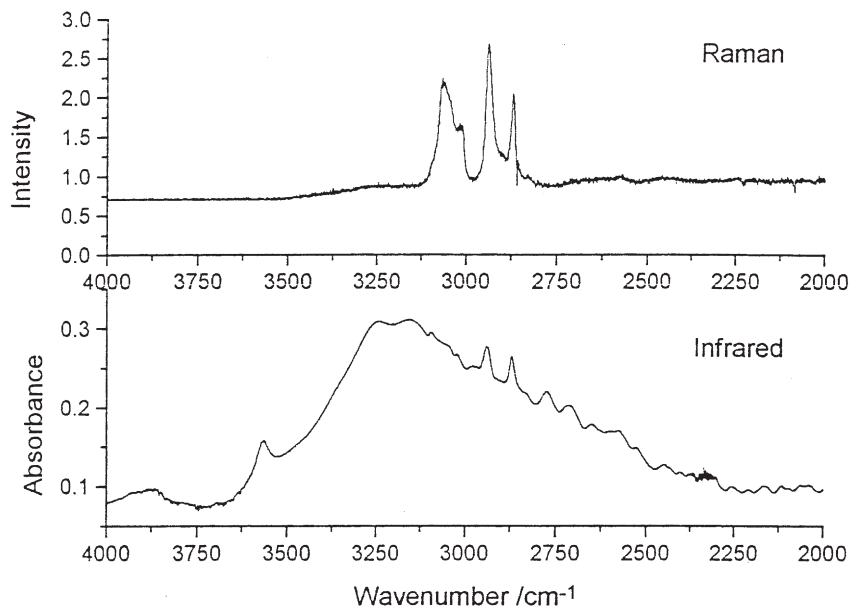


FIGURE 3 Infrared and Raman spectra of 25,26,27,28-tetrahydroxycalix[4]arene, 4000–2000 cm^{-1} .

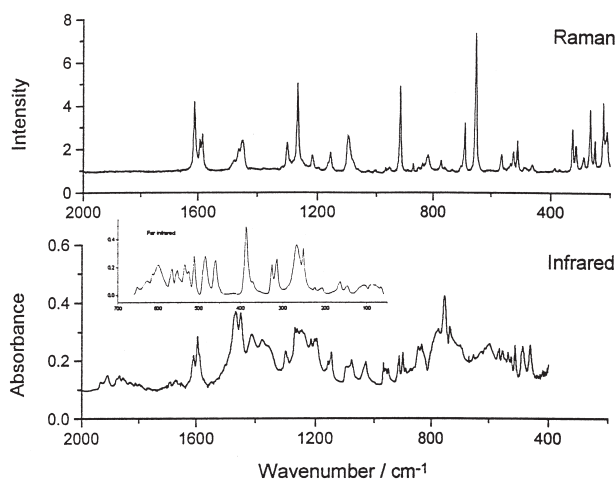


FIGURE 4 Medium infrared spectra of 25,26,27,28-tetrahydroxycalix[4]arene from 2000 to 400 cm^{-1} , far infrared spectra from 600 to 60 cm^{-1} , Raman spectra from 2000 to 200 cm^{-1} .

conditions, i.e. the relations under the simple internal coordinates of the ring.

During the second step the inverse kinetic energy matrix (\mathbf{G}) was calculated in the internal coordinate system and the force constants were transformed into this system (\mathbf{F}' matrix). Then the \mathbf{F}' matrix was fitted to the experimental frequencies (scaling of the force constants), consequently, the mean deviation between the frequencies calculated from the eigenvalues of the \mathbf{GF}' matrix and the corresponding experimental frequencies were minimized (\mathbf{F} matrix). Applying the scaled force constants and the eigenvalues of the \mathbf{GF} matrix, the potential energy distribution matrix (PED matrix) was calculated. The elements of the PED matrix indicate the participation of the individual internal coordinates in the individual normal modes, thus they characterize the normal modes of the molecule.

RESULTS AND DISCUSSION

The *infrared and Raman spectra* of CAL in the 4000–2000 cm^{-1} region are presented on Fig. 3, while Fig. 4 contains the same in the lower region of the spectra (IR, FIR and Raman).

The infrared and Raman spectra are very different. This is a consequence of their different mechanisms of generation. The very strong interactions between

the polar OH groups are reflected in IR spectra as intense overlapping bands. The Raman spectra, however, reflect the small charge shifts in the OH groups during the vibrations and therefore the corresponding bands are weak.

As apparent from the spectra, in the higher wavenumber region a strong, broad OH stretching IR band is observable superimposed on the CH stretching vibrations. In the Raman spectrum the OH stretches are very weak, and therefore the CH ones are clearly discernable. In the lower wavenumber region, the spectra are very complex, more than 100 bands being detected there. Furthermore, for the experimental evaluation of the overlapping bands, it was necessary to resolve them. Consequently, the assignment of these bands was impossible without the tools of QCC and NCA.

Calculations of the *structure* of CAL have yielded the following order of molecular energies for the four possible conformers (isolated molecules): cone < paco (partial cone), 1,2-alternate, 1,3-alternate (molecular mechanics, [12]). The type of the most stable conformer depends, however, on the chemical environment [13]. For quantum chemical calculations we choose the most stable cone conformer.

Investigating the symmetry of the cone conformer of CAL (Fig. 1) at first glance one may suppose the C_{4v} symmetry of the molecule (cone conformer), i.e. the symmetry elements are one tetragir, four digirs parallel with the tetragir and four symmetry planes, each of them containing one of the digirs and the tetragir. Molecular mechanics calculations [13] found the C_{2v} symmetry for the equilibrium geometry and structure with C_{4v} symmetry as the saddle point between the two possible equivalent C_{2v} formations.

The first attempt at a quantum chemical calculation was carried out with this approximation and restricted symmetry. The resultant frequency set contained, however, five imaginary vibrational frequencies, indicating a structure far from the equilibrium geometry (r_e) corresponding to the HF/4-31G* method. The next attempt was the assumption of the C_{2v} symmetry and non-restricted symmetry, but the calculations resulted in the C_s one. Although we found only one imaginary frequency in this case, the r_e geometry was not approached yet. The last calculation started with C_{4v} symmetry, the optimization being carried out without any restriction on symmetry. The resulting

TABLE I Facing angles and relative energies of calculated structures

Symmetry	Number of imaginary frequencies	Angles between facing rings (degrees)	Relative energies $E - E_{C_{4v}}$ (kJ mol^{-1})
C_{4v}	5	54.621	–
C_s	1	21.329	–94.826
		101.126	
C_2	0	23.212	–110.86
		105.818	

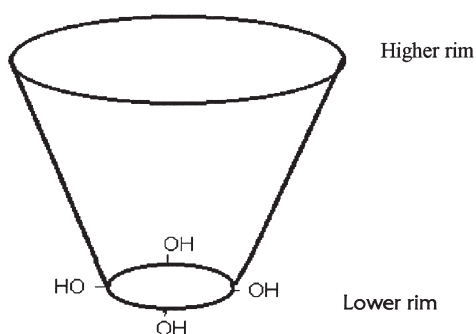


FIGURE 5 Approximate shape of the 25,26,27,28-tetrahydroxycalix[4]arene molecule.

symmetry was C_2 (cone conformer) and presented the winning solution with only positive frequencies. This calculation took 200h CPU time using a Power Challenge SGI computer with R10000 processors. The duration of these calculations shows that application of a better quantum chemical method with a larger basis set is out of the question. We regard our *ab initio* symmetry as a refinement of the molecular mechanics results.

Table I presents the calculated energies and Fig. 5 shows the approximate structure of the molecule. The calculated r_e geometric parameters of the molecule are listed in Table II.

Applying the method of *normal coordinate analysis*, the first problem was the choice of the independent internal coordinates. The choice of coordinates characterizing the lower rim seemed to be the most appropriate (Fig. 5). Therefore the linear combinations of bond stretching, in-plane deformation and torsional coordinates [32] were chosen. This choice gave us the possibility to equalize the four quarters of the lower rim in the internal coordinates. The other possibility, i.e. to choose the changes in the individual geometric parameters of this rim as internal coordinates, leads to an asymmetry of the rim quarters. This is chemically meaningless.

The aforementioned method was applied for the elimination of the redundant coordinates. Suitable coordinates for five and six membered rings have already been published [33] and are widely used. For a 16-membered ring like the lower rim, a similar proposition is not yet available. According to the program based on the theory of ring redundancy conditions [31], the redundant coordinates were calculated and simultaneously, independent symmetry coordinates were proposed (see Table III, Fig. 6). The first 42 coordinates, summarized in Table III, are proposed for the 16-membered ring (the lower rim).

Atoms other than those belonging to the lower rim (see Fig. 6) were regarded as substituents and each of

TABLE II Geometric parameters of 25,26,27,28-Tetrahydroxycalix[4]arene*

Distances†				Valence angles†					
$r(1,2)$	1.521	$r(14,39)$	1.083	$\varphi(2,1,24)$	119.9	$\varphi(10,11,12)$	119.1	$\varphi(22,23,24)$	119.1
$r(1,24)$	1.389	$r(14,40)$	1.083	$\varphi(2,1,25)$	121.8	$\varphi(10,11,37)$	120.5	$\varphi(22,23,47)$	120.5
$r(1,25)$	1.393	$r(15,16)$	1.385	$\varphi(24,1,25)$	118.3	$\varphi(12,11,37)$	120.4	$\varphi(24,23,47)$	120.4
$r(2,3)$	1.522	$r(15,28)$	1.390	$\varphi(1,2,3)$	113.0	$\varphi(11,12,13)$	121.6	$\varphi(1,24,23)$	121.6
$r(2,29)$	1.083	$r(16,17)$	1.380	$\varphi(1,2,29)$	110.0	$\varphi(11,12,15)$	119.5	$\varphi(1,24,48)$	118.8
$r(2,30)$	1.083	$r(16,41)$	1.075	$\varphi(1,2,30)$	108.2	$\varphi(13,12,38)$	118.8	$\varphi(23,24,48)$	119.5
$r(3,4)$	1.385	$r(17,18)$	1.380	$\varphi(3,2,29)$	110.6	$\varphi(12,13,27)$	118.3	$\varphi(1,25,21)$	121.0
$r(3,26)$	1.390	$r(17,42)$	1.075	$\varphi(3,2,30)$	108.8	$\varphi(14,13,27)$	121.8	$\varphi(1,25,49)$	123.6
$r(4,31)$	1.075	$r(18,19)$	1.387	$\varphi(29,2,30)$	106.0	$\varphi(12,13,14)$	119.9	$\varphi(21,25,49)$	115.4
$r(4,5)$	1.380	$r(18,43)$	1.075	$\varphi(4,3,26)$	118.2	$\varphi(14,15,16)$	120.1	$\varphi(3,26,7)$	122.3
$r(5,6)$	1.380	$r(19,28)$	1.388	$\varphi(2,3,26)$	121.6	$\varphi(14,15,28)$	121.6	$\varphi(3,26,51)$	118.6
$r(5,32)$	1.075	$r(19,20)$	1.521	$\varphi(2,3,4)$	120.1	$\varphi(16,15,28)$	118.2	$\varphi(7,26,51)$	119.0
$r(6,7)$	1.387	$r(20,21)$	1.518	$\varphi(3,4,5)$	120.7	$\varphi(15,16,17)$	120.7	$\varphi(9,27,13)$	121.0
$r(6,33)$	1.075	$r(20,44)$	1.078	$\varphi(5,4,31)$	120.0	$\varphi(15,16,41)$	119.3	$\varphi(9,27,53)$	115.4
$r(7,8)$	1.521	$r(20,45)$	1.085	$\varphi(3,4,31)$	119.3	$\varphi(17,16,41)$	120.0	$\varphi(13,27,53)$	123.6
$r(7,26)$	1.388	$r(21,22)$	1.381	$\varphi(4,5,6)$	119.9	$\varphi(16,17,18)$	119.9	$\varphi(15,28,55)$	118.6
$r(8,9)$	1.518	$r(21,25)$	1.397	$\varphi(4,5,32)$	120.1	$\varphi(16,17,42)$	120.1	$\varphi(19,28,55)$	119.0
$r(8,34)$	1.078	$r(22,23)$	1.384	$\varphi(6,5,32)$	120.0	$\varphi(18,17,42)$	120.0	$\varphi(15,28,19)$	122.3
$r(8,35)$	1.085	$r(22,46)$	1.076	$\varphi(5,6,7)$	121.3	$\varphi(17,18,19)$	121.3	$\varphi(25,49,50)$	115.4
$r(9,10)$	1.381	$r(23,24)$	1.377	$\varphi(5,6,33)$	119.6	$\varphi(17,18,43)$	119.6	$\varphi(26,51,52)$	110.1
$r(9,27)$	1.397	$r(23,47)$	1.074	$\varphi(7,6,33)$	119.1	$\varphi(19,18,43)$	119.1	$\varphi(27,53,52)$	115.4
$r(10,11)$	1.384	$r(24,48)$	1.076	$\varphi(6,7,26)$	117.6	$\varphi(18,19,20)$	120.1	$\varphi(28,55,56)$	110.1
$r(10,36)$	1.076	$r(25,49)$	1.342	$\varphi(8,7,26)$	122.3	$\varphi(18,19,28)$	117.6		
$r(11,12)$	1.377	$r(26,51)$	1.380	$\varphi(6,7,8)$	120.1	$\varphi(20,19,28)$	122.3		
$r(11,37)$	1.074	$r(27,53)$	1.342	$\varphi(8,9,10)$	121.5	$\varphi(20,21,22)$	121.5		
$r(12,13)$	1.389	$r(28,55)$	1.380	$\varphi(8,9,27)$	119.7	$\varphi(20,21,25)$	119.7		
$r(12,38)$	1.076	$r(49,50)$	0.951	$\varphi(10,9,27)$	118.8	$\varphi(22,21,25)$	118.8		
$r(13,14)$	1.521	$r(51,52)$	0.949	$\varphi(9,10,11)$	121.3	$\varphi(21,22,23)$	121.3		
$r(13,27)$	1.393	$r(53,54)$	0.951	$\varphi(9,10,36)$	119.1	$\varphi(21,22,46)$	119.1		
$r(14,15)$	1.522	$r(55,56)$	0.949	$\varphi(11,10,36)$	119.6	$\varphi(23,22,46)$	119.6		

*For the numbering of the atoms see Fig. 1b. †Distances (r) in angstroms, angles (φ) in degrees.

TABLE III 25,26,27,28-Tetrahydroxycalix[4]arene, C_2 symmetry, HF/4-31G* calculations

i^*	Internal coordinates†	Scale factor	$F(i,i)‡$
1	$r(1,25) - r(3,26) + r(7,26) + r(9,27) + r(13,27) + r(15,28) + r(19,28) + r(21,25)$	0.885	13.387
2	$r(1,2) + r(2,3) + r(7,8) + r(8,9) + r(13,14) + r(14,15) + r(19,20) + r(20,21)$	0.885	4.276
3	$\varphi(1,25,21) + \varphi(3,26,7) + \varphi(9,27,13) + \varphi(15,28,19)$	0.903	6.145
4	$\varphi(1,2,3) + \varphi(7,8,9) + \varphi(13,14,15) + \varphi(19,20,21)$	0.903	26.726
5	$r(1,25) - r(3,26) + r(7,26) - r(9,27) + r(13,27) - r(15,28) + r(19,28) - r(21,25)$	0.885	5.560
6	$r(1,2) - r(2,3) + r(7,8) - r(8,9) + r(13,14) - r(14,15) + r(19,20) - r(20,21)$	0.885	3.735
7	$\varphi(2,1,25) - \varphi(2,3,26) + \varphi(8,7,26) - \varphi(8,9,27) + \varphi(14,13,27) - \varphi(14,15,28) + \varphi(20,19,28) - \varphi(20,21,25)$	0.903	3.575
25	$\varphi(1,2,3) + \varphi(7,8,9) - \varphi(13,14,15) - \varphi(19,20,21)$	0.903	891.985
26	$\varphi(3,26,7) - \varphi(15,28,19)$	0.903	68.681
27	$\varphi(1,25,21) - \varphi(9,27,13)$	0.903	99.133
30	$\pi(2,1,25,21) + \pi(2,3,26,7) + \pi(3,26,7,8) + \pi(8,9,27,13) + \pi(9,27,13,14) + \pi(14,15,28,19) + \pi(15,28,19,20) + \pi(1,25,21,20)$	0.900	0.478
39	$\pi(3,26,7,8) - \pi(15,28,19,20)$	0.900	568.556
40	$\pi(2,1,25,21) - \pi(9,27,13,14)$	0.900	28.884
41	$\pi(3,2,1,25) - \pi(8,9,27,13) - \pi(15,14,13,27) + \pi(1,25,21,20)$	0.900	363.488
43	$r(21,22)$	0.897	6.878
44	$\varphi(20,21,22)$	0.901	14.135
45	$\pi(1,25,21,22)$	0.897	2.081
67	$r(22,23)$	0.896	8.930
69	$\pi(21,22,23,24)$	0.896	0.461
70	$r(4,5)$	0.896	9.166
71	$r(5,6)$	0.896	9.602
72	$\pi(3,4,5,6)$	0.896	0.462
73	$r(10,11)$	0.896	8.930
88	$r(28,55)$	0.876	5.235
89	$\varphi(15,28,55)$	0.895	2.505
90	$\pi(18,19,28,55)$	0.875	0.717
91	$r(49,50)$	0.874	6.957
92	$\varphi(25,49,50)$	0.899	0.770
93	$\pi(21,25,49,50)$	0.863	0.117

* Serial number. † r : Bond stretching, φ : in-plane bending, τ : torsion; for the numbering of the atoms see Fig. 1b. ‡ Diagonal force constants, units: 10^2 Nm^{-1} and 10^{-18} Nm , respectively. The full table is available as deposit.

them were added to the already defined part of the molecule as one stretching, one in-plane deformation and one torsional coordinate (Table III).

The calculated *force constants* were scaled to the experimental spectra. The scale factors and the diagonal force constants are also shown in Table III. At first sight, some of the data might appear very strange. Some diagonal force constants have extraordinarily high values. This fact was shocking. The very high values are consequences of the choice of the lower rim internal coordinates. However, as the equation:

$$|\mathbf{GF} - \lambda \mathbf{E}| = 0 \quad (7)$$

(λ is proportional to the square of the wavenumbers, \mathbf{E} is a unit matrix) yielded wavenumbers in the usual region and also acceptable scale factors, we concentrated on the evaluation of these data. Similarly high values resulted for the corresponding non-diagonal elements of the force constant matrix. The unusually high values of the diagonal \mathbf{F}' elements belong to more than half of the lower rim coordinates. The pivot element of the 25th coordinate has the highest value (nearly $830 \times 10^{-18} \text{ Nm}$). It is a linear combination of the CH_2 bends. Some force constants of the CH_2 group carbon atom-benzene ring carbon atom deformations are found between 100 and $200 \times 10^{-18} \text{ Nm}$ (coordinates 24, 28 and 29).

Several torsional force constants hit the region of $200\text{--}600 \times 10^{-18} \text{ Nm}$ (coordinates 38, 39, 41 and 42). These coordinates are linear combinations of the CH_2 group carbon atom-benzene ring carbon atom torsions or this kind of torsions, which take part in the combinations.

The aforementioned surprising force constant values are at least 100 times greater than the usual values of the diagonal force constants of deformational and torsional coordinates. It is known that the force constants present the value of the deformation force belonging to a unit change in the coordinate. The nature of the movements belonging to the coordinates with such extraordinarily high force constant values (having values up to $892 \times 10^{-18} \text{ Nm}$) were examined. They are all combinations of elementary coordinates where the symmetrically equivalent ones (corresponding to the C_2 symmetry) move in opposite directions, labeled by opposite signs in the combination (e.g. if one of the angles enlarges during the motion its equivalent pair narrows). This can be well demonstrated by examining, e.g. the ring stretching coordinates 21–23, the ring bending coordinates 10–11 and 24–29, or the ring torsional coordinates 38–42 (see Table III and Fig. 1). The extraordinary force constant values express a *certain rigidity of the ring* (the lower rim), although this ring is not planar.

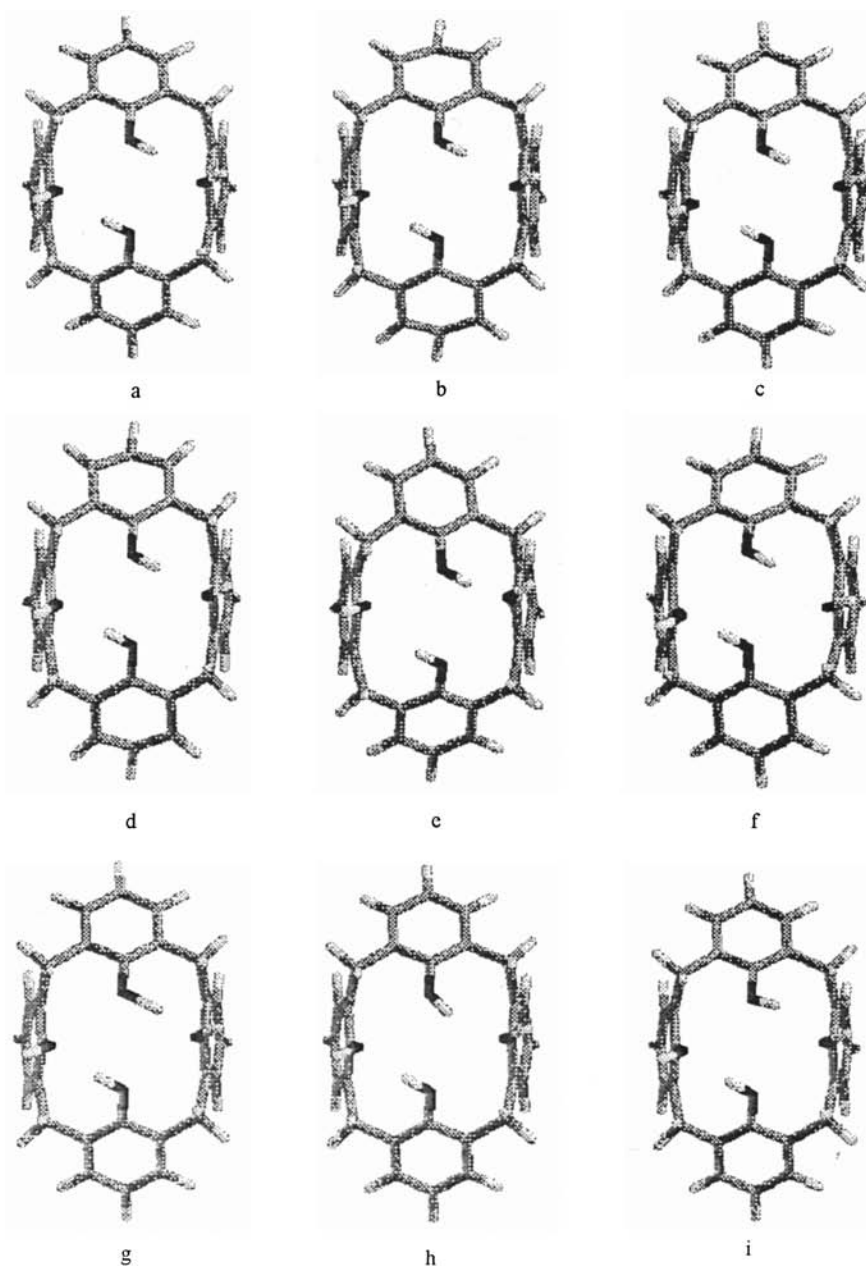


FIGURE 6 Effect of the some internal coordinates on the structure of 25,26,27,28-tetrahydroxycalix[4]arene molecule (oxygen: black, carbon: gray, hydrogen: white), a: equilibrium geometry, b: coordinate 1 (lower rim stretching), c: coordinate 5 (lower rim stretching), d: coordinate 8 (lower rim stretching), e: coordinate 25 (lower rim in-plane bending), f: coordinate 39 (lower rim torsion), g: coordinate 91 (OH stretching), h: coordinate 92 (OH in-plane deformation), i: coordinate 93 (OH out-of-plane deformation). For the definition of the coordinates see Table III.

The *scale factors* (Table III), as resulting from the scaling process, fall in a very narrow interval, between 0.860 and 0.910. The mean deviation between the experimental and calculated (scaled) frequencies is small, 9.31 cm^{-1} and 1.67%, respectively. Table IV presents the synopsis of experimental and scaled calculated wavenumbers of the fundamentals, together with the corresponding potential energy matrix (PED) elements. Only the OH and CH stretching modes are characteristic, which means that only one type of internal coordinate participates

in these vibrations. In all other modes, stretching, deformational and torsional vibrations of different groups are mixed.

Summing up, the 25,26,27,28-tetrahydroxycalix[4]arene molecule has rigidity to a certain extent. Their vibrational spectra have a high degree of complexity, and consequently, the assignment of the spectra was carried out overcoming several difficulties and complications. Therefore, the truncated cone structure (pinched cone or lamp-shade form) is relatively stable. This structure makes the calix[4]arene

derivatives suitable for application in artificial ion channel models, ion sensors and in cages for building molecular clathrates.

Acknowledgements

The authors would like to thank Professor J. Kristóf, Dr H. Mikosch, Dr A. Grün and Dr E. Horváth for their assistance in the realization of this work.

References

- [1] Lan, B.T.T. and Tóth, K. (1998), *Anal. Sci.* **14**, 191.
- [2] Shortreed, M., Bakker, E. and Kopelman, R. (1996), *Anal. Chem.* **68**(15), 2656.
- [3] O'Neill, S., Kane, P., McKervey, M.A. and Diamond, D. (1998), *Anal. Commun.* **35**, 127.
- [4] Schwing-Weill, M.-J. and Arnaud-Neu, F. (1997), *Gazzetta Chimica Italiana* **127**, 687.
- [5] Dozol, J.F., Rouquette, H., Eymand, S., Tournois, B., Simon, N. and Lamare, V. (1996), *ISEC '96*, 1333.
- [6] Kubinyi, M., Mohammed-Ziegler, I., Grofcsik, A., Bitter, I. and Jones, W.J. (1997), *J. Mol. Struct.* **408/409**, 543.
- [7] Mohammed-Ziegler, I., Kubinyi, M., Grofcsik, A., Grün, A. and Bitter, I. (1999), *J. Mol. Struct.* **480/481**, 289.
- [8] Mohammed-Ziegler, I., Poór, B., Kubinyi, M., Grofcsik, A., Grün, A. and Bitter, I. (1999), *J. Inclusion Phenomena Macrocyclic Chem.* **35**(1), 349–353.
- [9] Antipin, L.S., Stoikov, I.I., Fitseva, N.A., Stibor, I. and Konovalov, A.I. (1997) "Calix[4]arene based α -aminophosphonates as carriers for the membrane transport of the zwitterionic amino acids", *4th International Conference on Calixarenes*, Parma, Italy, Book of Abstracts, p. P80.
- [10] Arena, G., Contino, A., Magri, A., Sciotto, D. and Lamb, J.D. (1997) "Selective transport of cesium and strontium ions through polymer inclusion membranes containing calixarenes as carriers", *4th International Conference on Calixarenes*, Parma, Italy, Book of Abstracts, p. P131.
- [11] Fischer, F., Grootenhuis, P.D.J., Croenen, L.C., van Hoorn, W.P., van Veggel, F.C.J.M., Reinhoudt, D.N. and Karplus, M. (1995), *J. Am. Chem. Soc.* **117**, 1611.
- [12] van Hoorn, W.P., Briels, W.J., van Duynhoven, J.P.M., van Veggel, F.C.J.M. and Reinhoudt, D.N. (1998), *Org. Chem.* **63**, 1299.
- [13] Dominik, H., Roth, H.J., Schierbaum, K.D. and Göpel, W. (1994), *Supramol. Sci.* **1**, 11–19.
- [14] Golebiewski, J., Lamare, V. and Ruiz-López, M.F. (2000) "Quantum chemical investigation of calix-crown-ether binding properties towards alkali cations", *10th International Congress on Quantum Chemistry*, Menton, France, Book of Abstracts, p. B26.
- [15] Mushkin, V.B., Antipin, I.S. and Konovalov, A.I. (1997) "The quantum chemical calculations of geometry and energy of tert-butylcalix[4]arene complexes with aromatic guests", *4th International Conference on Calixarenes*, Parma, Italy, Book of Abstracts, p. 82.
- [16] Thondorf, I. and Brenn, J. (1997), *Theochem.* **398**, 307–314.
- [17] Hay, B.P., Nicholas, J.B. and Feller, D. (2000), *J. Am. Chem. Soc.* **122**, 10083.
- [18] Golebiewski, J., Lamare, V., Dozol, J.F., Martins-Costa, M.T.C., Millot, C. and Ruiz-Lopez, M.F. (2000) "Liquid phase affinity of 1,3-alt-calix[4]arene-bis-crown6 towards Cs[⊕] and Na[⊕]. A hybrid quantum chemical/molecular mechanical study", *10th International Congress on Quantum Chemistry*, Menton, France, poster.
- [19] Bernardino, R.J. and Costa Cabral, B.J. (2001) "Structure and inclusion properties of the four conformers of thiocalix[4]arene: a density functional study", *6th International Conference on Calixarenes*, Enschede, The Netherlands, Book of Abstracts, p. P-13.
- [20] Wipff, G. and Lauterbach, M. (1995), *Supramol. Chem.* **6**, 187–207.
- [21] Muzet, N., Wipff, G., Casnati, A., Dominiano, L., Ungaro, R. and Ugozzoli, F. (1996), *J. Chem. Soc. Perkin Trans. 2*, 1065–1075.
- [22] Varnek, A., Sirlin, C. and Wipff, G. (1996) In: Tsoucaris, G., ed, *Crystallography of Supramolecular Compounds* (Kluwer Academic Publishers, Dordrecht), pp 67–99.
- [23] Lauterbach, M., Muzet, N., Troxler, L., Varnek, A. and Wipff, G. (1997) "Adsorption of calixarenes and ionophores at the liquid-liquid interface: molecular dynamics investigations", *4th International Conference on Calixarenes*, Parma, Italy, Book of Abstracts, p. IL4.
- [24] Lamare, V., Dozol, J.-F., Asfari, Z., Vicens, J., Ugozzoli, F., Casnati, A., Ungaro, R., Arnaud-Neu, F., Fuangfwasdi, S., Thuery, P. and Nierlich, M. (1997) "New calix[4]arene bearing crown ether loops. Molecular modelling and experimental studies", *4th International Conference on Calixarenes*, Parma, Italy, Book of Abstracts, p. P74.
- [25] Krug, A., Thondorf, I. and Böhmer, V. (1997) "Molecular dynamics simulations on methylene-substituted resorcinarenes", *4th International Conference on Calixarenes*, Parma, Italy, Book of Abstracts, p. P74.
- [26] den Otter, W.K. and Briels, W.J. (1997), *J. Chem. Phys.* **107**, 4968.
- [27] den Otter, W.K. and Briels, W.J. (1998), *J. Am. Chem. Soc.* **120**, 13167.
- [28] Dormann, J., Ruoff, A. and Schatz, J. (2001) "Vibrational spectroscopic study of host-guest structures based on calix[n]arenes", *6th International Conference on Calixarenes*, Enschede, The Netherlands, Book of Abstracts, p. IL-5.
- [29] Vicens, J. and Böhmer, V. (1991) *Calixarenes—A Versatile Class of Macrocyclic Compounds* (Kluwer Academic Publishers, Dordrecht).
- [30] Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, Jr., J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S. and Pople, J.A. (1998) *GAUSSIAN 98*, Revision A.3, Gaussian, Inc., Pittsburgh PA.
- [31] Billes, F. (1966), *Acta Chim. Hung.* **49**, 97.
- [32] Wilson, E.B., Decius, J.C. and Cross, P.C. (1955) *Molecular Vibrations* (McGraw-Hill, London), pp 54–61.
- [33] Pulay, P., Fogarasy, G., Pang, F. and Boggs, J. (1979), *J. Am. Chem. Soc.* **101**, 2550.