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Dedicated to professor Gh. Marcu at his 80th anniversary

A QUANTUM CHEMICAL CONFORMATIONAL ANALYSIS OF P-TERT-BUTYL/PENTYL/OCTYL-CALIX[8]ARENES

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ABSTRACT. A conformational analysis of *p-tert*-butyl/*tert*-pentyl/ *tert*-octyl-calix[8]arenes has been performed by semiempirical calculations. The results are in agreement with the available experimental data, as predicted for the pleated-loop conformation. The relative stability of the conformers depends on the substituents located in the *para* position, however the energy difference between the most stable and the next conformations is low.

Keywords: *p-tert*-butyl-calix[8]arene, *p-tert*-pentyl-calix[8]arene, *p-tert*-octyl-calix[8]arene, conformations, PM3 semiempiric.

Introduction

Calixarenes are [1n]-metacyclophanes, obtained from the condensation of formaldehyde with *p*-alkylphenols, thus resulting structures in which phenol fragments are connected by methylene bridges[1]. They have received a special interest as their calix crater is suitable for accommodating guest molecules.

As the calix[8]arenes have many torsion possibilities they are much more flexible than smaller-cycle representatives: there are sixteen up-down conformations plus others in which phenolic fragments adopt an out arrangement[2].

The goal of this research is to identify and characterize the most stable *para*-substituted calix[8]arene conformations by means of semiempirical methods.

Computational procedure

The starting structures have been built using the graphical interface of Spartan 04 [3] and preoptimized by molecular mechanics. Optimizations were continued at the semiempirical level employing the PM3 model of Stewart[4,5] using Gaussian 98 package of programs[6]. Frequency analysis followed all optimizations in order to establish the nature of the stationary points found, so that all the structures reported in this study are genuine minima on the potential energy surface at this level of theory, without any imaginary frequencies. Only the lowest energy conformers (within 15 kcal/mol) have been retained for discussion.

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Results and discussion

The solid state structure of *p-tert*-butyl-calix[8]arene, determined by X-ray diffractometry[7,8] consists of four pleated fragments joined together. Indeed the global minimum structure found for the *p-tert*-butyl-calix[8]arene is the conformer having this pleated-loop shape, of an average D_{4d} symmetry, an arrangement that favors an internal circular hydrogen bonding stabilizing this conformation[9] (figure 1). The calculated average O·O distance of 2.74 Å is very close to the 2.71 Å average determined by Gutsche for an empty *p-tert*-butyl-calix[8]arene and the 2.70 Å average reported by Schatz et.al.[10] for the calix:chloroform 1:8 clathrate, thus proving the strong hydrogen bonds maintaining this conformation. The computed value of interplanar angle between two adjacent phenolic units is 111.6º comparable with the ~112º average reported for the chloroform clathrate.

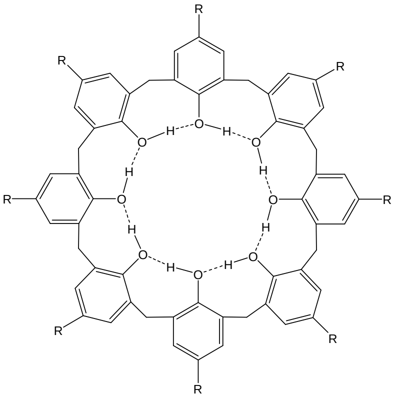


Figure 1. The internal circular hydrogen bonding in the calix[8]arene pleated loop conformer.

The next structure (*tert*-butyl-calix[8] **2** in figure 2) only 0.8 kcal/mole higher in energy may be described as consisting of two trimeric craters with the remaining two phenolic units ensuring a good linking through a “pleated motif” the result being again a stabilising internal circular hydrogen bonding.

The following two structures (*tert*-butyl-calix[8] **3** and **4**) consist of two calix[4] units joined together in an anti C_2 arrangement. Both calix[4] fragments adopt a cone conformation, which has already been proved to be the most stable one among the four possible conformations for a calix[4]arene[11,12]. Conformations **1**, **2**, **3** and **4** were identified in the case of rare earth (Eu and Lu) dinuclear calix[8]arenes complexes[13].

Conformer no. **5** at +4.18 kcal/mole above the global minimum is also based on two calix[4]arene fragments but this time having the same orientation although with a certain degree of crater distortion as the two connecting phenols have a parallel orientation. This conformer has been identified in the crystal structure of a tungsten complex trapping a WO group inside each of the calix[4] units[14]. This structure is also related to conformer no. **7**, the so-called ‘pinched’ conformer[15], whose calix[4] cones are more circular due to the lower distance between the connecting groups, but this definitely makes it less stable so its energy is higher than that of the other one.

This conformation was also found experimentally in the case of oligonuclear europium(III) derivatives of *p-tert*-butyl-calix[8]arene crystallized with DMSO[16,17].

The presence of pseudoconic calix[4] units should not be surprising: researchers noticed the remarkable similarity between the temperature dependent ^{1}H-NMR spectra of *p-tert*-butyl-calix[8]arene and *p-tert*-butyl calix[4]arene[15].

Tert-butyl-calix[8] **6** originates from the lowest energy pleated loop conformer but in this case one of the pleatings has an anti orientation as compared to all the other ones leading to a non-planar structure which makes hydrogen bonding more difficult although the circular shape is well-maintained.

Tert-butyl-calix[8] **8** is also based on two calix conic units joined together, but this time a calix[3] with a calix[5]. The calix[3] unit is slightly tensioned making this conformer less stable but the general orientation of the hydroxyl groups at the lower rim is almost circular, stabilizing this conformation.

Structure *tert*-butyl-calix[8] **9** may be depicted as a distorted two calix[4] structure with the units' connecting fragments adopting an almost out orientation, while the last remaining structure *tert*-butyl-calix[8] **10** may be described as reunion of a large opened calix[4]arene unit connected to a pleated motif by two phenolic fragments having an out orientation.

Interestingly, the global minimum conformer for the *tert*-pentyl-calix[8]arene is the one based on two calix[4]arene cone units joined together in an anti orientation and not the pleated loop conformer found for the *tert*-butyl-calix[8]arene. This arrangement provides enough space for the bulky upper rim substituents and also preserves the stabilizing hydrogen bonding at the lower rim. It is related to *tert*-pentyl-calix[8] **4** which has a similar conformation but with larger calix cavities.

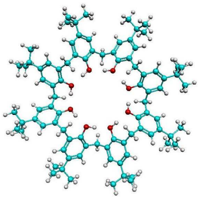
The pleated loop conformer is the next structure at 4.3 kcal/mole above the global minimum, and at the same energy a structure based on two calix[3] units plus a pleated connection fragment is located. All the other structures found for *tert*-pentyl-calix[8]arene have practically the same geometries as the conformers already reported for the *tert*-butyl species respecting the same stability order.

For each class of compounds the corresponding structures are ordered upon their stability, with the corresponding relative energy towards the global minimum conformer indicated (in kcal/mole).

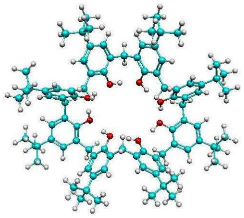
The lowest energy conformer found for the *tert*-octyl-calix[8]arene is the one based on two calix[3] fragments and a V-shaped cleft. Although it shouldn't be so stable from the calix crater point of view, watching the structure not from above but from the calix "plane" side, offers the image of a half-circle geometry, this arrangement providing the necessary space for these large substituents.

The following structure is based on two calix[4] *anti*-oriented units with the calix craters wide opened so that an internal hydrogen bonding can be established between these two units. The space requirement for the bulky octyl fragments is also satisfied, leading to a conformation of only 0.8 kcal/mole above the global minimum structure.

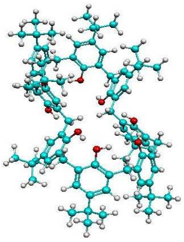
Other two conformers (*tert*-octyl-calix[8] **3** and **7** at 3.0 and 6.8 kcal/mole, respectively) are also based on calix[4] fragments but as they are not so opened the upper rim ligands are more sterically hindered so that these conformers are less stable. The pleated loop conformer is only the sixth one in terms of energy. This is due to the fact that the pleated structure although stabilized in the interior, can not easily accommodate voluminous ligands at the external V-shaped cleft area.



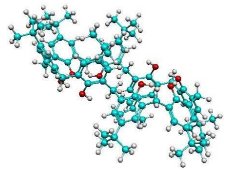
tert-butyl-calix[8] **1** (0.0)



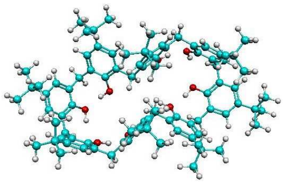
tert-butyl-calix[8] **2** (+0.8)



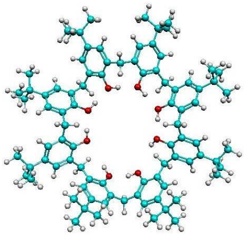
tert-butyl-calix[8] **3** (+2.3)



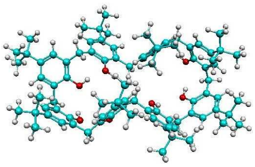
tert-butyl-calix[8] **4** (+3.3)



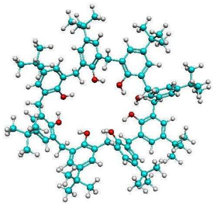
tert-butyl-calix[8] **5** (+4.2)



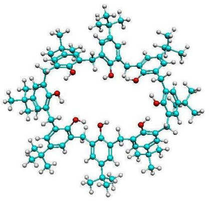
tert-butyl-calix[8] **6** (+4.4)



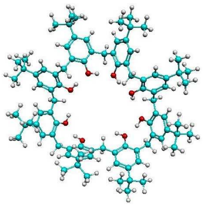
tert-butyl-calix[8] **7** (+6.0)



tert-butyl-calix[8] **8** (+6.9)



tert-butyl-calix[8] **9** (+7.5)



tert-butyl-calix[8] **10** (+10.5)

Figure 2. The ten lowest energy conformers found for *p*-*tert*-butyl-calix[8]arene.

tert-pentyl-calix[8] **1** (0.0)

tert-pentyl-calix[8] **2** (+4.3)

tert-pentyl-calix[8] **3** (+4.3)

tert-pentyl-calix[8] **4** (+5.8)

tert-pentyl-calix[8] **5** (+6.4)

tert-pentyl-calix[8] **6** (+7.3)

tert-pentyl-calix[8]] **7** (+8.2)

tert-pentyl-calix[8] **8** (+10.8)

tert-pentyl-calix[8] **9** (+12.2)

tert-pentyl-calix[8] **10** (+15.2)

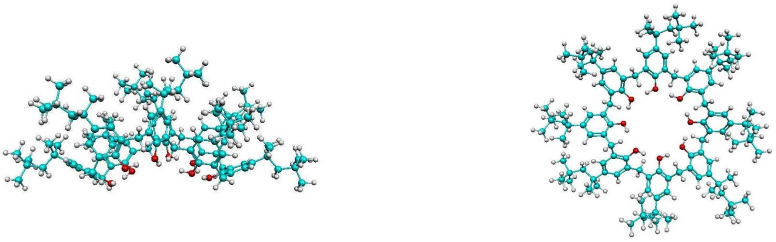
Figure 3. The ten lowest energy conformers found for *p*-*tert*-pentyl-calix[8]arene.

tert-octyl-calix[8] **1** (0.0)

tert-octyl-calix[8] **2** (+0.8)

tert-octyl-calix[8] **3** (+3.0)

tert-octyl-calix[8] **4** (+4.4)



tert-octyl-calix[8] **5** (+4.5)

tert-octyl-calix[8] **6** (+5.5)

tert-octyl-calix[8] **7** (+6.8)

tert-octyl-calix[8] **8** (+6.9)

tert-octyl-calix[8] **9** (+7.8)

tert-octyl-calix[8] **10** (+10.5)

Figure 4. The ten lowest energy conformers found for *p*-*tert*-octyl-calix[8]arene.

Conclusions

Thirty conformers of *p-tert*-butyl/pentyl/octyl-calix[8]arenes have been investigated by PM3 semiempirical method. Their stability is influenced by the hydrogen bonding established at the lower rim and also depends on the volume of the para substituents: thus the most stable geometry for the *p-tert*-butyl-calix[8]arene corresponds to a pleated-loop shape, as exepected from the experimental data. For the *p-tert*-pentyl analogue however the lowest energy conformer is the one consisting of two calix[4] pseudoconic units with an opposed orientation. Their stability is in agreement with the NMR data, as the calix[8]arenes' spectra are similar to those of calix[4]arenes. The most stable conformer for the *p-tert*-octyl-calix[8]arene is the one composed of three fragments including two calix[3] units, an arrangement providing the necessary space for the bulky *tert*-octyl substituents.

Aknowledgements

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REFERENCES

1. C.D. Gutsche, "Calixarenes revisited", RSC **1998**.
2. C.D. Gutsche, L.J. Bauer, *J. Am. Chem. Soc.*, **1985**, *107*, 6052-6059.
3. Spartan '04, Wavefunction Inc., 18401 Von Karman Avenue, Suite 370 Irvine, CA 92612.
4. J.J.P. Stewart, *J. Comput. Chem.*, **1989**, *10*, 209-220.
5. J.J.P. Stewart, *J. Comput. Chem.*, **1989**, *10*, 221-264.
6. Gaussian 98, Revision A.11.3, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J. J. Dannenberg, D.K. Malick, A. D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J. V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **2002**.
7. C.D. Gutsche, A.E. Gutsche, A.I.J. Karoulov, *J. Inclusion Phenom.*, **1985**, *3*, 447-451.
8. K.H. Ahn, S.-G. Kim, J.S. U, *Bull. Korean Chem. Soc.*, **2000**, *21*, 813-816.
9. S.H. Dale, M.R.J., Elsegood, C. Redshaw, *CrystEngComm*, **2003**, *5*, 368-373.
10. J. Schatz, F. Schildbach, A. Lentz, S. Rastätter, T. Debaerdemaeker, *Z. Kristallogr.*, **2001**, *216*, 182-186.
11. T.-N. Ursaleş, A. Ursaleş, I. Silaghi-Dumitrescu, *Rev. Chim.*, **2003**, *54*, 229-231.
12. T.-N. Ursaleş, I. Silaghi-Dumitrescu, *Rev. Roum. Chim.*, **2004**, *49*, 143-147.

13. J.-C. G. Bünzli, F. Ihringer, P. Dumy, C. Sager, R.D. Rogers, *Dalton Trans.*, **1998**, 497-503.
14. C. Redshaw, M.R.J. Elsegood, *Eur. J. Inorg. Chem.*, **2003**, 2071-2074.
15. C.D. Gutsche, L.J. Bauer, *Tetrahedron Lett.*, **1981**, *22*, 4763-4766.
16. S. Fleming, C.D. Gutsche, J.M. Harrowfield, M.I. Ogden, B.W. Skelton, D.F. Stewart, A.H. White, *Dalton Trans.*, **2003**, 3319-3327.
17. J.M. Harrowfield, M.I. Ogden, A.H. White, *Austr. J. Chem.*, **1991**, *44*, 1237-1247.