

[*n*]Peristylanes and [*n*]oxa[*n*]peristylanes (*n* = 3–6): A theoretical study

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Received (in Cambridge) 7th September 1998, Accepted 5th November 1998

Theoretical studies at the HF and Becke3LYP levels using 6-31G* basis sets were carried out on a series of [*n*]peristylanes and [*n*]oxa[*n*]peristylanes (*n* = 3–6) to understand their structure and energetics. The structures of the [3]- and [4]peristylanes (**1**, **2**) and their oxa-derivatives (**5**, **6**) were calculated to have the anticipated high symmetry, *C_m*. In contrast, a *C_s* structure (**9**) at HF/6-31G* and another (**25**) at the Becke3LYP/6-31G* level were calculated for the [5]oxa[5]peristylane. The energy difference between them is extremely small even though there are major differences in the structures indicating a very soft potential energy surface. On the other hand, the potential energy surface of [6]oxa[6]peristylane is not as soft. Similar structures were also calculated for the top rings. Calculations on the seco-compounds **11–14** and **15–19** (Table 4) indicate that there is no unusual strain involved in the formation of **27** from **19**. The Li⁺ interaction energies of the [*n*]oxa[*n*]peristylanes are 61.7 (*n* = 3), 72.8 (*n* = 4), 84.2 (*n* = 5) and 91.7 (*n* = 6) kcal mol⁻¹ at the Becke3LYP/6-31G* level. Dramatic differences between the C–C bond lengths obtained from the solid state X-ray diffraction studies and those from the calculations for the [*n*]oxa[*n*]peristylanes were also observed.

Introduction

The [*n*]peristylanes, **1–4** (*n* = 3–6), constitute a fascinating series of bowl-shaped molecules. These molecules have *n* vertical C–C bonds reminiscent of the colonnade structures (peristyles) of Greek civilization. The first three members of the series and several of their derivatives have been reported.^{1–4} Recently, a new family of symmetric [*n*]oxa[*n*]peristylanes with *n* = 3–6 (**5–8**) was conceived as being novel host systems and synthesis and structural characterization of a member of the family, [5]oxa[5]peristylane (**7**), was reported.⁵ Efforts towards the synthesis of [6]oxa[6]peristylane⁶ (**8**) were also outlined and a seco-derivative was successfully prepared. Several derivatives of [4]oxa[4]peristylane are known⁴ in the literature but data on detailed structural characterization are not available. The ongoing interest⁷ in this family of compounds and some unusual observations in the X-ray crystal structure of [5]oxa[5]peristylane⁸ encouraged us to study the structure of these compounds in detail and, in particular, the carbon compounds **1–4** and their hetero analogues **5–8**.

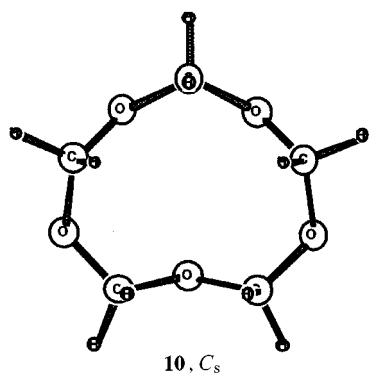
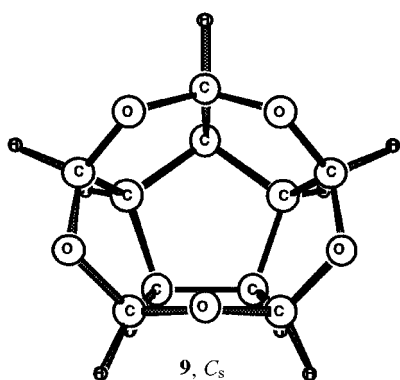
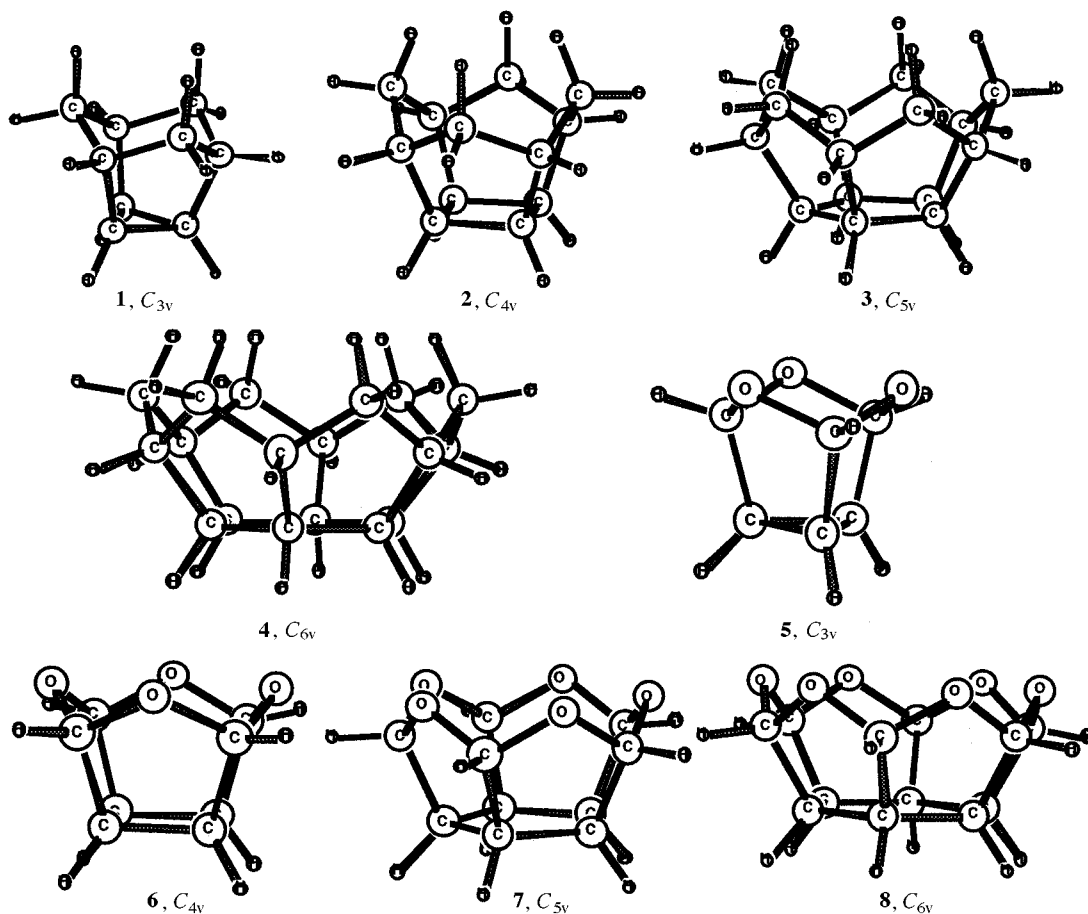
It is natural to look for the *C_n* axis in peristylanes and its oxa-derivatives. Crystal structures of the derivatives of **1** and **2** indicate a *C₃* and *C₄* axis, except for the substituents.^{1,2} However, the X-ray structures of the derivatives of **3** show that none of these retain a pseudo *C₅* axis. However, according to the ¹³C and ¹H NMR spectral data, [5]oxa[5]peristylane (**7**) has *C_{5v}* symmetry.^{5a} The solid state structure shows *C_s* symmetry where one of the oxygen atoms is pushed towards the *C₅* axis, **9**.⁸ Is the decrease in symmetry a consequence of the packing? Or is the *C_s* structure a characteristic of the top *C₅O₅* ring (**10**) in [5]oxa[5]peristylane? If the molecule has an inherent symmetry lower than *C_{5v}*, only a dynamic equilibrium can explain the solution structure. Our attempts to freeze the dynamic process by lowering the temperature have not been successful so far. We also want to know the possible structures for **8**, the target of our current synthetic efforts.⁶ Are there any unfavourable factors present in it that prevents its formation? For this purpose, the increase

in strain energy in forming the [*n*]peristylanes and the [*n*]oxa[*n*]peristylanes from their seco-structures (**11–14**) and (**15–19**) have also been estimated.

Anomalies in the C–C bond lengths of the structurally characterized derivatives of **1–8** are an added incentive for this theoretical study. For example, the cyclopropane ring in **1** is short (~1.50 Å) but the cyclobutane ring in **2** is long (1.55 Å).^{1,2} However, the cyclobutane ring in a tetra-*tert*-butyl derivative of **6** has a shorter average C–C bond length of 1.527 Å.^{4b} Is this decrease in bond length a characteristic of oxygen substitution? Will the short bond lengths persist in the gas-phase as well? The C–C distance of the cyclopentane ring in **7** appears shorter than is anticipated for a derivative of a ring of this size.⁵ There could be several possible reasons for these unusual bond lengths. Purely electronic effects could also manifest themselves in the form of short bond lengths in the isolated molecules. Alternatively, are the geometric parameters controlled by the dense packing in the crystal structures arising from the maximal C–H···O hydrogen bonding interactions?⁸ Is there any unusual libration⁹ effect? One of the factors that make the oxa-bowls attractive targets of synthesis is their potential affinity for metal ions. To this end, the structure and energetics of the Li⁺ complexes of **5–8** (**20–23**) have also been studied.

Computational methods

All calculations were carried out using *ab initio* MO (HF/6-31G*)¹⁰ and DFT¹¹ (Becke3LYP/6-31G* termed as B3LYP¹² in this paper) employing the GAUSSIAN94¹³ program. Frequency analyses,¹⁴ which characterize the stationary points on the PES, were carried out both at HF/6-31G* and B3LYP levels. Structures **1–8** were initially optimized with the *C_m* symmetry restrictions and the nature of the stationary points were determined. Transition structures and higher order stationary points were appropriately distorted and optimized until ground state structures were obtained.



Results and discussion

Geometric and energetic comparisons of the pairs of $[n]$ peristylanes and their oxa-analogues will be discussed first. General

trends in the structures and energetics are given next. This is followed by a discussion of the strain energy increase in the formation of the peristylanes based on their seco-structures. The energetics of the Li^+ interactions with **5–8** are discussed towards the end.

[3]Peristylanes and [3]oxa[3]peristylanes

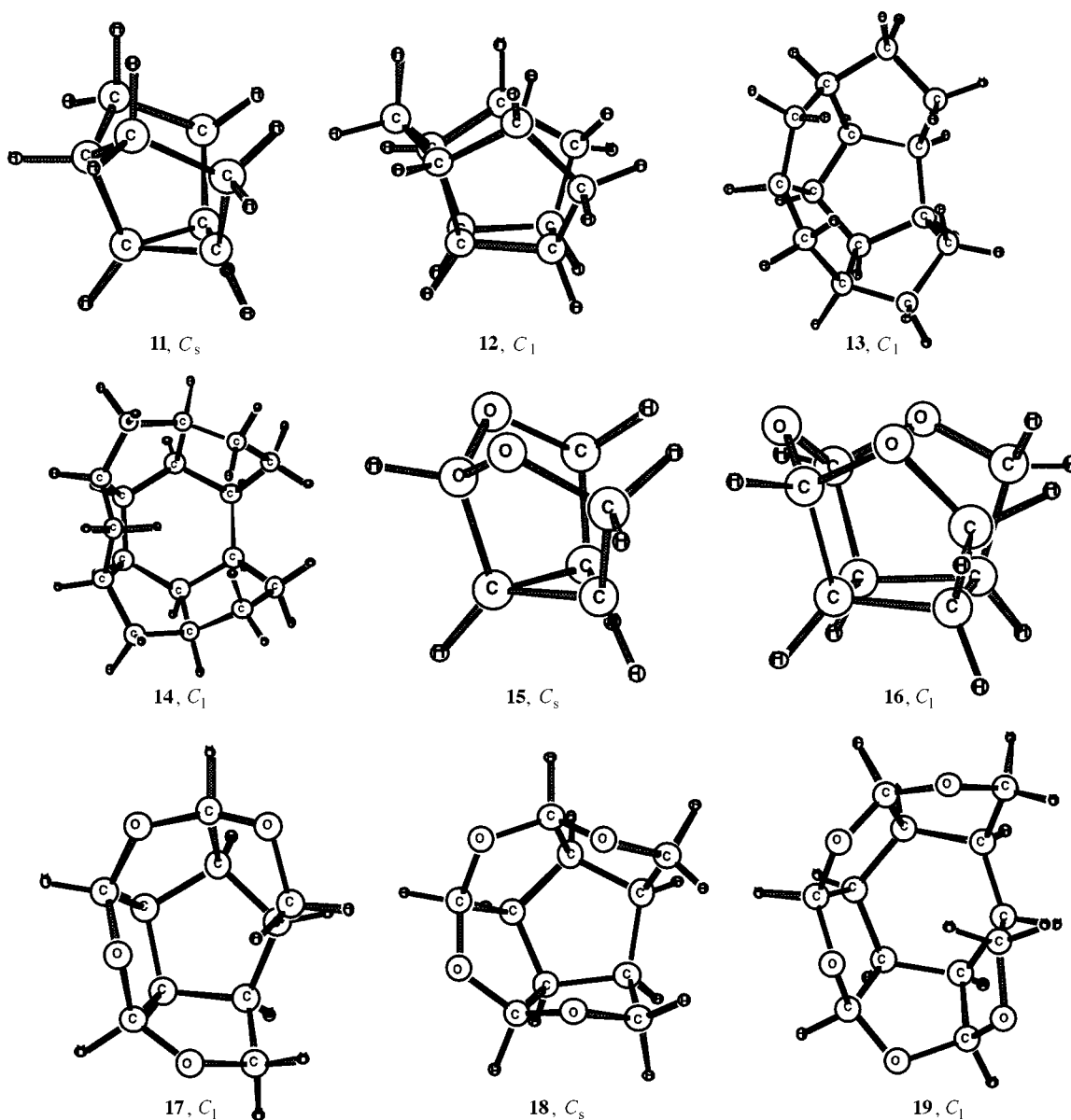
Both at the HF and B3LYP levels, the C_{3v} structures (**1**, **5**) are minima. The C–C distance of the three membered rings (Table 1) are around the 1.50 Å anticipated for a three membered ring (cyclopropane C–C distance = 1.509 Å at the B3LYP level). There are several derivatives of **1** characterized by X-ray crystallography and all of these three membered rings have short C–C distances.¹ The C–C bond lengths aligned along the C_3 axis is in the standard sp^3 C– sp^3 C range. We could not find any experimental data for a structure corresponding to **5**.

[4]Peristylanes and [4]oxa[4]peristylanes

The derivatives of [4]peristylane (**2**)² and its oxa-analogue (**6**)⁴ are well characterized structurally. They provide important yard-sticks for comparison with experimental structures in the solid state, calculated structures expected for isolated molecules at 0 K and the influence of hetero-substitution. Several derivatives of [4]peristylanes have been studied by X-ray crystallography.² The C–C bonds in four membered rings are all considerably longer than standard C–C single bonds as is expected for four-membered rings (Table 2, 1.55–1.56 Å). The calculated values are also comparable. The tetra-oxa derivatives provide a dramatic contrast in this respect. Several structures of these are known experimentally.⁴ Most of these have very short C–C bond lengths in the base four-membered ring. For example, the tetra-*tert*-butyl derivative of **6** has an average cyclobutane C–C bond length of 1.520 Å. A recent X-ray dif-

Table 1 Important bond length data (Å) for [3]- and [4]peristylanes and their oxa-analogues at HF/6-31G* and B3LYP levels

	1		2		5		6	
	HF/6-31G*	B3LYP	HF/6-31G*	B3LYP	HF/6-31G*	B3LYP	HF/6-31G*	B3LYP
Base C–C Dist./Å	1.501	1.515	1.551	1.561	1.492	1.504	1.540	1.550
Base C–Cap C Dist./Å	1.541	1.547	1.546	1.553	1.537	1.547	1.538	1.546
Cap C–CH ₂ (O) Dist./Å	1.540	1.548	1.544	1.551	1.436	1.427	1.392	1.417
Total Energy ^a /au	–347.77094	–350.14908	–463.71471	–466.88812	–455.23326	–457.85182	–607.02810	–610.51999

^a 1 au = 1 E_h

fraction study on parent compound **6** carried out by us gave a value of 1.538 Å, shorter than that observed for **2** or anticipated for a cyclobutane derivative.² Both the HF and B3LYP calculations (Table 2) lead to considerably longer cyclobutane C–C distances for **2** (1.551, 1.561 Å) and **6** (1.540, 1.550 Å). The shortening of the C–C distances in the case of the oxa-analogues may be a result of libration. If the compound has large anisotropic thermal motion in the crystal such that the molecule has a rocking motion about its main rotation axis, this can cause an apparent shortening of the tangential bonds. Qualitative analysis of the crystal structure (ORTEP diagram) shows that there is a molecular motion in the crystal, which is indicated by the shape and the direction of the ellipsoids.⁷ The

molecule rotates about an axis perpendicular to the cyclobutane ring, resulting in the short bond lengths. Despite the shrinking, these structures retain a rough C₄ axis.

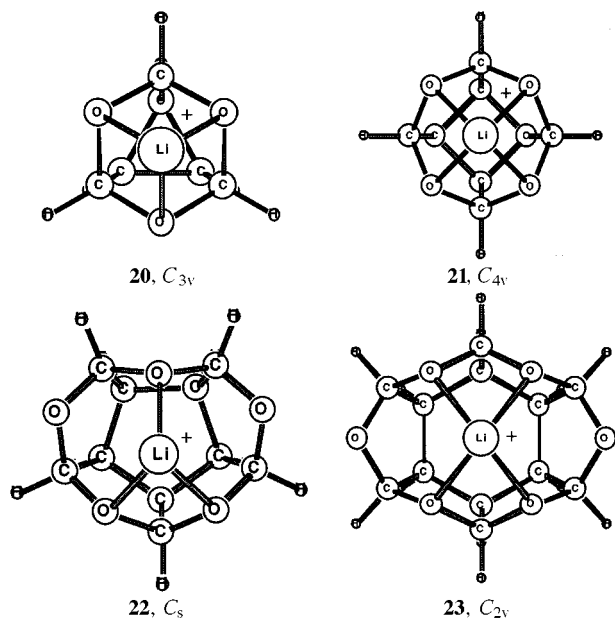
[5]Peristylanes and [5]oxa[5]peristylanes

The [5]peristylane (**3**), and the [5]oxa[5]peristylane (**7**) do not conform to C_{5v} symmetry. The C_{5v} structures are calculated to be higher order saddle points for both **3** and **7** (Table 2) indicating that the overall C_{5v} symmetry determined for **7** from the NMR data in solution is a result of a dynamic process.^{5a} Minimum energy structures with C_s symmetry (**24**, **9**) obtained at the HF level are very close in energy to the symmetric systems.

Table 2 Total energies (au) and frequencies of structures 1–27 at HF/6-31G* and B3LYP levels

System symmetry	HF/6-31G*			B3LYP		
	Total energy ^a /au	Frequencies	Ignored Freq.	Total energy ^a /au	Frequencies	Ignored Freq.
1, C _{3v}	-347.77094 (0)	377.1, 497.5	-1.8, 4.3	-350.14908 (0)	351.5, 354.4, 463.6	-36.6, 22.7
2, C _{4v}	-463.71471 (0)	32.2, 331.3, 359.9	-3.6, 3.2	-466.88812 (0)	67.2, 312.9, 340.6	27.9, 49.4
3, C _{5v}	-579.66646 (2)	-136.5, 356.7, 381.2	-4.2, 5.3	-583.63332 (2)	-126.5, 333.5, 356.8	-18.7, -7.5
4, C _{6v}	-695.57759 (3)	-183.0, -125.6, 348.4	-3.0, -2.7	-700.34194 (3)	-171.3, -116.8, 326.7	3.7, 8.5
5, C _{3v}	-455.23326 (0)	537.6, 630.6, 692.9	-5.3, -4.1	-457.85182 (0)	486.4, 486.9, 576.0	13.5, 24.8, 40.4
6, C _{4v}	-607.02810 (0)	130.3, 444.1, 546.9	1.4, 3.8	-610.51999 (0)	128.9, 464.5, 490.9	25.9, 31.9
7, C _{5v}	-758.82096 (2)	-68.9, 489.1, 503.6	-3.2, 2.5	-763.18276 (2)	-59.0, 423.0, 433.0	-32.0, -23.8
8, C _{6v}	-910.56072 (3)	-147.6, -98.3, 408.4	-0.7, -0.3, 3.1	-915.79695 (3)	-132.7, -90.3, 362.0	-5.0, 18.5
9, C _s	-758.82202 (0)	27.2, 103.6, 394.5	-1.2, -0.6	-763.18340 (1)	-27.9, 74.6, 360.3	-17.1, 5.8, 11.9
10, C _s	-569.40741 (0)	47.3, 68.0, 84.6	-2.9, 2.5, 3.0	-572.59855 (0)	55.0, 75.2, 83.6	-11.5, 16.3, 24.9
11, C _s				-312.04438 (0)	120.8, 255.6, 364.4	-27.6, -24.2, 11.6
12, C ₁				-428.77886 (0)	54.3, 209.1, 245.4	-11.7, -8.5, 16.6
13, C ₁				-545.53615 (1)	-56.0, 187.1, 204.9	-25.8, 16.8, 23.7
14, C _s				-662.25632 ^b		
15, C _s				-383.84128 (0)	121.8, 236.7, 438.4	-17.6, 9.8, 14.7
16, C _s				-536.48863 (0)	89.7, 150.1, 271.0	-17.1, 12.8
17, C ₁				-689.14984 (1)	-97.2, 114.9, 147.2	-4.9, 16.2, 20.2
18, C ₁				-689.15134 (0)	23.6, 142.3, 153.4	-7.7, 16.2, 18.7
19, C _s				-841.78546 (1)	-15.9, 156.7, 200.4	-21.6, -12.4, -8.4, 12.6
20, C _{3v}	-462.55946 (0)	243.4, 423.1, 562.5	1.7, 3.3	-465.23476 (0)	260.1, 433.3, 510.2	-21.4, 10.3
21, C _{4v}	-614.37398 (0)	73.1, 260.6, 402.9	5.0, 10.9	-617.92057 (0)	102.8, 253.2, 402.1	13.8, 43.5
22, C _s	-766.18784 (0)	107.1, 204.2, 264.4	-3.1, -1.8, -1.4	-770.60209 (0)	81.5, 180.3, 253.8	-22.5, 16.6, -12.1
23, C _{2v}	-917.94876 (0)	103.2, 203.6, 215.4	-4.1, -1.0	-923.23699 (0)	95.4, 189.5, 197.6	-19.2, -17.6, -15.4
24, C _s	-579.67817 (0)	115.4, 182.7, 271.9	-5.3, -4.5, -4.0	-583.64347 (0)	118.8, 169.4, 260.6	-9.8, 2.1, 12.1
25, C _s	-758.82198 (1)	-15.2, 105.2, 396.3	-3.3, 3.7	-763.18337 (0)	20.8, 73.8, 357.4	-19.5, -15.8, 1.2, 22.9
26, C _{3v}	-695.60756 (0)	138.9, 238.2, 274.6	-1.3, 1.1	-700.36816 (0)	130.6, 133.2, 226.4	-9.7, 10.1, 19.8
27, C _{3v}	-910.57163 (0)	105.5, 191.0, 360.1	-4.1, 3.2, 3.3	-915.80638 (0)	94.5, 94.8, 174.5	-12.2, -7.9, 14.0

^a 1 au = E_h. ^b Frequency calculations were not carried out.

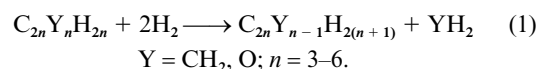


At the B3LYP level, structure 9 is not a minimum energy structure. Another C_s structure (25) where two oxygen atoms are pushed in is found to be a minimum even though the energy difference between 9 and 25 at either of these levels is very small. It was not possible to find a minimum energy structure for [5]peristylane corresponding to 25. The tendency for distortion away from the C_{5v} structure is also seen in the top ring skeleton of 7; our calculations indicated that 1,3,5,7,9-pentoxecane (10) has a similarly distorted structure. An X-ray structure of 1,3,5,7,9-pentoxecane, however, shows yet another distorted structure.^{5c} Thermal ellipsoids have suggested a considerable amount of intramolecular or torsional motion in this crystal.^{5c}

Several derivatives of 3 have been studied by X-ray diffraction.³ Bond lengths from these studies are comparable to those of the theoretical values. However, the X-ray structure of 7 indicates shorter than usual (average C–C distance of the base five-membered ring = 1.531 Å) bond lengths (Table 3). The decrease in bond length is noticed for other bonds as well. Interestingly, the solid state structure indicates a highly compact structure with every C–H bond and oxygen involved in the C–H···O bonding.⁸ This yields a high density solid similar to 6.⁸ Reasons similar to those discussed for [4]oxa[4]peristylane may be applicable here as well.

[6]Peristylane and [6]oxa[6]peristylane: Steric influence on synthesis

The C_{6v} symmetry structures are calculated to be higher order stationary points. A C_{3v} structure (26) is calculated to be a minimum and is lower in energy by 6.8 kcal mol⁻¹ (5.9 kcal mol⁻¹) at HF/6-31G* (B3LYP) for the parent system and 18.8 kcal mol⁻¹ (16.5 kcal mol⁻¹) at HF/6-31G* (B3LYP) for the [6]oxa derivative (27). Unlike 3 and 7, both 4 and 8 exhibit minimum energy structures of the same symmetry at both the levels of theory considered here. In view of our continuing attempts towards the synthesis of 8,⁶ we have estimated the increase in strain in going from a seco-structure (19) to 8. Similar estimates are made for all the systems for comparison purposes. This is established by reaction (1). Table 4 gives the energy of reaction (1) for the [n]peristylanes and [n]oxa[n]peristylanes (n = 3–6).



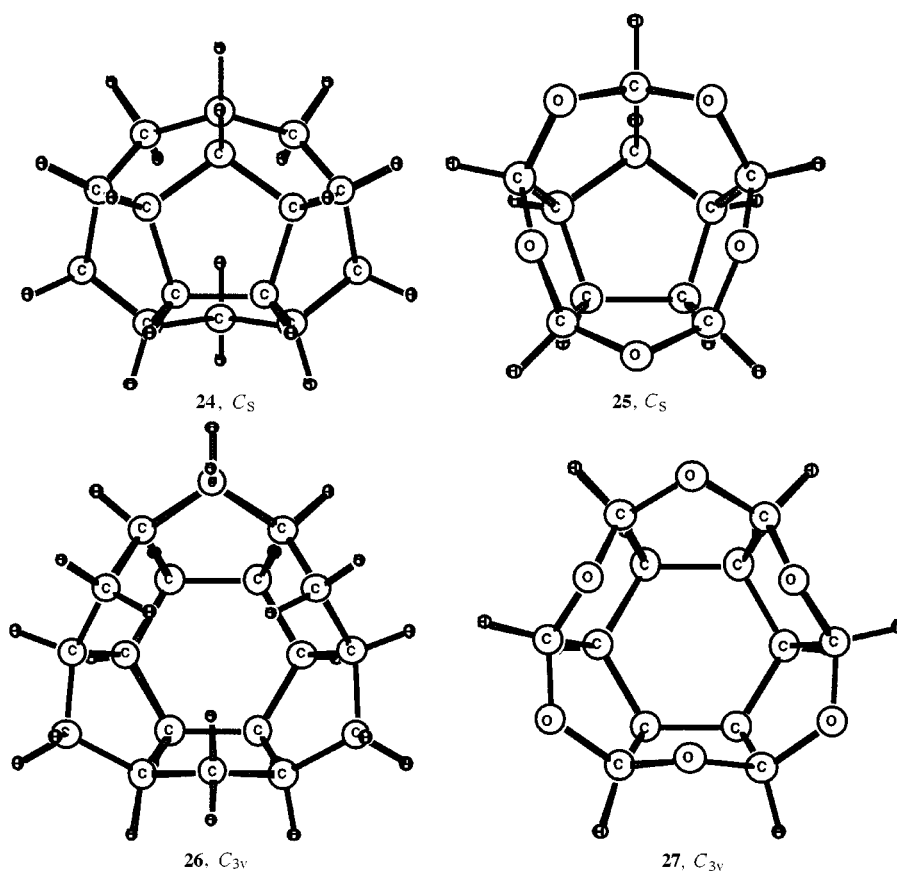
Interaction with metal ions

The symmetrical and crown-like disposition of the oxygen atoms in the oxaperistylanes make them attractive targets for

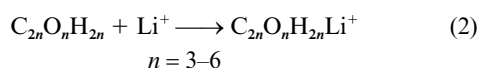
Table 3 Important bond length (Å) data for different structures (**7**, **9**, **25**) of [5]oxa[5]peristylanes at HF/6-31G* and B3LYP levels and from X-ray diffraction^a

Symmetry	HF/6-31G*			B3LYP			Expt. C _s
	7, C _{5v}	9, C _s	25, C _s	7, C _{5v}	9, C _s	25, C _s	
Base C–C Dist./Å	1.537	1.541, 1.531, 1.534	1.531, 1.538, 1.542	1.544	1.541, 1.549, 1.537	1.545, 1.538, 1.550	1.530, 1.536, 1.528
Base C–Cap C Dist./Å	1.540	1.540, 1.541	1.541, 1.540	1.550	1.551, 1.550	1.550, 1.551	1.529, 1.527, 1.525
Cap C–O Dist./Å	1.387	1.388, 1.381, 1.391, 1.389, 1.393	1.384, 1.392, 1.391, 1.390	1.413	1.413, 1.404, 1.417, 1.415	1.407, 1.415, 1.416, 1.408	1.408, 1.413, 1.407, 1.408, 1.420
Tot. energy ^b /au	–758.82096 (2)	–758.82202 (0)	–758.82198 (1)	–763.18276 (2)	–763.18340 (1)	–763.18337 (0)	

^a Ref. 8. ^b 1 au = 1 E_h.



metal ions. We have studied the energetic and the structural consequences of metal complexation by taking Li⁺ as a model. The resulting complexes retain the high symmetry for the [3]- and [4]oxa systems (**20**, **21**). The Li⁺ complex (**22**) has three oxygens coordinated to Li⁺ and the symmetry is reduced to C_s. The following reaction [reaction (2)] is always exothermic (Table 4).



The complexation energy increases with size, going from 56.9 kcal mol⁻¹ (61.7 kcal mol⁻¹) for **5** to 88.8 kcal mol⁻¹ (91.7 kcal mol⁻¹) for **8** at HF/6-31G* (B3LYP) level. **5** and **6** retain the high symmetry even after complexation (**20**, **21**). The unusual flexibility observed for **7** is reduced on complexation; only one minimum energy structure corresponding to **9** could be located (**22**). The interaction of Li⁺ with **8** is most exothermic (Table 4).

Conclusions

Calculations at the HF and B3LYP levels using the 6-31G* basis set on [n]peristylanes and [n]oxa[n]peristylanes indicate that the high symmetry structures are minima for n = 3 (C_{3v} **1**, **5**) and n = 4 (C_{4v} **2**, **6**). The C_{5v} structures (**3**, **7**) are not minima. A distorted C_s structure (**9**) is calculated to be a minimum for the pentoxa[5]peristylyane system. The energy difference between **7** and **9** is very small, in accordance with the C_{5v} structure observed in solution at all temperatures studied. The distorted structure is a characteristic of the top ten-membered ring: **10** is calculated to have a similar distorted structure. The [6]oxa[6]peristylyane also has a distorted geometry (**27**) which is similar in shape to its top ring. Calculations on the seco complexes **11–14** and **15–19** indicate that there is no unusual strain increment in going from **19** to **27**. The exothermicity of the Li⁺ interaction increases from **5** to **8** (Table 4). The lithiated structures (**20–23**) are more rigid.

Table 4 Reaction energies of reactions (1) and (2) calculated at HF/6-31G* and B3LYP levels^a

Reaction	HF/6-31G*	B3LYP
1 + 2H ₂ →11 + CH ₄		-39.4
2 + 2H ₂ →12 + CH ₄		-36.5
24 + 2H ₂ →13 + CH ₄		-37.7 ^b
27 + 2H ₂ →14 + CH ₄		-34.9 ^b
5 + 2H ₂ →15 + H ₂ O		-29.8
6 + 2H ₂ →16 + H ₂ O		-16.7
9 + 2H ₂ →17 + H ₂ O		-15.3
25 + 2H ₂ →18 + H ₂ O		-16.3
27 + 2H ₂ →19 + H ₂ O		-23.3 ^b
5 + Li ⁺ →20	-56.9	-61.7
6 + Li ⁺ →21	-69.2	-72.8
9 + Li ⁺ →22	-81.8	-84.2
27 + Li ⁺ →23	-88.8	-91.7

^a Reaction (1) calculated at the B3LYP level only. ^b The seco-structures considered for the calculation of the strain energy are not minima.

Acknowledgements

The authors thank the Department of Science and Technology (DST), New Delhi for financial support. P. K. S. thanks the Council of Scientific and Industrial Research (CSIR), New Delhi for financial assistance in the forms of Junior and Senior Research Fellowships. E. D. J. and P. K. S. thank the Maui High Performance Computing Center (MHPCC), Hawaii for a generous grant of computer time. Professor K. Venkatesan is thanked for valuable discussions.

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Paper 8/06955G