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DFT Calculations on Heterocyclacenes

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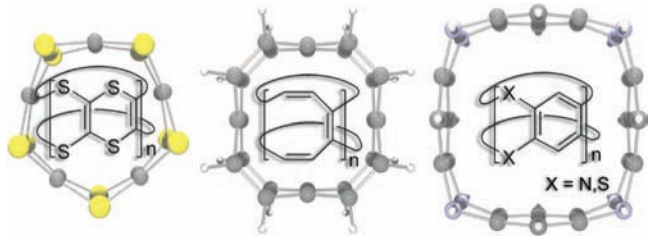
ABSTRACT



Two different types of cyclacenes utilizing eight-membered or six-membered rings containing divalent sulfur and nitrogen atoms have been investigated by theoretical means with respect to their geometries and relative energies using DFT calculations. In all four cases, we predict thermodynamically stable macrocycles which are built from linear annelation of conjugated rings to a hoop shape.

The preparation of hoop-shaped systems which are fully conjugated has been a topic of research for the past two decades.[1] During the past 5 years, successful examples have been reported for the first time.[2−4] The research has mainly focused on [6]$_n$cyclacenes (**1**, Figure 1) being prime examples of such species. However, attempts at their synthesis have been in vain so far. Two obstacles have to be overcome: the bending of a ribbon of annelated six-membered rings into a torus and the high reactivity of the resulting cyclacenes.

The latter characteristic is mainly due to the fact that [6]$_n$cyclacenes are lacking any aromaticity.[5] This can be circumvented in angularly annelated systems such as cyclo[10]phenacene (**2**). For these species, singlet ground states have been predicted.[6] The bending problem could also be avoided when C_{60} was used as starting material for the

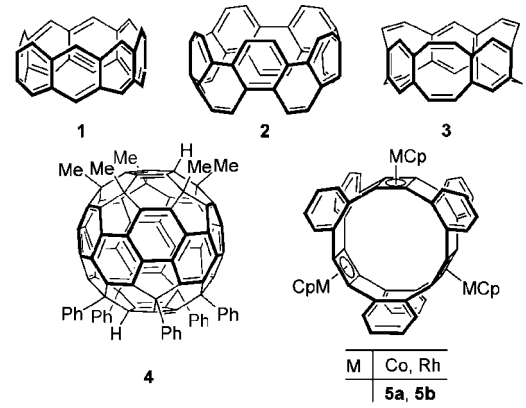


Figure 1. [6]$_8$Cyclacene (**1**), cyclo[10]phenacene (**2**), C_{60}-embedded cyclo[10]phenacene **4** as derivative of **2**, [6.8]$_3$cyclacene **3**, and [4.8]$_3$cyclacene derivatives **5a** and **5b**.

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derivative **4** which has a cyclo[10]phenacene as equatorial belt (Figure 1).[2]

Our approach to circumvent the obstacles mentioned above was the use of eight-membered rings as building blocks in combination with four-membered and six-membered rings. Cyclooctatetraene naturally adopts a boat conformation providing for the bending to a torus (Figure 2).[1e] This concept was recently underlined by DFT calculations on cyclacenes **6** and **7**[7] and validated through the syntheses of the first derivatives of $[4.8]_3$cyclacene **5**[3] and $[6.8]_3$cyclacene (**3**)[4] (Figure 1).

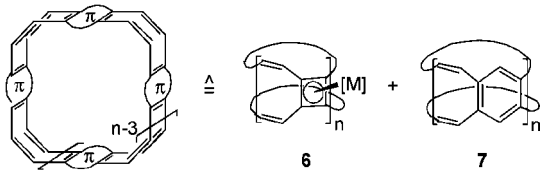


Figure 2. Linearly annelated cyclacenes with 4π- (**6**) or 6π-systems (**7**) alternating with cyclooctatetraene fragments.

In this paper, we present our results of model calculations on novel types of cyclacenes: $[8]_n$cyclacenes being composed of linearly annelated conjugated eight-membered rings (**8**$_n$ in Figure 3) and hetero(thia- and aza)cyclacenes. Cyclooctatetraene rings can be replaced by 1,4-dithiine[8] and 1,4-dihydropyrazine units without altering the number of eight π-electrons. Thus, cyclacenes **10**$_n$ and **11**$_n$ correspond to $[6.8]_n$cyclacenes **7**. Cyclacenes **9**$_n$ parallel $[8]_n$cyclacenes (**8**$_n$) and represent further examples of $(CS)_n$ compounds.[9]

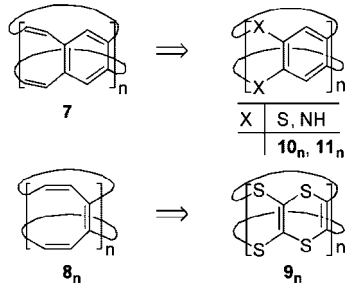


Figure 3. Deduction of heterocyclacenes **9**$_n$, **10**$_n$, and **11**$_n$ and $[8]_n$cyclacenes (**8**$_n$).

The geometrical parameters of **8**$_n$−**11**$_n$ were optimized using the density functional theory (DFT)[10] by applying the three-parameter hybrid functional by Becke (B3)[11] and the correlation functional suggested by Lee, Yang, and Parr (LYP).[12] As basis set we used 6-31G* as recommended by Pople et al.,[13] implemented in Gaussian03.[14] All minima were characterized by harmonic vibrational frequency calculations, and all energies are corrected by zero-point vibrational energies.

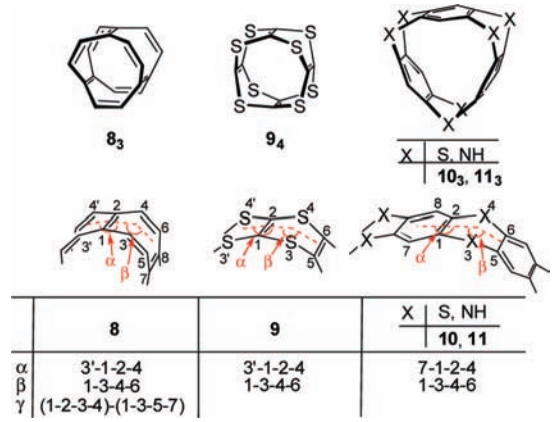
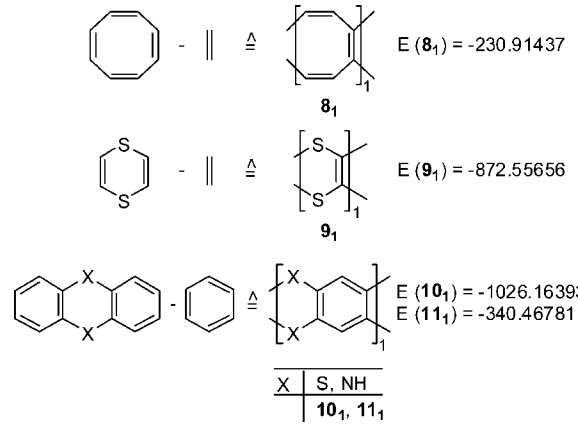


Figure 4. Schematic drawings of **8**$_3$, **9**$_4$, **10**$_3$, and **11**$_3$, atom numbering in **8**−**11**, and definition of the angles α, β, and γ.

Scheme 1. Definitions and Energies (in au) of the Strain-Free Subunits **8**$_1$−**11**$_1$



In Figure 4 we have shown as examples the formulas of **8**$_3$, **9**$_4$, **10**$_3$, and **11**$_3$. In Table 1, the dihedral angles α and β

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Table 1. Most Relevant Calculated Geometrical Parameters and Calculated Point Groups for $\mathbf{8}_n-\mathbf{11}_n$ and the Energy Differences ΔE between the Subunits of $\mathbf{8}_n-\mathbf{11}_n$ and the Strain-Free Subunits $\mathbf{8}_1-\mathbf{11}_1$

	n	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
$\mathbf{9}_n$	ΔE (kJ/mol)	76.3	41.5	30.4	27.4	27.8	24.1	22.0	21.9	20.7	21.6	18.8	19.2	19.7
	α (deg)	156.5	163.9	172.8	177.0	179.8	176.5	176.5	175.5	177.9	172.1	175.7	177.2	181.9
			169.0				175.4	175.3	175.6	178.8	173.6	178.3	181.0	178.1
			164.8				173.8	175.7	179.9	179.1	174.4	178.0	181.7	178.4
			166.4				172.0		178.7		173.8	175.4	178.7	
			167.9				170.8		178.2		177.0			
									179.4		178.1			
											176.4			
	β (deg)	113.5	121.4	127.2	131.6	135.2	123.4	225.3	135.2	232.7	124.8	131.0	130.7	131.7
			121.6				216.0	127.2	134.7	132.1	217.4	128.3	231.9	133.8
			121.7				125.9	130.6	130.1	134.4	125.8	228.3	131.9	131.8
			121.2				131.5		229.4	134.5	127.2	128.3	134.5	232.5
			121.8				126.0		128.4		227.4		131.9	
									130.4		128.5			
											132.0			
	PG	D_{4h}	C_1	D_{6h}	$D_{7h}{}^a$	D_{8h}	C_{2v}	D_{2h}	$C_{2v}{}^a$	$D_{2h}{}^a$	C_{2v}	D_{2h}	C_{2v}	C_{4h}

	n	**2**	**3**	**4**	**5**	**6**	**7**	**8**
$\mathbf{8}_n$	ΔE (kJ/mol)		46.7	7.2	2.4	9.0	18.0	27.0
	α (deg)		165.3	177.6	190.4	194.8	197.1	198.5
	β (deg)		127.4	133.8	138.8	142.6	145.8	148.3
	γ (deg)		67.6	62.3	57.9	54.2	51.1	48.3
	PG		D_{3h}	D_{4h}	$D_{5h}{}^a$	$D_{6h}{}^a$	$D_{7h}{}^a$	$D_{8h}{}^a$
$\mathbf{10}_n$	ΔE (kJ/mol)	317.6	97.0	37.5	16.3	7.8	4.4	3.3
	α (deg)	140.0	159.2	168.5	173.7	177.0	179.3	179.1
	β (deg)	100.7	107.7	114.6	119.7	123.7	126.7	129.1
	PG	D_{2h}	D_{3h}	D_{4h}	D_{5h}	D_{6h}	D_{7h}	D_{8h}
$\mathbf{11}_n$	ΔE (kJ/mol)	592.2	191.6	100.1	62.0	42.7	32.2	26.0
	α (deg)	152.1	155.2	164.3	169.7	173.0	175.2	176.7
	β (deg)	97.7	116.6	124.0	129.8	134.3	137.9	141.1
	PG	D_{2h}	$D_{3h}{}^a$	$D_{4h}{}^a$	D_{5h}	D_{6h}	D_{7h}	D_{8h}

[a] Symmetry from comparison of structural parameters.

are listed describing the bending along the central scaffold as well as the angle γ for $\mathbf{8}_n$. The definitions of the angles α, β, and γ are shown in Figure 4.

To get an estimation of the strain energy opposed by the hoop shape of the cyclacenes, we calculated the energies of the strain free subunits $\mathbf{8}_1$, $\mathbf{9}_1$, $\mathbf{10}_1$, and $\mathbf{11}_1$ as shown in Scheme 1. The energy differences between a subunit of each $\mathbf{8}_n-\mathbf{11}_n$ (total energy divided by n), and the strain-free subunits $\mathbf{8}_1-\mathbf{11}_1$ are denoted as ΔE in Table 1.

For $\mathbf{8}_n$, the ΔE value rapidly decreases with increasing numbers of n and has its minimum for $n = 5$. For the larger congeners the strain energy increases again. The calculated structures of $\mathbf{8}_3$, $\mathbf{8}_5$, and $\mathbf{8}_8$ are shown in Figure 5. As the C−C bond lengths have average values for localized double bonds (C1−C2, 1.35 and 1.36 Å; C3−C5, 1.34 and 1.35 Å) and localized single bonds (C1−C3, 1.49 and 1.48 Å), the strain energy can be deduced to an unfavorable distortion from planarity of the central double bond units (C1−C2, angle α) and a more or less favorable bending of the cyclooctatetraene rings (angle β). The minimal strain energy for $n = 5$ stems from an optimal bending β of the cyclooctatetraene rings. In this case, it is closest to that found in cyclooctatetraene itself with 138.4°.[15]

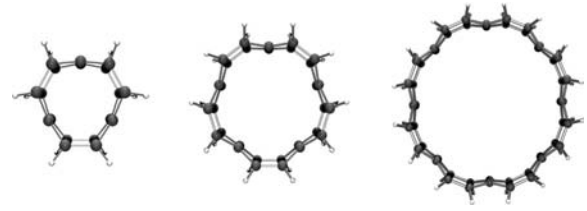

Figure 5. Calculated structures of $\mathbf{8}_3$, $\mathbf{8}_5$, and $\mathbf{8}_8$.

The distortion from planarity (180°) of the central double bond unit, characterized by the angle α, is smallest for $n =$

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4 and increases again with growing n as the C1−C2 bonds point inside the cavity. As a measure for the π-orbital overlap and thus the conjugation around the belt we measured the angles γ between the planes of the peripheral and those of the central double bonds. Assuming that the overlap between orbitals is proportional to the cosine of the angle between them, the conjugation around the torus of $\mathbf{8}_n$ rises from 38% for $n = 3$ to 67% for $n = 8$.

In the case of $\mathbf{9}_n$, the relative energies ΔE almost steadily decrease with growing n still leaving a strain energy of about 20 kJ/mol per subunit for the largest systems. The smaller members $\mathbf{9}_3$−$\mathbf{9}_8$ have D_{nh}-symmetrical structures which change to lower symmetries for $n \geq 9$ as the sulfur bridges allow for a fair amount of flexibility in the cage. As a result, structures were found in which four ($\mathbf{9}_9$−$\mathbf{9}_{12}$) or eight ($\mathbf{9}_{13}$−$\mathbf{9}_{16}$) sulfur centers point to the inside of the cavities. The calculated structures of $\mathbf{9}_6$, $\mathbf{9}_9$, and $\mathbf{9}_{16}$ are shown in Figure 6.

Figure 6. Calculated structures of $\mathbf{9}_6$, $\mathbf{9}_9$, and $\mathbf{9}_{16}$.

The deviation from planarity at the central double bond units (C1−C2) is substantial only for $n = 3$−5; in the larger systems, these units remain rather rigid and the bending is mostly accomplished by the thioether bridges. The dihedral angles β through the sulfur centers are smallest for $n = 4$−5 and range for $n \geq 6$ between 126.7° and 135.2° for sulfur bridges pointing outside the cavity and 216.0°−232.7° for those pointing to the inside. The bond lengths C1−C2 have values of 1.34 and 1.35 Å; the lengths of the C−S bonds lie between 1.78 and 1.81 Å.

In the case of the hoop-shaped systems $\mathbf{10}_n$ and $\mathbf{11}_n$, the strain energy is very large for the smallest systems with $\mathbf{10}_2$ and $\mathbf{11}_2$ being [1$_4$](1,2,4,5)cyclophanes and steadily decreases with growing n with the steepest descent from $n = 2$−4. The bond lengths in the phenyl rings are equalized with 1.40−1.41 Å (1.43/1.45 Å for $\mathbf{11}_2$). The C−S bond lengths in $\mathbf{10}_n$ range between 1.79 and 1.84 Å, the C−N bond lengths in $\mathbf{11}_n$ between 1.42 and 1.46 Å. In Figure 7 are shown the calculated structures of $\mathbf{10}_3$, $\mathbf{10}_5$, $\mathbf{10}_8$, $\mathbf{11}_4$, $\mathbf{11}_6$, and $\mathbf{11}_7$. In both ring systems we find that the shape of the macrocyclic scaffolds is determined by the tetrasubstituted aromatic rings which maintain their planarity. Responsible for the strain energy are the bending at the heteroatom bridges (dihedral angle β) and the deviation from planarity at the phenyl−heteroatom bonds (angle α). For the thio-systems $\mathbf{10}_n$, the dihedral angle α describing the coplanarity of the phenyl rings and the C−S bonds grows very close to 180° from

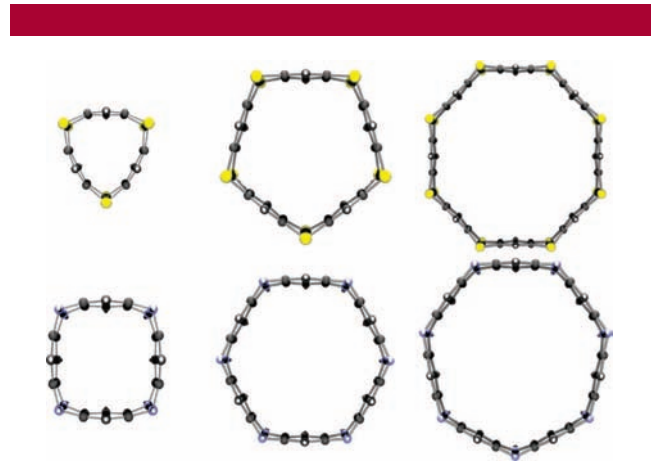

Figure 7. Calculated structures of $\mathbf{10}_3$, $\mathbf{10}_5$, and $\mathbf{10}_8$ (top row) and $\mathbf{11}_4$, $\mathbf{11}_6$, and $\mathbf{11}_7$ (bottom row).

$n = 6$ upward. The bending at the thioether bridges starts with an angle β of 100.7° for $n = 5$ and grows to 129.1° for $n = 8$, very close to the value found in the strain free subunit $\mathbf{10}_1$ of 129.8°. In the azacyclacenes $\mathbf{11}_n$, both angles α and β grow in similar increments with increasing n parallel to a decrease in strain energy. The dihedral angle α almost approaches its optimal value found in the strain free subunit $\mathbf{11}_1$ (178.5°) for $n = 8$ (176.7°). β, on the other hand, describing the bending at the nitrogen centers is for $n = 8$ (141.1°), still far from the ideal angle of 160.1° explaining the considerably high strain energy. This strong bending at the sulfur and nitrogen centers in $\mathbf{10}_n$ and $\mathbf{11}_n$ differs considerably from the recently described *N*,*N*-dihydrodiazatetracenes,[16] which are almost planar. The bending at the heteroatoms in $\mathbf{10}_n$ and $\mathbf{11}_n$ is indicative for a reduced conjugation in the 4n π subunits.

To conclude, our calculations strengthen the concept to incorporate eight-membered rings into cyclacenes and show that it can be expanded to heteroanalog but electronically equivalent systems. We obtained structures that are electronically stable and have only little strain energy. The novel cyclacenes provide large cavities with donor groups in the case of the heterocyclacenes which partly point inside the cavity. These novel cyclacenes represent a target worthwhile synthetic investigations.

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Supporting Information Available: Tables listing electronic energies, Cartesian coordinates, and zero-point vibrational energies for all calculated species. This material is available free of charge via the Internet at http://pubs.acs.org.

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