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DFT Calculations on [6.8]Cyclacenes and CpCo-Capped [4.8]Cyclacenes

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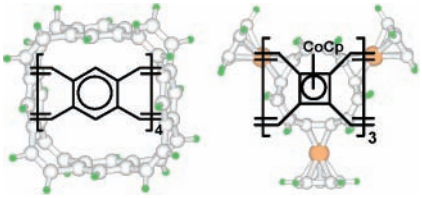
ABSTRACT



Two different types of cyclacenes, utilizing eight-membered and six-/four-membered rings as building blocks ([6.8]$_n$ and CpCo-capped [4.8]$_n$cyclacenes), have been theoretically investigated with respect to their geometries, relative energies, and magnetic properties (aromaticity).

Hoop-shaped linearly annelated benzene rings (**1**, Figure 1), called [6]$_n$cyclacenes,[1] have been discussed since 1954[2] with respect to their conjugation properties (aromaticity) and their energetic and spectroscopic characteristics.[3,4] The main outcome of model calculations was that [6]$_n$cyclacenes, especially those with an even number of rings, should show a small singlet−triplet splitting, indicating a high reactivity. In those types of cyclacenes in which benzene rings are not linearly annelated (e.g., hoops consisting of a repeating phenanthrene (**2a**)[5a,6] or pyrene (**2b**)[5a,7] unit (Figure 1)), the singlet−triplet splitting is expected to be large based on Clar's aromatic sextet rules.[8]

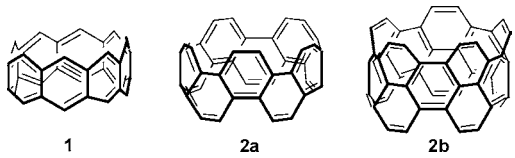


Figure 1. [6]$_8$Cyclacene (**1**), phenanthrene-type (**2a**), and pyrene-type (**2b**) cyclacenes.

The challenge of a [6]$_n$cyclacene synthesis has been met several times but could not successfully be accomplished.[5,9]

(1) In accordance with the notation [m.8]$_n$cyclacenes, we will use the term [6]$_n$cyclacenes for **1** instead of [n]cyclacenes which is commonly used.

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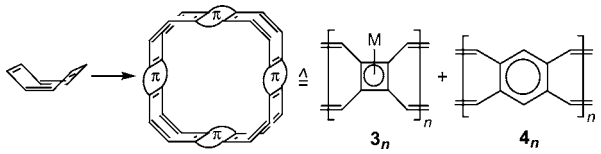
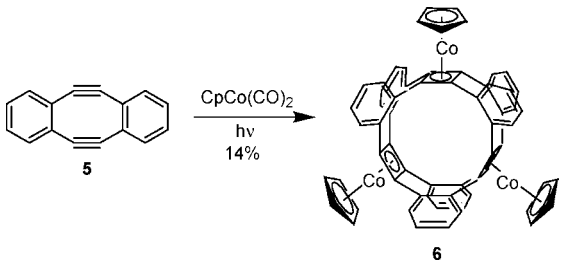
The main reason might be the above-mentioned high reactivity predicted for linear [6]$_n$cyclacenes.[4] The synthesis of a nonlinear cyclacene from [60]fullerene, named [10]-cyclophenacene and consisting of phenanthrene units, however, has been reported.[6] An alternative approach to linearly annelated cyclacenes utilizes conjugated eight-membered rings combined with four- or six-membered rings.[5c] The eight-membered ring facilitates the bending of the linear assembly to a ring (Scheme 1).

Scheme 1. Construction of [4.8]$_n$ and [6.8]$_n$Cyclacenes by Annelation of Eight- and Four-Membered Rings (**3**$_n$) and Eight- and Six-Membered Rings (**4**$_n$), Respectively



Using this concept, we arrive at [4.8]$_n$- and [6.8]$_n$cyclacenes **3**$_n$ and **4**$_n$ (Scheme 1) where the cyclobutadiene units of the latter are stabilized by metal fragments. In this case, we were successful by utilizing a transition metal supported [2+2] cyclodimerization of the cyclic diyne **5** (Scheme 2).[10]

Scheme 2. Synthesis of the [4.8]$_3$Cyclacene **6**



In this paper, we report the results of model calculations for [6.8]$_n$cyclacenes (n = 3−8) and for CpCo-capped [4.8]$_n$cyclacenes (n = 3, 4).

The geometrical parameters were optimized using the density functional theory (DFT)[11] by applying the three-parameter hybrid functional by Becke (B3)[12] and the correlation functional suggested by Lee, Yang, and Parr (LYP).[13] As basis sets, we used for C and H those recommended by Pople et al.[14] (6-31G*) as implemented in Gaussian 03.[15] For Co, we used the SDD basis set that includes the Dunning−Huzinaga valence double-ζ on the first row and Stuttgart−Dresden ECPs on the cobalt atom.[16] All minima were characterized by harmonic vibrational frequency calculations, and energies are corrected by zero-point vibrational energies. To derive the NMR data, single-point GIAO-NMR[17] calculations with B3LYP/6-311G** and B3LYP/6-311+G** were carried out on the above geometries.

The optimized geometries of the [6.8]$_n$cyclacene series (**4**$_n$) all show a D_{nh} symmetry. The structure of the smallest member, **4**$_3$, is shown in Figure 2. The most interesting

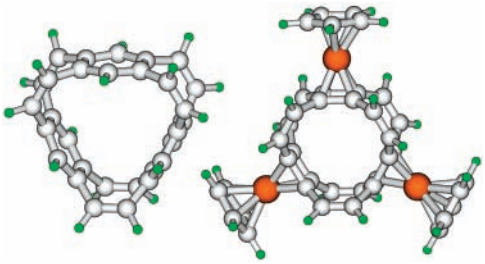


Figure 2. Calculated molecular structures of **4**$_3$ (B3LYP/6-31G*) and **3**$_3$ (B3LYP/6-31G* for C, H; B3LYP/SDD for Co).

geometrical parameters of **4**$_n$ are listed in Table 1: $a-d$ stand for the C−C bond lengths and δ_1 and δ_2 define the dihedral angles between bonds C2−C3/C6−C5 and C11−C12/C9−C8 (Figure 3) characterizing the deviation from planarity of the cyclooctatetraene and benzene rings, respectively. The cavity diameter is given by the parameter ρ.[18]

To compare the energies per subunit of **4**$_n$ with growing n, we set the energy of the smallest cyclacene **4**$_3$ to zero and plotted the energies of each **4**$_n$ divided by n (ϵ_1) against n (Figure 4). To get an estimation for the strain energy opposed by the hoop shape of the cyclacene, we calculated the energy of the strain-free subunit **4**$_1$ by subtracting the

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Table 1. Most Interesting Geometrical Parameters $a-d$, δ_1, δ_2, and ρ[a] (See Figure 3 and Text), Relative Energies ϵ_1 and ϵ_Δ[a] (See Text), and NICS Values[b] (See Figure 5) of the $[6.8]_n$Cyclacenes $\mathbf{4}_n$

n	3	4	5	6	7	8
a [Å]	1.489	1.483	1.479	1.476	1.475	1.474
b [Å]	1.341	1.341	1.342	1.343	1.344	1.345
c [Å]	1.410	1.411	1.411	1.412	1.412	1.412
d [Å]	1.400	1.400	1.401	1.402	1.402	1.403
δ_1 [°]	50.7	44.3	39.5	35.8	32.4	30.1
δ_2 [°]	6.6	4.7	3.6	2.8	2.2	1.7
ρ [Å]	5.65	6.96	8.79	10.94	12.75	14.91
ϵ_1 [kcal/mol]	0.0	−6.0	−6.8	−6.3	−5.5	−4.7
ϵ_Δ [kcal/mol]	6.8	0.7	0.0	0.5	1.3	2.1
NICS 0/0/0	−8.00/ −7.24	−3.99/ −3.61	−2.10/ −2.02	−1.12	−0.64	−0.36
NICS 0	−8.96/ −7.92	−8.06/ −7.18	−7.08/ −6.42	−6.19	−5.43	−4.82
NICS −1	−12.02/ −10.70	−9.82/ −8.53	−8.18/ −7.52	−6.99	−6.09	−5.56
	−9.78/ −7.95	−10.19/ −9.13	−10.04/ −9.00	−9.58	−9.10	−8.45

[a] B3LYP/6-31G*. [b] First value: B3LYP/6-311G**//B3LYP/6-31G*. Second value: B3LYP/6-311+G**//B3LYP/6-31G*.

energies of the fragments **F2** and **F1** (Scheme 3).[19] The energy difference between ϵ_1 and the strain-free subunit $\mathbf{4_1}$ is denoted as ϵ_Δ in Table 1.

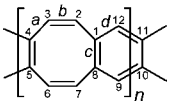


Figure 3. Definition of the parameters $a-d$ for $[6.8]_n$cyclacenes $\mathbf{4}_n$.

Interestingly, the smallest strain energy is induced in the five-membered cyclacene $\mathbf{4_5}$ having a bending of $\delta_1 = 39.5°$ in the cyclooctatetraene moiety which is closest to the

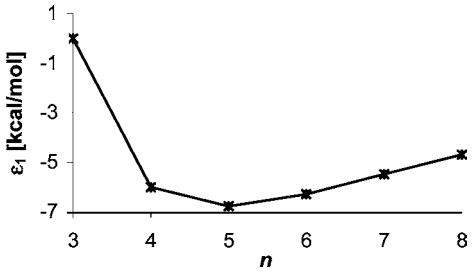
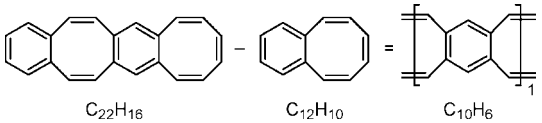


Figure 4. Calculated relative energies per subunit ϵ_1 of $[6.8]_n$-cyclacenes $\mathbf{4}_n$. The energy of $\mathbf{4_3}$ was set to 0 kcal/mol.

experimentally found angle in cyclooctatetraene itself of 41.9°.[20] The three-membered cyclacene $\mathbf{4_3}$ with a dihedral angle δ_1 of 50.7° holds the highest strain energy. The benzene rings are slightly distorted from planarity, as described by

Scheme 3. Strain-Free Model of $\mathbf{4}_n$ ($n = 1$) Derived by the Energy Difference between the Strain-Free Subunits **F2** and **F1**[19]



the dihedral angle δ_2. It steadily decreases toward zero with growing n and seems to exert less influence on the strain energy of the cyclacene. A bending of the same kind is found in the benzene rings in [2.2.2.2](1,2,4,5)cyclophane (12.7°)[21] and its tetrabenzannelated congener (12.2°).[22] A comparison of the bond lengths shows a slight diminishing of the bond alternation in the cyclooctatetraene rings (a and b) with growing n, whereas the CC bond lengths in the benzene rings essentially remain unaffected (c and d). The cavity diameter almost triples going from $\mathbf{4_3}$ (5.65 Å) to $\mathbf{4_8}$ (14.91 Å).

To obtain a measure of the aromaticity in the cavity center and in the benzene rings, we calculated nucleus-independent chemical shift (NICS) values as defined in Figure 5. The

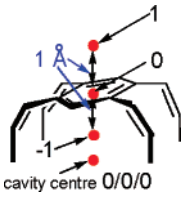


Figure 5. Definition of the NICS values.

results are listed in Table 1 and graphically represented in Figure 6. The center of the cavity shows significantly negative NICS values for the smaller cyclacenes which considerably decrease in absolute value with growing cavity diameter.[23] The NICS values of the benzene rings are also substantially negative for the cyclacenes with small n compared to benzene itself with a NICS 0 of −8.91/−8.04 and a NICS 1 of −11.12/−10.19 (B3LYP/6-311G**//B3LYP/6-31G* and B3LYP/6-311+G**//B3LYP/6-31G*, respectively). With growing n, NICS 0 and NICS −1 increase to less negative numbers pointing toward a slightly decreasing aromaticity, whereas NICS 1 only marginally varies.

(18) The cavity diameter ρ is defined as the distance between the centers of a benzene and cyclooctatetraene ring opposite each other (for uneven numbers of n) or the distance between the centers of two benzene rings opposite each other (for even numbers of n), which in the latter case is smaller than the distance between the centers of two cyclooctatetraene moieties.

(19) Calculation of the energy difference between the corresponding fragments **F3** and **F2** gives the same result. From the two different conformers possible for **F2**, the one with a bending of the cyclooctatetraene units in a circlewise manner was chosen.

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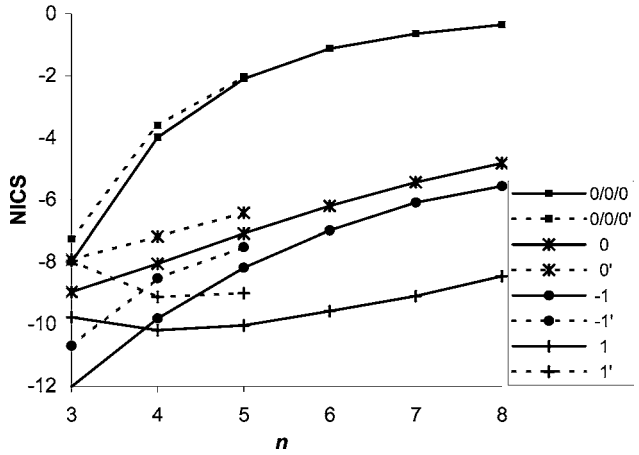


Figure 6. NICS values for $[6.8]_n$cyclacenes $\mathbf{4}_n$ (Figure 5, Table 1). B3LYP/6-311G**//B3LYP/6-31G*; dashed values: B3LYP/6-311+G**//B3LYP/6-31G*.

As representatives for the CpCo-capped $[4.8]_n$cyclacene series, the structures of $\mathbf{3}_3$ and $\mathbf{3}_4$ were optimized. For $\mathbf{3}_3$, no minimum could be found, but a first-order saddle point with a negligible negative frequency (5.8 cm^{-1}) was found showing a rotation of one of the Cp rings around the Co−Cp axis. Its structure is shown in Figure 2. The most interesting geometrical parameters of $\mathbf{3}_n$ are listed in Table 2 as well as a comparison with the X-ray crystallographic structure of **6**.[10] *a*−*d* stand for the C−C bond lengths; *e* stands for the distance from the Co atom to the center of the cyclobutadiene unit; δ defines the dihedral angle between bonds C1−C2/C7−C6 (Figure 7) characterizing the deviation from planarity of the cyclooctatetraene ring; and the cavity diameter is given by the parameter ρ. The energy of the strain-free subunit $\mathbf{3}_1$ was calculated analogously to Scheme 4 and subtracted from the energy per subunit of $\mathbf{3}_n$ to give ϵ_Δ. The geometrical parameters of **6** are very close to those calculated for $\mathbf{3}_3$. The longer bonds *d* in **6** (1.406 Å) compared to $\mathbf{3}_3$ are due to the annelated benzene rings which favor bond lengths of around 1.390 Å (1.390 Å,[24] 1.397 Å (B3LYP/6-31G*)).

Table 2. Most Interesting Geometrical Parameters *a*−*e*, δ, and ρ (See Figure 7 and Text) of the $[4.8]_n$Cyclacenes $\mathbf{3}_n$ and **6**[10] and Relative Energies ϵ_Δ (See Text) of $\mathbf{3}_n$[a]

n	**6**	$\mathbf{3}_3$	$\mathbf{3}_4$
a [Å]	1.474	1.478	1.481
b [Å]	1.458	1.456	1.456
c [Å]	1.487	1.465	1.454
d [Å]	1.402	1.349	1.352
e [Å]	1.675	1.693	1.696
δ [°]	135.5	138.6	149.0
ρ [Å]	4.50	4.49	5.78/6.15[b]
ϵ_Δ [kcal/mol]	−	18.3	9.4

[a] B3LYP/6-31G* for C, H; B3LYP/SDD for Co. [b] Distances between the centers of two cyclobutadiene rings/two cyclooctatetraene rings opposite each other.

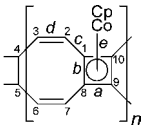
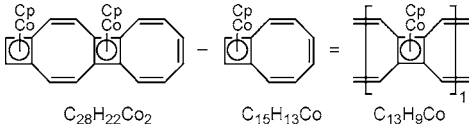


Figure 7. Definition of the parameters *a*−*e* for $[4.8]_n$cyclacenes $\mathbf{3}_n$.

Scheme 4. Strain-Free Model of $\mathbf{3}_n$ ($n = 1$) Derived by the Energy Difference between the Strain-Free Subunits **CoF2** and **CoF1**



The larger strain energy of the $[4.8]_n$cyclacenes compared to their $[6.8]_n$ congeners might be opposed by the, in the former case, more unfavorable bending of the cyclooctatetraene moiety to a tub shape. In **CoF1** as well as **CoF2**, the cyclooctatetraene rings adopt a near planar geometry which is consistent with theoretical and experimental results for similar bicyclo[6.2.0]decapentaene systems.[25]

In conclusion, our calculations reveal that the $[4.8]_n$cyclacenes with $n = 3$ and 4 and the $[6.8]_n$cyclacenes with $n = 3-8$ should be thermodynamically stable species and in contrast to the $[6]_n$cyclacenes be within reach of experiment. The GIAO-NMR calculations predict for $[6.8]_n$cyclacenes aromatic delocalization only in the benzene subunits.

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

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(23) Deletion of the etheno bridges in $\mathbf{4}_n$ and recalculation of NICS values in the cavity center and the benzene rings (as done for $\mathbf{4}_3$, $\mathbf{4}_5$, and $\mathbf{4}_7$) essentially yielded the same result. Thus, the significantly negative values of NICS 0/0/0 seem to stem from the proximity of the benzene subunits and do not indicate a diatropic ring current around the belt.

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