AM1 Study of [C,C]8Carbo- and [C,H]8Carbo-cyclooctatetraene and Smaller Carbomers†

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The results of AM1 semi-empirical SCF MO calculations are reported for [C,C]8carbo-cyclooctatetraene, [C,H]8carbo-cyclooctatetraene and smaller carbomers, derived from benzene and cyclobutadiene.

The cyclooctatetraene molecule **1** has two skeletal orbits: one constituted by the eight carbon sites and the other constituted by the eight hydrogen sites. Thus, compound **1** can undergo two distinct molecular expansion processes: (i) insertion of a linear acetylenic group −C≡C− into each C−H bond of the molecule, which leads to octaethynylcyclooctatetraene **2** and (ii) insertion of the −C≡C− unit at the position *a* and the linear cumulene group (=C=C=) at position *b*, which produces 1,2,4,5,7,8,10,11,13,14,16,17,19,20,22,23-hexadecadehydro[24]annulene **3**. The protons in these expanded structures are in a similar environment to those in cyclooctatetraene. Since structures **2** and **3** mostly retain both the symmetry and the electronic relationships between original atoms (general vinylogy effect), and since they differ only by the number of carbon atoms (and thus by size), these expanded structures are termed as 'carbomers'[1] of cyclooctatetraene. Compounds **2** and **3** contain $4N$ out-of-plane π-electrons and they are expected to show a paramagnetic ring current.[2]

1   **2**

3
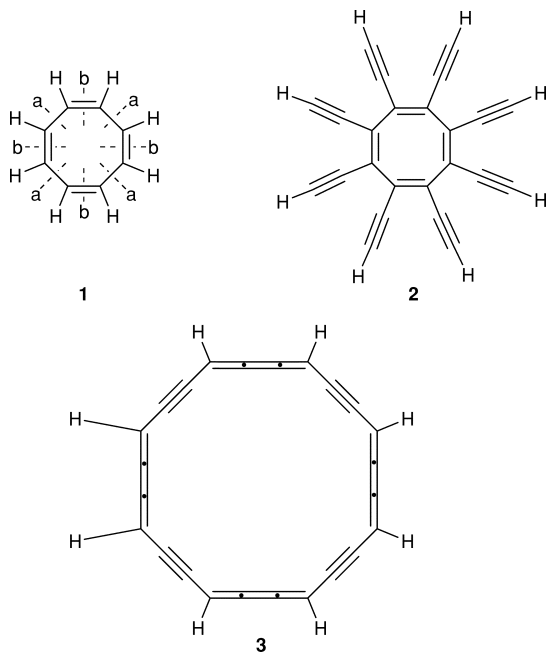
Intrigued by the exceedingly interesting molecular structures of compounds **2** and **3**, we carried out AM1 semi-empirical SCF MO calculations[3] on these expanded systems and smaller carbomers **4**–**7** derived from benzene and cyclobutadiene. Although there is presently no published experimental or theoretical data on the synthesis or structural properties of carbomers **2**, **3**, **6** and **7**, the synthesis of

hexaethynylbenzene **4**[4] and 1,4,7,10,13,16-hexasubstituted derivatives of **5**[5] have been reported. The NMR spectra of the expanded system **5** provides strong evidence for the existence of a diamagnetic ring current.[5]

4   **5**

6   **7**
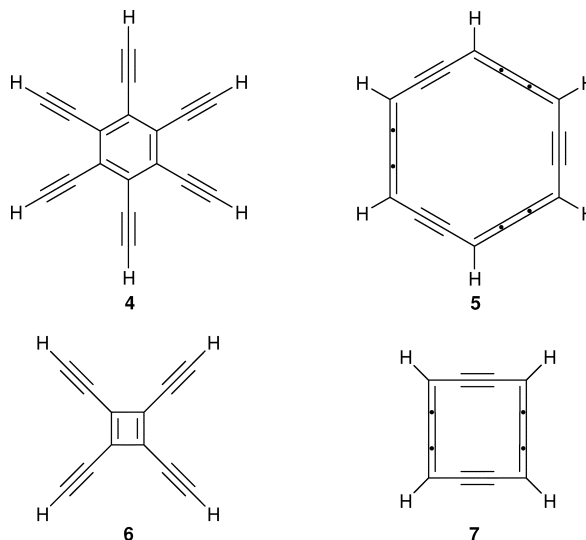
Calculations

Initial estimates of the geometry of structures **1**–**7** was obtained by a molecular-mechanics program PCMODEL (88.0)[6] followed by full minimization using semi-empirical AM1[3] method in the MOPAC 6.0 computer program,[7–9] implemented on a VAX 4000-300 computer. Optimal geometries were located by minimizing energy, with respect to all geometrical coordinates, and without imposing any symmetry constraints. The structures of the transition-state geometries were obtained using the optimized geometries of the equilibrium structures according to the procedure of Dewar *et al.*[10] (keyword SADDLE). All geometries were characterized as stationary points, and true local energy-minima and transition states on the potential energy surface were found using keyword FORCE. All energy-minima and transition state geometries obtained in this work are calculated to have $3N$-6 and $3N$-7 real vibrational frequencies, respectively.[11]

Results and discussion

Cyclooctatetraene **1**[12] has been the subject of electron diffraction[13] and NMR[14] studies. In order to gauge the AM1 reliability for annulenes **1**–**7**, we have optimized the geometry of **1** without restriction. As shown in Table 1, the tub conformation is 12.1 kcal mol^{-1} (1 cal = 4.184 J) more stable than the planar geometry. Although the AM1 method underestimates the energy barrier for ring inversion in **1**, the agreement between the experimental data and the calculated quantities is generally quite good.

Table 1 Heats of formation (kcal mol^{-1}) and selected structural parameters[a] (bond lengths r in Å, bond angles θ and dihedral angles ϕ in °) for compounds **1–7**

Feature	1 Tub	1 Planar	2 Tub	2 Planar	3 Tub	3 Planar	4 Planar	5 Planar	6 Planar	7 Planar
ΔH_f^o	63.48	75.58	517.52	559.71	505.32	506.49	359.41	378.33	318.71	278.42
$\Delta\Delta H_f^{o\,b}$	0.0 (0.0)[c]	12.10 (13.7)[c]	0.0	42.12	0.0	1.17	—	—	—	—
r_{C-H}	1.106 (1.090)[d]	1.114	1.060	1.060	1.110	1.112	1.060	1.107	1.060	1.100
$r_{C_{sp}^2-C_{sp}^2}$	1.452 (1.562)[d]	1.441	1.470	1.466	1.398	1.396	1.412	1.398	1.546	1.413
$r_{C_{sp}^2-C_{sp}}$	—	—	1.410	1.432	1.315	1.315	1.410	1.319	1.377	1.322
$r_{C_{sp}^2=C_{sp}^2}$	1.338 (1.344)[d]	1.336	1.365	1.367	—	—	1.409	—	1.369	—
$r_{C_{sp}=C_{sp}}$	—	—	—	—	1.258	1.258	—	1.256	—	1.263
$r_{C\equiv C}$	—	—	1.198	1.198	1.202	1.202	1.198	1.203	1.199	1.203
$\theta_{C=C-C}$	126 (126)[d]	135	122	135	125	126	120	122	90	115
$\theta_{C\equiv C-C}$	—	—	180	180	178	176	180	179	180	168
$\theta_{C=C=C}$	—	—	—	—	178	176	—	179	—	167
ϕ_{ring}	57	0	67	0	49	0	0	0	0	0

[a]Experimental values are given in parantheses. [b]The standard strain energy in each geometry of a molecule is defined as the difference between the standard heats of formation ($\Delta H°$) for that geometry and the most stable conformation of the molecule.[15] [c]Ref. 14. [d]Ref. 13.

Heats of formation and selected structural parameters for ground-state and transition-state geometries of compounds **2**–**7** are shown in Table 1. The [C,C]$_8$carbomer **3** and [C,C]$_4$carbomer **7** are more stable than the corresponding [C,H]$_n$carbomers (**2** and **6**) by 12.2 and 40.3 kcal mol^{-1}, respectively. On the other hand, the [C,C]$_6$carbomer **5** is calculated to be 18.9 kcal mol^{-1} less stable than hexaethynyl-benzene **4**. Thus, antiaromatic rings prefer to undergo expansion at the carbon orbit, while the benzene ring favours expansion at the hydrogen orbit. The reason for this behaviour might be conservation of the aromatic nucleus.

Carbomers **2** and **3** are not planar but tub-shaped. Interestingly, the energy difference between the tub confor-mation and the planar geometry in **3** is only 1.17 kcal mol^{-1}, while the planar structure of **2** is 42.12 kcal mol^{-1} higher than the tub form. The unusually high energy of the planar geometry of octaethynylcyclooctatetraene **2** can be attributed to large distortions in the bond angles as well as repulsion between the acetylenic moieties. Furthermore, substituents are expected to increase the energy required for angle expansion. In [C,C]$_8$carbomer **3**, the strain due to planarity of the ring skeleton is not concentrated solely in the sp^2-hybridized carbon atoms (as in **1** and **2**), but rather is expressed by adjustments, particularly in bond angles, throughout the molecule. This feature may account for the low energy barrier for ring inversion in **3**.

The planar geometries of **1–3** exhibit interesting structural features. While C=C–C bond angles in **1** and **2** are the same as that observed for a regular octagon (135°), the olefinic angles in the planar geometry of **3** are expanded by 1°. The tub conformation of octaethynylcyclooctatetraene **2** is more puckered than that of **1** by 10°, while the tub form of **3** is flattened by about 8°.

In conclusion, AM1 semi-empirical SCF MO calcu-lations provide a fairly clear picture of [C,C]$_8$-carbo- and [C,H]$_8$carbo-cyclooctatetraene and smaller carbomers de-rived from benzene and cyclobutadiene from both structural and energetic points of view. Although the benzene ring favours expansion at the hydrogen orbit, the antiaromatic systems prefer to undergo expansion at the carbon orbit. It would be valuable, of course, to have direct structural data on **2**–**7** for comparison with the results of the AM1 calculations.

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