## Supporting Information

for

# **Coarctate and Möbius – the Helical Orbitals of Allene and Other Cumulenes**

Marc H. Garner<sup>1, 2, 3\*</sup>, Roald Hoffmann<sup>3</sup>, Sten Rettrup<sup>1</sup>, Gemma C. Solomon<sup>1, 2</sup>

<sup>1</sup>Dept. of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100, Copenhagen Ø, Denmark.

<sup>2</sup> Nano-Science Center, University of Copenhagen, Universitetsparken 5, DK-2100, Copenhagen

Ø, Denmark.

<sup>3</sup> Dept. of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 4850, USA.

1. Orbital coefficients of [4]cumulene and Möbius cyclooctatetratene	S2
2. Distributing the twist in Möbius systems	
3. Unitary transformations of matrices	S10
4. Algorithm for Reporting Twist in Möbius Molecules	S11
5. 1,1-disubstituted [4]cumulene	S12

#### **1. Orbital coefficients of [4]cumulene and Möbius cyclooctatetratene**

As discussed in detail in the manuscript, the basis of [4]cumulene (Scheme S2) is different from that of cyclooctatetraene (Scheme S1) in that the twist of the basis cannot be evenly distributed. Consequently both the eigenvalue spectrum and the eigenvectors (the LCAO-MOs) are different as can be seen in Figure 9 in the manuscript, and in Table S1 and Table S2 shown below.

The distinctive distribution of the helical twist shown in Figure 6 in the manuscript, and the orbital "sizes" along the helix is inevitably also linked to the basis of [4]cumulene. Although we first described it in a rectilinear basis, the  $C_2$ -adapted wavefunctions are, of course, the same. The difference between Table 1 (see manuscript) and Table S2 is the basis set, which is linked by a basis set rotation at the three central carbon atoms, cf. Scheme 2 and Scheme 5 in the manuscript.

Scheme S1. The Hückel Matrix and Basis Set for Möbius Cyclooctatetraene

Basis	: <b>p</b> 1	$\mathbf{p}_2$	$\mathbf{p}_3$	$\mathbf{p}_4$	$\mathbf{p}_5$	$\mathbf{p}_6$	<b>p</b> 7	p <sub>8</sub>
	α	k·β	0	0	0	0	0	$-k\cdot\beta$
	k·β	α	k·β	0	0	0	0	0
	0	k·β	α	k·β	0	0	0	0
<u>и</u> _	0	0	k·β	α	k·β	0	0	0
··-	0	0	0	k·β	α	k·β	0	0
	0	0	0	0	k·β	α	k·β	0
	0	0	0	0	0	k·β	α	k·β
	- <i>k</i> ·β	0	0	0	0	0	k·β	α

Scheme S2. The Hückel Matrix and Basis Set for Pentatetraene.



**Table S1.** Bonding Hückel MOs for Möbius cyclooctatetraene from the model in Scheme 4, and
 visualized in Figure 9, in the manuscript.

		LCAO								
	Atom	1	2	3	4	5				
		n	<sup>p</sup> 2	р <sub>3</sub>	р <sub>4</sub>	n				
ε·β <sup>−1</sup>	MO	P <sub>1</sub>	р <sub>8</sub>	р <sub>7</sub>	<i>р</i> 6	$P_5$				
0.74	0		- 0.19	- 0.50	- 0.19					
0.71	20	+ 0.35	- 0.46	+ 0.00	+ 0.46	+ 0.35				
0.74	0	+ 0.35	+ 0.46	+ 0.00	- 0.46					
0.71	Za		+ 0.19	+ 0.50	+ 0.19	- 0.35				
4 74			+ 0.19	+ 0.00	- 0.19	0.05				
1./1	10	+ 0.35	- 0.46	- 0.50	- 0.46	- 0.35				
			+ 0.46	+ 0.50	+ 0.46					
1.71	1a	+ 0.35	- 0.19	+ 0.00	+ 0.19	+ 0.35				

**Table S2.** Bonding Hückel MOs for [4]cumulene from the model shown in Scheme 5, and

 visualized in Figure 10, in the manuscript.

		LCAO								
	Atom	1	2	3	4	5				
		n	<sup>p</sup> 2	P3	$P_4$	n				
ε·β <sup>-1</sup>	MO	P <sub>1</sub>	р <sub>8</sub>	р <sub>7</sub>	<i>p</i> <sub>6</sub>	$P_5$				
0.00		. 0.40	- 0.11	- 0.37	- 0.11	. 0.40				
0.62	20	+ 0.43	- 0.49	+ 0.00	+ 0.49	+ 0.43				
0.00	0		+ 0.49	+ 0.00	- 0.49					
0.62	Za	+ 0.43	+ 0.11	+ 0.37	+ 0.11	- 0.43				
4.00	20 41-		+ 0.11	+ 0.00	- 0.11	0.00				
1.62	10	+ 0.26	- 0.49	- 0.60	- 0.49	- 0.26				
1.00			+ 0.49	+ 0.60	+ 0.49					
1.62	1a	+ 0.26	- 0.11	+ 0.00	+ 0.11	+ 0.26				

#### 2. Distributing the Twist in Möbius Systems

Though our concern in this paper is in the coarctate helical orbitals of even [n]cumulenes, we were drawn to consider in detail the potential twist as one proceeds along a hypothetical Möbius system, measured by the attenuation factor k, be it for a Möbius annulene or an even [n]cumulene. As we have seen, the eigenvalues of the Möbius annulene and coarctate analogue Hückel matrices are identical for 4-orbital systems (Möbius cyclobutadiene and allene). But they are slightly different for the 8-orbital systems, as well as for higher n.

Moving from the specific systems considered to a more general Möbius system, the corresponding Hückel matrices have the general form (1)

Here the *k*'s are overlap attenuation factors,  $k^i = \cos(\theta_i)$ , alternatively expressed by the cosines of the angles between adjacent *p* orbitals. The construct—a very important one—is either that the <u>sum</u> of all the angles is 0° (a Hückel system) or 180° (a Möbius one). Notice that this formulation allows a variable angle along the cyclic chain, and not necessarily an equalized progressive twist. For instance, in Möbius cyclooctatetraene, the angles can be (5 of an infinity of choices) as shown in Table S3. More results are shown at the end of the section (Table S4). The corresponding energies of the bonding levels are also shown in tabular form.

	S	equent	ial ove	Positive eigenvalues <sup>a</sup>					
Α	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	0.71 (2), 1.71 (2)
В	0	45	0	45	0	45	0	45	0.71 (2), 1.58 (2)
С	0	0	0	0	45	45	45	45	0.56, 0.71, 1.41, 1.79
D	0	0	45	45	0	0	45	45	0.62 (2), 1.62 (2)
Ε	0	0	0	90	0	0	0	90	0.62 (2), 1.62 (2)

**Table S3.** Positive eigenvalues for different twist distributions in a Möbius 8-ring.

<sup>a</sup>In units of  $\beta$ . The number in parenthesis indicates the number of degenerate levels.

It will be noticed first that some distributions of twist keep degeneracies (**A**, **B**, **D** and **E**), others do not. The degeneracies stem from  $S_n$  axes,  $n \ge 4$ , in the matrix. The Hamiltonian matrix, as simplified for our systems, may have symmetries that are greater than those of the underlying topology. Second, we can compute the total energy for 8 electrons (e.g. 9.66 $\beta$  for **A**) or per electron (1.21 $\beta$  for **A**). There is a danger in focusing our attention on the total  $\pi$ -electron energy – this led people astray in early days of aromaticity. But it is interesting to note that the lowest energy is obtained for an equalized distribution of the attenuation along the chain. We postulate this is a general result, but have not yet found a proof.

In a coarctate Möbius system, the distribution of twist has inherent constraints and so cannot be evenly distributed for cumulenes larger than allene. In annulenes one has (in principle) more flexibility for measures of attenuation along the ring. Some distributions of twist give rise to identical eigenvalues of the Hückel matrix, such as **D** and **E** in Table 3; the latter is a case of broken conjugation, as two angles are 90°. The identical eigenvalues are the result of a unitary transformation relating the two matrices; a more detailed example is given in the next section. Actually we have encountered this situation twice for [4]cumulene. First we started out from the perpendicular basis (Scheme 2 in the manuscript), and then from the coarctate Möbius basis (Scheme 5 in the manuscript). It might seem that the apparent difference in distribution of twist along the coarctate basis would give different energy levels. But this cannot be. The result is, of course, the same, cf. Figure 4 and 9 in the manuscript, Table 1 and S2. The difference between the two starting points is a basis set rotation.

There is an interesting effect of attenuation in a 4n+2 cyclic <u>Möbius</u> system, easiest seen in Figure S1 for two distributions of  $180^{\circ}$  twist in the 6-membered ring.



**Figure S1.** Hückel models of two hypothetical Möbius conformations of 6-ring (benzene) where the 180° twist is continuous (left) and where the twist is localized (right).

We see that a "localized" twist model (right) breaks the degeneracy of the highest occupied level, and in this way achieves a lower energy than an equalized/continuous twist model. The 4n+2 Möbius system is in a high energy (antiaromatic, even as we hesitate to use the word) situation. And almost any symmetry breaking deformation, a Jahn-Teller distortion, will stabilize the molecule. More examples are listed in Table S5. Unequal distribution of bond lengths, another type of structural deformation, has the same effect (and is treated in the exact same way) as deformation through twist at the Hückel level of theory.

The effect we saw may not be a general one for stabilizing open-shell (Hückel 4n, Möbius 4n+2) systems. So when we look at the planar (Hückel antiaromatic) cyclooctatetraene, we do not find a distribution of twists (summing to  $0^{\circ}$ ) that is asymmetrical that is also stabilizing overall.

A final comment: the presence of degeneracies in the various cases is not obvious. Yet it must be traced to higher symmetries in the Hamiltonian, even if the point group of the actual molecule is lower ( $C_2$ ).

**Table S4.** Positive eigenvalues for different twist distributions in a Möbius 8-ring. Continued fromTable S3.

		Seque	Positive eigenvalues <sup>a</sup>						
Α	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	0.71 (2), 1.71 (2)
F	45	45	0	45	45	0	0	0	0.52, 0.75, 1.49, 1.72
G	0	30	30	30	0	30	30	30	0.69 (2), 1.67 (2)
Η	30	15	30	15	30	15	30	15	0.71 (2), 1.69 (2)
I	30	22.5	22.5	22.5	15	22.5	22.5	22.5	0.68, 0.73, 1.68, 1.73

<sup>a</sup>In units of  $\beta$ . The number in parenthesis indicates the number of degenerate levels.

	Sequ	uential ov	verlap ar	Positive eigenvalues <sup>a</sup>			
Α	30	30	30	30	30	30	0.00 (2), 1.50 (2)
В	60	0	60	0	60	0	0.5, 1.32 (2)
С	30	0	60	30	60	30	0.35, 1.21, 1.55
D	0	0	90	0	90	0	0.62, 1.00, 1.62
Ε	0	45	45	0	45	45	0.00 (2), 1.41 (2)
F	0	0	90	0	0	90	0.00 (2), 1.41 (2)

**Table S5.** Positive eigenvalues for different twist distributions in a Möbius 6-ring.

<sup>a</sup>In units of  $\beta$ . The number in parenthesis indicates the number of degenerate levels.

#### 3. Unitary transformations of matrices

It may seem strange that systems with different twist distribution can yield the same eigenvalue spectrum. This occurs because the Hamiltonian matrices are linked by a unitary transformation or, to put it in the context of molecules, a basis set rotation. [4]cumulene is one such system, where the rectilinear basis can be rotated into a Möbius basis. The simplest example is allene, and the basis rotation is shown in Figure S2. From mere inspection of the Hamiltonian matrices, it is far from obvious that the eigenvalue spectrum is the same; yet from the visual depiction of the corresponding basis it is clear that the matrices are linked simply by a basis rotation.



**Figure S2.** Change in internal twist of Möbius cyclobutadiene, corresponding to a basis rotation of allene. The Hamiltonian matrices are linked by a unitary transformation and therefore the eigenvalue spectrum is the same in all three cases.

#### 4. Algorithm for Reporting Twist in Möbius Molecules

To estimate the orbital overlap change along a Möbius ring is nontrivial. Geometries at threecoordinate carbons (to take a simple case) arise from a complex set of adjustments and distortions of molecular geometry. Dihedral angles along the chain are one good way to do this. We suggest an alternative algorithmic procedure of along the following lines to estimate the overlap of orbitals at A and B, illustrated in Scheme S3.

#### Scheme S3: *p* orbitals at two three-coordinate centers



- 1. Form at A and B a set of unit vectors pointing along AB, A1, A2 directions and separately for AB, B3, B4.
- 2. Form the planes including the unit vectors, which may or may not contain A + B.
- 3. Form the perpendiculars to those planes that pass through A and B.
- 4. Calculate the angle between these normals.

This approach ignores a  $\sigma$ -contribution (from 2s admixture into 2p orbitals), but should help.

### 5. 1,1-disubstituted [4]cumulene

As discussed in the manuscript, the helicogenic symmetry of  $\alpha, \omega$ -disubstituted even [*n*]cumulenes is a special situation and most coarctate systems do not have helicogenic symmetry. To our knowledge, no other realistic substituent pattern of the even [*n*]cumulenes satisfy the helicogenic symmetry requirement. An example is 1,1-dimethyl-[4]cumulene; its optimized structure and frontier  $\pi$  orbitals are shown in the left column of Figure S3. The molecule has  $C_{2\nu}$  symmetry and the orbitals are non-degenerate. Still, due to the mirror symmetry and the non-helicogenic rotation axis, the orbitals are not helical.



**Figure S3.** Optimized structure and frontier  $\pi$  orbitals of 1,1-dimethyl-[4]cumulene (left) and 1,1-diamino-[4]cumulene (right). Calculations are performed using same details as described in the manuscript (M06-2X/6-311G(*d*,*p*)).

By using single-faced  $\pi$  donor substituents, such as amine groups, it is possible to further reduce the symmetry of the 1,1-disubstituted species to  $C_2$ . While this breaks the mirror

symmetry it does not change the fact that the remaining  $C_2$ -axis is not helicogenic.

Consequently the frontier  $\pi$  orbitals of 1,1-diamino-[4]cumulene, shown in the right column of Figure S3, is not helical. It should be noted that the molecule (this particular conformation of it) is chiral, but the carbon  $\pi$  system does not have clear helicity.