

Double-twist Möbius aromaticity in a $4n + 2$ electron electrocyclic reaction†

Henry S. Rzepa

Received 22nd July 2005, Accepted 9th September 2005

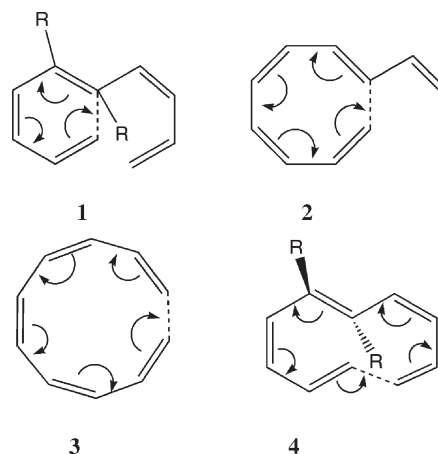
First published as an Advance Article on the web 22nd September 2005

DOI: 10.1039/b510508k

One transition state for the 10 electron ($4n + 2$) electrocyclisation of *Z,E,Z*-decapentaene is predicted to have the properties of a double-twist Möbius strip, with delocalised bond lengths and the NICS(0) magnetic index typical of aromaticity; a 5,6-di-*t*Bu substituted decapentaene is predicted to react in this mode in preference to the competitive six-electron electrocyclisation.

Heilbronner's¹ suggestion of conjugated stability for a population of $4n$ π electrons in molecular orbitals derived from an array of p-atomic orbitals arranged around a Möbius strip has had a widespread influence. Notable was Zimmerman's² incorporation of the Möbius concept into his reformulation in terms of transition state stability of the original Woodward–Hoffmann selection rules for pericyclic reactions. Schleyer³ showed how this stability could be quantitatively associated with transition state aromaticity, illustrating this for the electrocyclisation of (*Z,Z*)-octa-1,3,5,7-tetraene, which involves *e.g.* $4n$ electrons and proceeds *via* a geometry which has a C_2 axis of symmetry and Möbius topology. The corollary follows that a transition state with a local C_s plane of symmetry and $4n + 2$ electrons is Hückel rather than Möbius aromatic. In the considerable and regular discussion of Möbius-conjugated cyclic systems over the last 40 years,⁴ including the notable recent first synthesis of a $4n$ Möbius annulene,⁵ virtually no mention has been made of the possibility of higher order Möbius bands. The parent topology is derived from a 180° (π) twist imparted to a cylinder to form a Möbius band; the electronic analogue being one phase shift (π) in a basis of p-orbitals arranged continuously around a ring. If a further 180° twist is imposed (2π overall) on such a ring, then a higher order double-twisted Möbius strip is formed. This has two sides and two edges, unlike the single-twisted band which has only one of each. Both single and double-twisted bands (in ideal form) have at least one C_2 symmetry axis and are therefore chiral. A double-twisted p-atomic orbital basis in Möbius cyclic form may be deduced^{1,2} to have particular stability if populated with $4n + 2$ electrons as a closed shell. The first example of such a doubly-twisted Möbius-aromatic transition state is here proposed for one mode of the thermal electrocyclisation of decapentaene (Scheme 1).

Decapentaenes can in principle undergo many different pericyclic reactions, including the three thermal electrocyclic



Scheme 1

reactions involving respectively 6, 8 and 10 electrons ($4n + 2$, $4n$ and $4n + 2$) shown in Scheme 1. These conventionally² would be assigned to Hückel (1), Möbius (2) and again Hückel (3) transition state topologies. The calculated geometry (B3LYP/6-31G(d)) of the pericyclic Hückel transition state 1 deriving from (*Z,E,Z*)-decapentaene deviates little from planarity in the six-membered ring (Fig. 1a), since the angular strain at each carbon is minimal. For the Möbius transition state 2 deriving from (*Z,Z,E*)-decapentaene, the greater strain inherent in the eight-membered ring is largely avoided by adoption of a helical geometry (Fig. 1b).

The ten-membered ring in 3 for electrocyclisation of (*Z,Z,Z*)-decapentaene is less able to adopt a planar Hückel-like geometry, since this would induce significant angular strain at each carbon. Most 10π mono-cyclic annulenes are only planar if contained within an eight-membered (or smaller) ring, tending instead to adopt non-planar forms when part of nine- or ten-membered rings because of this strain.⁷ This is certainly true for 3, the geometry of which (although C_s symmetric) is non planar and high in energy (Table 1). In contrast, the ten-electron electrocyclisation (Fig. 1c) of the isomeric (*Z,E,Z*)-decapentaene can adopt a double helical “figure of eight” conformation 4 contained within a ten-membered ring as the mechanism for avoiding planar strain, with resulting C_2 symmetry at the transition state. The analogy with the folding modelled for a double-twisted Möbius cyclacene (Fig. 1d)⁶ implies that the $4n + 2$ electron reaction of (*Z,E,Z*)-decapentaene can be regarded as passing through a double-twist Möbius transition state 4, the free energy of which is only about 6 kcal mol⁻¹ higher than 1, the alternative reaction possible with (*Z,E,Z*)-decapentaene. The isomeric *Z*-configuration at the central double bond does not allow reaction 2 to compete with 1 or 4. The reaction free energy

Department of Chemistry, Imperial College London, South Kensington Campus, Exhibition Road, London, UK SW7 2AY

† Electronic supplementary information (ESI) available: Calculated (B3LYP/6-31G(d)) Geometries and transition normal modes for the electrocyclic ring openings 1–4 and calculated five highest energy molecular orbitals for 3 at the B3LYP/6-31G(d) level, contoured at 0.01 au. See DOI: 10.1039/b510508k

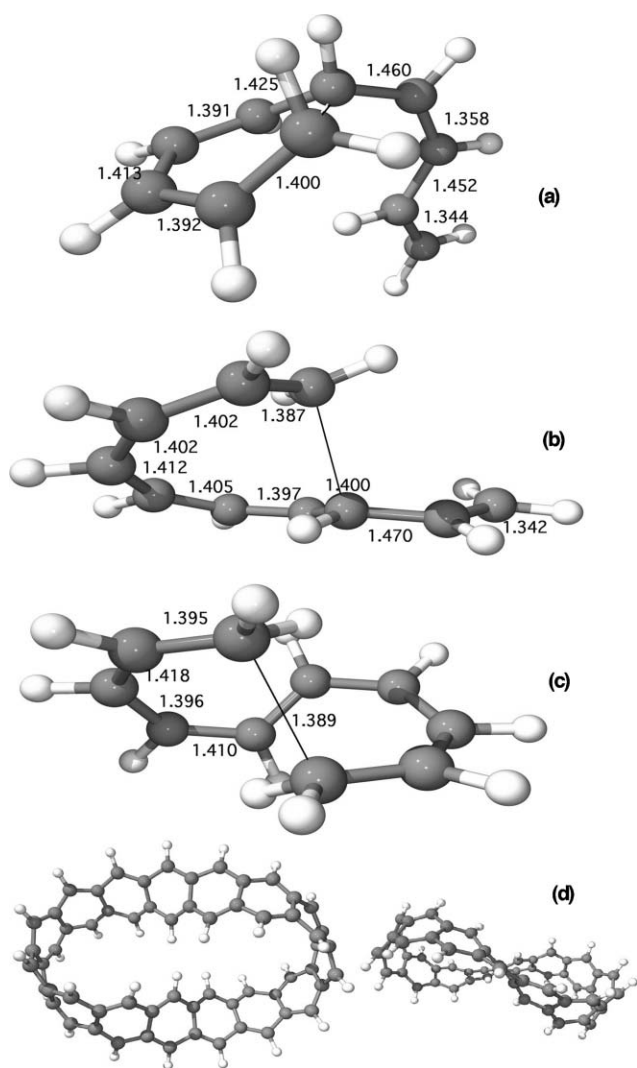


Fig. 1 Calculated bond lengths (B3LYP/6-31G(d), in Å) for (a) electrocycloisomerization of **1**, (b) **2**, (c) **4** and (d) a double-twist cyclacene, taken from ref. 7 and shown in two views. The perspective is better viewed as 3D rotatable models, for which see the electronic supporting information at <http://www.rsc.org/>.

from (*Z,E,Z*)-decapentaene to (*Z,Z,Z,Z*)-cyclodecatetraene is slightly endothermic (Table 1, R = H), implying this specific reaction would instead proceed as a ring-opening rather than

closing. Pericyclic reaction *via* such a double-twist Möbius-aromatic conformation could formally be regarded as an extension to the selection rules originally formulated by Zimmerman.²

To ascertain if a double-twist Möbius topology does indeed result in ten-electron aromaticity, two indices of this property were computed (Table 1). The bond lengths around the periphery of **4**, expressed as the maximum difference between the longest and shortest bond (Δr , excluding the forming bond itself), reveal the small degree of bond alternation typical of aromatic ring transition states (Δr 0.02–0.04 Å).³ The NICS(0) magnetic index, which Schleyer has formulated and calibrated⁸ has a typically highly aromatic value (−14.9 ppm, *cf* −10 ppm for the archetypal benzene itself). These observations are duplicated for **1** and **2**, confirming transition state aromaticity along the entire series, but with each arising from a different mode!

The B3LYP density functional hybrid, although much used and tested, has been criticised for over-emphasizing the degree of bond equality in 10 π and higher planar annulenes.⁶ To verify that the results above are not simply an artifact of this procedure, two further correlated methods were evaluated, the KMLYP rehybridisation⁹ (which is thought to result in more realistic bond alternation for larger planar Hückel systems)¹⁰ and the coupled cluster (CCSD) method which is thought to be the most reliable in this regard.⁶ Essentially similar values are obtained (Table 1).

These results suggest a double-twist Möbius conformation may be energetically accessible for systems where ring and angular strain is best eliminated by adoption of a helical rather than a near-planar ring conformation. Indeed, if the alternative pathway *via* **1** is sterically inhibited (R = *t*Bu), **4** is now predicted to offer a similar or lower free energy route than *via* **1** (Table 1); such substitution now also makes the electrocycloisomerization exothermic. Another feature of **4** is the chirality associated with the double-helical figure-of-eight conformation. If the two groups R are themselves chiral, then the transition state would have two diastereomeric configurations. Using the simple group R = CHFI as a chiral prototype, the two resulting transition states are indeed found to have slightly different properties, but most significantly a difference in their free energies of 8–10 kcal mol^{−1} (Table 1). This surprisingly large value suggests that transfer of chirality in double-twist Möbius pericyclic transition states might be particularly specific. Characterisation of stable molecules exhibiting a double-twist Möbius feature or of systems bearing even higher order Möbius twists is also a tantalising possibility.¹¹

Table 1 Calculated properties for **1–4**

System	Total energy, E_h [relative ΔG_{298} /kcal mol ^{−1}], NICS(0) (ppm) and $\Delta r/\text{Å}$	
	B3LYP	KMLYP
1, R = H 6-31G(d)	−388.15213 ^a [11.8], −12.4, 0.034	−387.36968 [12.3], −14.0, 0.020
2, R = H 6-31G(d)	−388.17284 [0.0], −10.5, 0.025	−387.39136[0.0], −10.8, 0.045
3, R = H 6-31G(d)	−388.14151 [19.0], −9.8, 0.043	−387.35329 [24.4], −9.7, 0.047
4, R = H 6-31G(d)	−388.14569 [18.1 ^b], −14.9, 0.029	−387.36432 ^c [18.4], −16.4, 0.043 ^c
4, R = H cc-pVTZ	−388.28902, −15.6, 0.023	−387.49993, −17.0, 0.031
1, R = <i>t</i> Bu 6-31G(d)	−702.62260 [2.2], −11.4, 0.064	−701.31155 [0.0], −12.7, 0.052
4, R = <i>t</i> Bu 6-31G(d)	−702.62853 [0.0 ^d], −11.9, 0.043	−701.31484 [0.2], −13.5, 0.046
4, R = (<i>R,R</i>)-CHF ₂ 6-31G(d)	−686.85064 [0.0 ^e], −13.2, 0.032	−685.61205 [0.0], −14.8, 0.038
4, R = (<i>S,S</i>)-CHF ₂ 6-31G(d)	−686.83526 [8.4 ^e], −13.0, 0.036	−685.59555 [10.2], −15.4, 0.041

^a Value for 1,2 divinyl isomer, −388.1499 E_h ; ^b ΔG_{298}^\ddagger 27.2 kcal mol^{−1}; ΔG_{298} (reaction) +4.4 kcal mol^{−1}. ^c Values for CCSD/6-31G(d) calculation, −386.8525 E_h and 0.037 Å ^d ΔG_{298}^\ddagger , 28.1 kcal mol^{−1}; ΔG_{298} (reaction) −10.0 kcal mol^{−1}. ^e Stuttgart–Dresden SDD effective core potential for iodine.

Notes and references

- 1 E. Heilbronner, *Tetrahedron Lett.*, 1964, 1923–1928.
- 2 H. E. Zimmerman, *J. Am. Chem. Soc.*, 1966, **88**, 1564–1565; H. E. Zimmerman, *Acc. Chem. Res.*, 1971, **4**, 272–280.
- 3 H. Jiao and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1763–1765; H. Jiao and P. von R. Schleyer, *J. Chem. Soc., Perkin Trans. 2*, 1994, 407–410.
- 4 H. S. Rzepa, *Chem. Rev.*, 2005, DOI: 10.1021/cr030092l.
- 5 D. Ajami, O. Oeckler, A. Simon and R. Herges, *Nature*, 2003, **426**, 819–821.
- 6 H. M. Sulzbach, H. F. Schaefer, K. Klopffer and H. P. Lüthi, *J. Am. Chem. Soc.*, 1996, **118**, 3519–3520; R. A. King, T. D. Crawford, J. F. Stanton and H. F. Schaefer, *J. Am. Chem. Soc.*, 1999, **121**, 10788–10793; H. S. Rzepa and N. Sanderson, *Phys. Chem. Chem. Phys.*, 2004, **6**, 310–313.
- 7 M. Martin-Santamaria and H. S. Rzepa, *J. Chem. Soc., Perkin Trans. 2*, 2000, 2378–2381.
- 8 P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317–6318; P. v. R. Schleyer, M. Manoharan, Z. Wang, X. B. Kiran, H. Jiao, R. Puchta and N. J. van Eikema Hommes, *Org. Lett.*, 2001, **3**, 2465–2468; C. Corminboeuf, T. Heine, T. Gotthard, P. von R. Schleyer and J. Weber, *Phys. Chem. Chem. Phys.*, 2004, **6**, 273–276.
- 9 J. K. Kang and C. B. Musgrave, *J. Chem. Phys.*, 2001, **115**, 11040–11051; H. J. P. Senosiain, C. B. Musgrave and D. M. Golden, *Faraday Discuss.*, 2001, **119**, 173–189.
- 10 C. S. Wannere and P. v. R. Schleyer, *Org. Lett.*, 2003, **5**, 865–868; C. S. Wannere, K. W. Sattelmeyer, H. F. Schaefer and P. von R. Schleyer, *Angew. Chem., Int. Ed.*, 2004, **43**, 4200–4206.
- 11 H. S. Rzepa, *Org. Lett.*, 2005, **7**, DOI: 10.1021/ol0518333.