ORGANIC LETTERS

2005
Vol. 7, No. 21
4637−4639

A Double-Twist Möbius-Aromatic Conformation of [14]Annulene

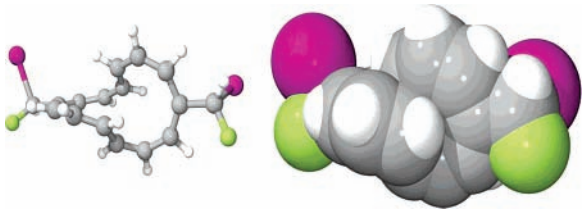
Henry S. Rzepa

Department of Chemistry, Imperial College London, South Kensington Campus, Exhibition Road, London SW7 2AY, U.K.

rzepa@imperial.ac.uk

Received August 1, 2005

ABSTRACT



B3LYP and KMLYP/6-31G(d) calculations predict a double-helical and chiral conformation of [14]annulene with the topological properties of a double-twist Möbius band as highly aromatic; its energy with respect to the known Hückel-aromatic conformation is predicted to be stabilized by suitable ring substitution.

The topological object known as a Möbius strip or band can be formed by cutting, imparting a half-twist (π), and rejoining a cylinder. Heilbronner[1] was the first to demonstrate theoretically using Hückel MO theory that when this is done to a cylindrical array of p atomic orbitals, maximum electronic stability is achieved when the resulting molecular orbitals are populated with $4n$ (n is an integer) electrons in a closed shell configuration. In the two decades following this proposal, the most successful application of this concept was its use by Zimmerman for rationalizing pericyclic reactivity and stereoselectivity.[2] A wide variety of allowed pericyclic transition states have been attributed to half-twist Möbius stability.[2] It has also been demonstrated that Möbius conjugation at a transition state also results in significant aromaticity.[3] It is only recently, however, that the successful synthesis of a stable crystalline half-twist $4n$ π-electron Möbius [16]annulene has enabled its structure and properties to be measured.[4] Previously, several single half-twist Möbius conformations of [12]-, [16]-, and [20]annulenes had been located computationally, although non-Möbius forms were lower in energy in all cases.[5]

Very much less attention has been given to the related family of topological objects formed by imparting further half-twists to a cylinder, and in particular to Möbius (the topological term is paradromic) bands formed from two (2π) or three (3π) such operations.[6] All of the resulting objects are in fact chiral, a property which is potentially exploitable in many areas of modern chemistry. It has recently been suggested[7] that the pericyclic electrocyclic reaction of (*Z*,*E*,*Z*) decapentaene **1**, formalized as a double-twist Möbius system with an $4n + 2$ electron count, may be competitive in energy and aromaticity with the more conventional achiral $4n + 2$ electron Hückel transition state bearing no topological twist. It was speculated that examples of not only further double and triple-twist transition states, but also stable molecule

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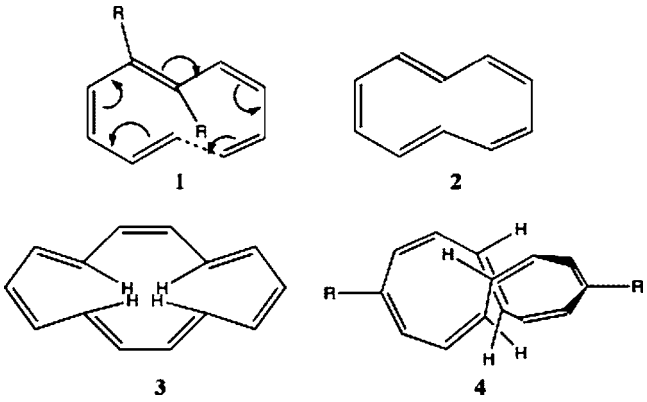
10.1021/ol0518333 CCC: $30.25
Published on Web 09/22/2005

examples of such higher order Möbius aromaticity might be discoverable.[7] Here, an exploration of this last suggestion is made, applied to a double-twist conformation of the $4n + 2$ π-electron [14] annulene.



Previously,[7] the transition state **1** was reported as having C_2 symmetry, with a geometry predicted to show little bond length alternation (Δr 0.029Å)[3] and a magnetic NICS(0) index (−14.9 ppm)[8] typical of ring aromaticity. By analogy, the annulene **2** is an obvious starting point to apply this concept to a stable molecule rather than to a transition state. Compound **2** has previously been shown[9] to prefer a C_2-symmetric "twist" conformation as the overall conformational minimum. In this conformation, the bond alternation is high[4] (Δr 0.139Å), and the NICS(0) value (−0.3 ppm)[8] shows no evidence of aromaticity. Inspection of the geometry shows why; the C−C dihedral angles around this ring (109, 9, 46, 3, 46, 150, −46, 3, −46, −9°) show one almost orthogonal value which strongly inhibits the cyclic "p_π" conjugation. The 10-membered ring is simply too small to accommodate any even distribution of a double-twist, and the resulting molecule is nonaromatic and alkene-like in character. This is in contrast to the transition state **1**, where the longer C−C forming bond and its local geometry better accommodates the angular strain, allowing better cyclic conjugation.

The obvious solution to this problem is to increase the ring size to a [14]annulene **3**. A double-helical D_2-symmetric conformation **4** (Figure 1) emerges as accommodating ring strain with little penalty compared to the known conformation **3**. When all of the ring substituents are hydrogens, **4** is predicted as 15 kcal/mol higher in free energy than **3** (Table 1). In part at least, **3** may be stabilized with respect to **4** by "H−H" interactions for the hydrogens shown, which Bader and co-workers have suggested[10] may be worth up to 10 kcal mol^{-1}.

The calculated ^{1}H NMR shifts for the hydrogens in **4** are the typically aromatic ∼7.1 ppm for the outer atoms but a more unusual 2.8 ppm for the four hydrogens shown for **4**. The bond length alternation (Δr 0.010 Å) and the NICS(0) value at the overall ring centroid (−18.3 ppm) is also indicative of a conjugated aromatic system. When compared with **3** (Δr 0.014 Å, NICS(0) −15 ppm) it is apparent that the aromaticity is not merely retained but enhanced, despite the lower p-orbital overlap resulting from the double-twist present. This twist is, however, reasonably evenly distributed around the ring (CCCC dihedral angles 176, −24, −17, −7, −7, −17, −24, 176, −24, −17, −7, −7, −17, −24°) with no orthogonality present to inhibit conjugation. That a double-twist conjugated Möbius ring can be even more aromatic than a Hückel system and not unfeasibly less stable has not previously been anticipated.

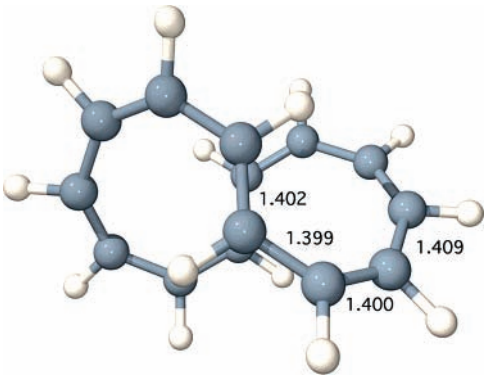


Figure 1. Calculated (B3LYP/6-31G(d)) structure showing the helical structure for **4**. 3D rotatable structures and computed properties are available in the Supporting Information.

Schleyer, Schaefer, et al.[11] have suggested that the B3LYP method underestimates bond length variation in both [14]- and [18]annulene, and so it is important to evaluate whether the above result may be simply an artifact. The KMLYP density functional rehybridization[12] has been shown to more reliably predict the relative bond length in nontwisted Hückel annulenes, while being computationally very much faster than the most reliable method (CCSD(T)).[13] Applied to **4**, KMLYP reveals almost no bond alternation (Δr 0.012 Å, NICS(0) −21.8 ppm), retaining D_2 symmetry (any bond alternation would reduce the symmetry to C_2). In marked contrast, as reported previously,[11] the bond alternation in **3** increases at the KMLYP level, the symmetry is reduced to C_s from C_{2h} (Δr 0.096 Å), and the NICS(0) value increases to −7.0 ppm. The free energy difference between **3** and **4** is reduced to 12.8 kcal mol^{-1}.

Although **4** is *only* 13−15 kcal mol^{-1} higher than **3**, the equivalent equilibrium concentration of this conformation

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Table 1. Calculated[a] Properties for **2**−**4**

system, method	energy, hartree	Corrected for ΔG_{298} {relative, kcal mol^{-1}}	NICS(0), ppm	Δr,[b] Å
2, R = H B3LYP/6-31G(d)	−386.96236	–	−0.3	0.139
3, R = H B3LYP/6-31G(d)	−541.81229[e]	−541.61347 {0.0}	−14.9	0.014
3, R = H KMLYP/6-31G(d)	−540.70861[f]	−540.49899 {0.0}	−7.0	0.096
3, R = F[c]B3LYP/6-31G(d)	−1930.95347	−1930.88694 {3.0}	−4.6	0.117
4, R = H B3LYP/6-31G(d)	−541.78948[e]	−541.58966 {15.0}	−18.3	0.010
4, R = H KMLYP/6-31G(d)	−540.68963[f]	−540.47858 {12.8}	−21.8	0.012
4, R = F[c]B3LYP/6-31G(d)	−1930.96208	−1930.89178 {0.0}	−15.9	0.012
4, R = (*R*,*R*)-CHFI B3LYP/6-31G(d)[d]	−840.48090	−840.27618 {1.3}	−17.3	0.021
4, R = (*S*,*S*)-CHFI B3LYP/6-31G(d)[d]	−840.48266	−840.27820 {0.0}	−17.3	0.023

[a] Calculations performed using Gaussian 03, Revision C.01, Gaussian, Inc., Wallingford CT, 2004 (see the Supporting Information for the full citation). [b] Difference, in Å, between the shortest and longest ring C−C bond lengths. [c] Ring perfluorinated. [d] Stuttgart−Dresden SDD effective core potential for iodine. [e] B3LYP/cc-pVQZ energies, respectively, −542.0445, −542.0212, ΔE 14.5 kcal mol^{-1}. [f] CCSD/6-31G(d) single point energies, −540.0382, −540.0163, ΔE 13.7 kcal mol^{-1}.

would be far too small to be experimentally detectable. However, the possible stabilization of **3** by "H−H" interactions, something not possible in **4**, and the differing steric environments, suggests one strategy for inverting the stability of these two isomers. Replacing these hydrogens with, e.g., F would replace any H−H stabilization in **3** with F−F lone-pair repulsion. Calculations suggest that indeed **4** (fully perfluorinated) is now predicted to be the more stable conformation by ΔG 3.0 kcal mol^{-1}, while **3** is destabilized and also dearomatized by such substitution.

Another feature unique to **4** is its prominent chirality, which suggests another interesting experiment. If the groups R are replaced with a chiral auxiliary (e.g., R= CHFI), then two diastereoisomers are possible with respect to the helical ring chirality.[14] The diastereomeric energy difference is predicted to be 1.3 kcal mol^{-1} if substituted at R, which would result in a detectable unequal equilibrium mixture of two diasteroisomers. The achiral conformation **3**, having only C_s symmetry, cannot sustain such isomerism.

The synthesis of a 4*n* Möbius [16]annulene was a challenging undertaking, and indeed only one such successful synthesis has been reported to date.[4] The present calculations suggest that double-twist and perhaps even triple-twist Möbius systems may be an equally viable target for synthetic attention.

Supporting Information Available: 3D coordinates for **1**−**4** presented using the Jmol applet. This material (Copyright 2005 Henry Rzepa) is available free of charge as OpenData via the Internet at http://pubs.acs.org.

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