Geometric localisation in Möbius π systems

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Abstract

Evaluation of the eigenvalues of the bond–bond polarisability matrix for Möbius monocycles indicates that the apparent natural C_2 symmetry of Möbius π systems is not a consequence of π distortivity but rather is due to the release of strain in the σ-skeleton.
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1. Introduction

The Möbius band (a.k.a. Möbius strip) is a well-known object in both recreational and formal mathematics [1,2]. It is single-edged, single-sided and non-orientable. In the classical construction, a Möbius band is formed by joining the ends of a rectangular piece of paper, after a half twist has been introduced (Fig. 1). When viewed through the line of the join in the paper, the physical model shows instantaneous C_2 symmetry, but as manipulation of the paper model easily reveals, the C_2 axis can be rotated through a full circle, so that any two antipodal points on the central circular line can in turn become the poles of a binary rotation (R). The full symmetry group of the band is therefore a direct product of C_2 and cyclic translation (S) groups, and is isomorphic to D_∞ (D_{2m} if a cyclic structure of m translationally equivalent units is embedded in the band [3]).

Realisation of the Möbius topology in molecular form has long been a target of synthetic chemistry (Fig. 2) [4], but in all reported examples, experimental or computer-generated [5–12], the object turns out to have *fixed* C_2 geometry. Why do molecular Möbius strips lock into C_2 symmetry? Why does the free motion of the D_∞ mathematical ideal not survive as an ultra-low-energy mode of the C_2

structure? The present Letter suggests that this configuration locking is not caused by π distortivity [13–19]. It is found that the natural symmetry of a Möbius π system is C_2, for the same reason, i.e., release of strain in the σ-skeleton, that the symmetry of 1,3,5,7-cyclooctatetraene (COT) is D_{2d} [20] rather than D_{4h}.

2. Results and discussion

For planar and spherical systems, Hückel π energies and orbitals are obtained from the Hamiltonian matrix $\mathbf{H} = \alpha\mathbf{1} + \beta\mathbf{A}$, i.e., as eigenvalues and eigenvectors of the adjacency matrix $\mathbf{A}$ of the carbon skeleton. An identical spectrum of eigenvalues (in appropriate reduced units) is found for an untwisted network of atoms interacting through σ bonds. In Möbius σ systems, diagonalisation of $\mathbf{A}$ again yields Hückel energies, but for a Möbius π system, the matrix to be diagonalised is not $\mathbf{A}$ but $\mathbf{A}'$. In the weighted adjacency matrix $\mathbf{A}'$, all edges crossing the 'seam' of the Möbius band carry a factor of -1 to take account of the effect of the twist on the overlap of neighbouring p_π orbitals (Fig. 3) [21,22]. Eigenvalue spectra of Möbius σ and π systems are thus in general different. In fact, as the Möbius band is doubly covered by the cylinder (in the sense that identification of antipodal points on a cylinder produces a set of points with the topology of the band [2]), the eigenvalue spectra of σ and π systems for a fixed Möbius carbon skeleton form complementary halves of the spectrum of a centrosymmetric graph with twice as

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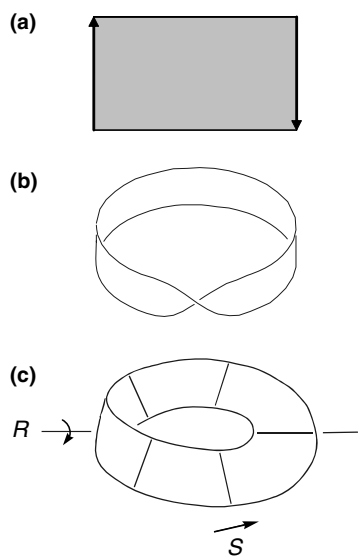
(a)

(b)

(c)

$R \rightarrow$

S

Fig. 1. Construction of a Möbius band (a) by joining two opposite edges of a rectangle, with a half twist, leading to (b) an object with an instantaneous C_2 symmetry, but in fact (c) a total symmetry group isomorphic to D_∞, generated by the binary rotation R and a translation S of the band (here illustrated for a division of each face of the original rectangle into five square cells).
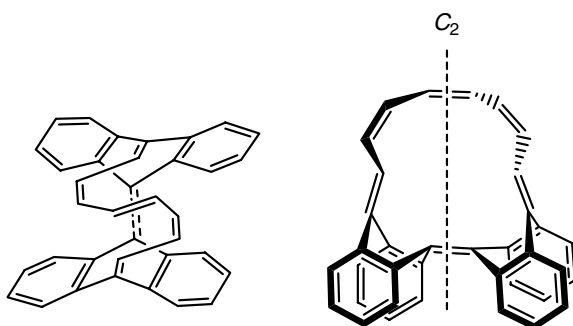
C_2

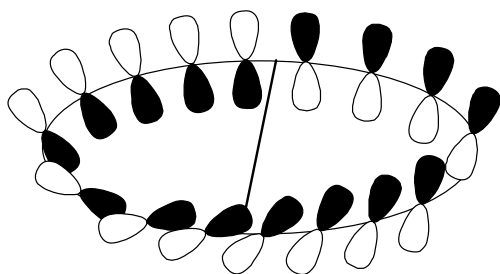Fig. 2. A Möbius [16]-annulene with C_2 symmetry [4,12].

Fig. 3. Unavoidable phase interruption in a Möbius annulene. For a cycle of carbon atoms embedded on the central circle of a Mobius band, overlap of neighbouring p_π orbitals has a uniform sign at all positions but at one pole of the instantaneous C_2 axis of the band.

many vertices, a graph that can be embedded on the cylinder [23]. *Gerade* eigenvectors of the cylindrical graph give σ, *ungerade* π, solutions for the smaller Möbius graph. Rules for stability of $4n + 2$ and $4n$ cycles reverse between

Hückel and Möbius systems, and the mnemonic constructions such as the Frost–Musulin [24] diagram for the eigenvalue spectra need modification, but the double-cover property allows both Hückel and Möbius cycles to be included in a single diagram for the cycle with double the number of vertices [23].

A link between geometric and electronic structure is made through the theory of π distortivity [13–16]. In one persuasive view, π electron delocalisation in a conjugated system is a *consequence* rather than a *cause* of high molecular symmetry. The claim for a Hückel $[4n + 2]$-annulene is that, whereas the σ bonds of a cyclic array have a strong energetic motive for the preservation of an equilateral geometric structure, the π electrons are inherently distortive, since π stabilisation energy is always increased by introduction of bond alternation to localise and strengthen some π bonds at the expense of others. A quantitative tool for the description of such distortions is the bond-polarisability matrix **π** [13], the entries of which are the derivatives $(\partial p_{rs}/\partial \beta_{tu})$ of the mobile π bond order p of one bond with respect to changes in the Hückel resonance parameter β of another, and hence, apart from scaling, the $(\partial p_{rs}/\partial \beta_{tu})$ are second derivatives of π energy with respect to σ bond lengths.

Diagonalisation of **π** predicts the independent directions of distortion of the σ framework that would favour π-electron delocalisation. In particular, when the magnitude of the maximum eigenvalue $|\lambda_{max}^\pi|$ exceeds $\sim 1.8\beta^{-1}$ for a conventional Hückel system, it is expected that actual geometric distortion will occur [13]. Thresholds for distortion of annulenes, polyenes, and other Hückel π systems accord qualitatively with data from more sophisticated calculations and from experiment, e.g., benzene, with $|\lambda_{max}^\pi| = 1\beta^{-1}$ is, of course, undistorted, whereas bicyclic pentalene, with $|\lambda_{max}^\pi| = 2.357\beta^{-1}$ is predicted by *ab initio* calculations to undergo $D_{2h} \rightarrow C_{2h}$ distortion [25].

Heilbronner gave a heuristic account [14] of this unrealised tendency to π distortivity in benzene, from which a simple rule-of-thumb for prediction of the inherently most distortive mode of a Hückel π system has been devised. The *Heilbronner vectors* [16] of a conventional π system are sets of changes $\delta\beta_{tu}$ (which imply changes in bond lengths) such that the sum $\Sigma_t \delta\beta_{tu}$ vanishes when taken over all bonds tu radiating from a common vertex t, i.e., $\Sigma_t A_{tu}\delta\beta_{tu} = 0$. The space spanned by these vectors is easily identified, by analogy with the graphical construction of non-bonding orbitals, and it is typically found to contain a match to the most distortive eigenvector(s) of **π**. This association is easily rationalized in terms of the alternating character of entries in **π** along a series of elements $\pi_{rs,tu}$ associated with the bonds tu in a conjugated pathway starting from a given bond rs. Thus, for Hückel annulenes of even size, the **π** eigenvector of maximum $|\lambda^\pi|$ is entirely determined by symmetry. It is exactly the sole Heilbronner vector and is the bond alternation (Kekulé) mode associated with in-plane first-order Jahn–Teller distortion in the

case of [4n]-annulenes. For [4n + 2]-annulenes the series $|\lambda^\pi_{max}|\beta^{-1} = 1.0000, 1.3416, 1.5602, 1.7219, 1.8506, 1.9575,$ $2.0489, 2.1288, \ldots$ for $n = 1$–8 predicts loss of $D_{(4n+2)h}$ symmetry by the second-order mechanism at $\sim$22 carbon centres, coinciding with *ab initio* SCF estimates for the distortion threshold and falling somewhat below the DFT estimate of 30 [17–19]. For pentalene, the vertex-sum requirement imposes loss of mirror symmetry in the Heilbronner vector, which indeed leads from ideal D_{2h} down to the C_{2h} point group and has entries $\delta\beta_{tu}$ that closely match the maximal eigenvector of π (Fig. 4).

Amongst Möbius π systems, the 'aromatic' cycles are those with $4n$ π electrons [21], and π can be calculated with the usual second-order perturbation expression, but based on the eigenvectors of A' rather than A. Maximum eigenvalues, $|\lambda^\pi_{max}|$, for Möbius [4n]- and Hückel [4n + 2]-annulenes fall on the same curve (Fig. 5), and predict distortion at a similar threshold, if we assume the same β value for both conventional and Möbius annulenes [21]. It may be argued that β should be reduced by a factor of $\cos(\pi/4n)$ in the Möbius annulene, giving a reduction of 8% for $4n = 8$ and less than 1% for $4n = 20$. The most dis-
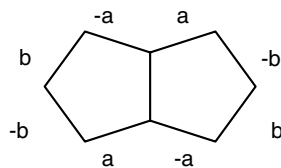

Fig. 4. Match of Heilbronner vectors and direction of maximum π distortivity. In pentalene, the unique normalised Heilbronner vector [16] has $a = b = 0.3536$, indicating equal and opposite increases and decreases of the Hückel β parameter in alternation around the molecular perimeter, with no change to the central bond. In the *exact* eigenvector of π (eigenvalue 2.357 β^{-1}), the pattern of distortion is essentially identical, with $a = 0.3428$ and $b = 0.3639$ [13,25].
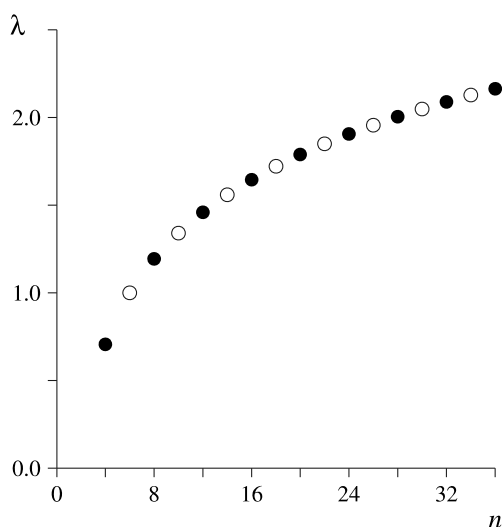

Fig. 5. Variation of maximum eigenvalue $|\lambda^\pi_{max}|\beta^{-1}$ with ring size, n, for the aromatic Hückel [4n + 2]- and Möbius [4n]-annulenes. Hückel systems are denoted by open circles ($\circ$) and Möbius systems by filled circles ($\bullet$).

tortive eigenvector has a characteristic form, obtainable by a simple modification of the Heilbronner construction: sets of changes $\delta\beta_{tu}$ are now found subject to a zero-sum $\Sigma_t A'_{tu}\delta\beta_{tu} = 0$. Thus, effectively, we may construct the Heilbronner vector as though the system were of the normal Hückel type, and then reverse the entry $\delta\beta_{tu}$ for any bond that crosses the seam. This procedure produces a distortion vector with at most C_2 symmetry about the chosen seam position. With the usual correlation of β with bond length, we see that the Heilbronner vector corresponds to alternant shortening and lengthening of bonds around the Möbius cycle: in a bond that does not cross the seam, a change of $A'_{tu}\beta_{tu}$ to $(1 + \delta)\beta_{tu}$ corresponds to bond shortening; in a bond that crosses the seam it is a change of $A'_{tu}\beta_{tu}$ to $(-1 - \delta)\beta_{tu}$ that corresponds to bond shortening. The instantaneous molecular symmetry remains C_2, but the full symmetry group falls from D_{8n} to D_{4n}, as the translational repeat unit is now larger. The π distortion has the same origin as the tendency of conventional large [4n + 2]- and [4n]-annulenes to break symmetry [17–19], though it is likely to occur sooner as a result of the extra σ strain and the reduced π overlap (which follows a cosine function $\cos(\pi/n)$ [21]) in the Möbius band. The fact that the occupied molecular orbitals of small Mobius annulenes can be partitioned into those of a polyene and a twisted ethene fragment [10] is consistent with the dominance of σ factors. The energetic cost of such twisting can be estimated by a modified version of the Sandorfy C model [26] taking explicitly into account 1,3-interactions [27,28].

3. Conclusion

Qualitative chemical calculations based on the Heilbronner approach to π distortivity indicate that the locking of configuration of Möbius-type molecules and structures is not a consequence of any special features of their π electronic structure, but should rather be ascribed to steric effects within their σ systems.

Acknowledgement

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