

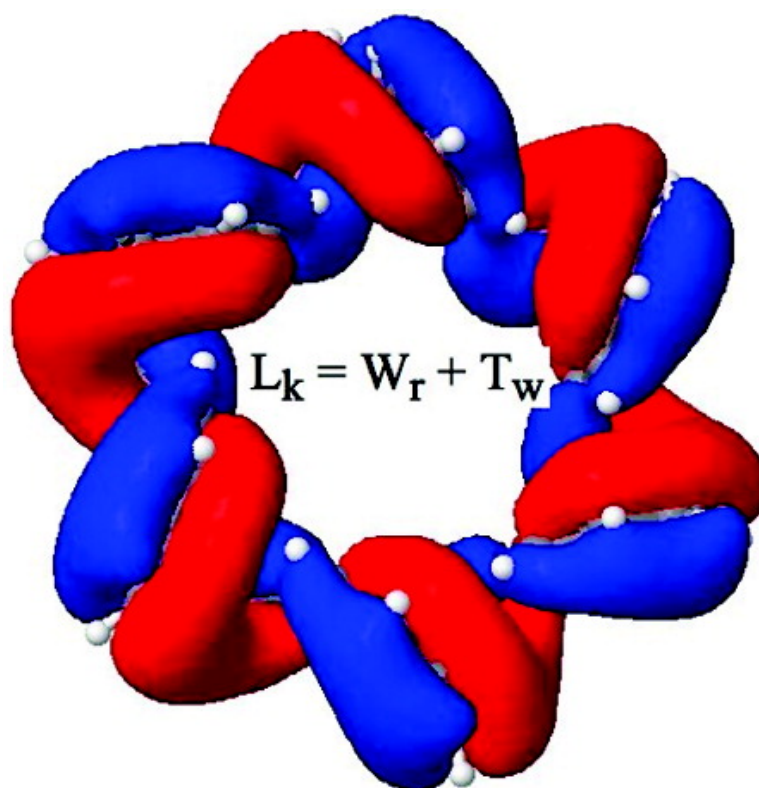
Article

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## Intrinsically Chiral Aromaticity. Rules Incorporating Linking Number, Twist, and Writhe for Higher-Twist Möbius Annulenes

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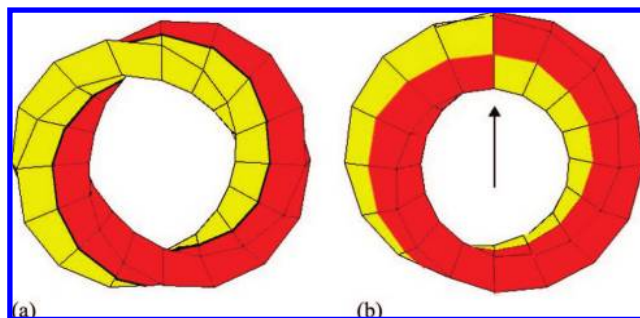
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**Abstract:** The geometries of coiled annulenes belonging to the chiral  $C_2$  and  $D_n$  ( $n = 2, 7$ ) point groups are defined by two chiral indices,  $W_r$  and  $T_w$ , respectively (writhe and twist), which sum to give an overall integer linking number,  $L_k$  (the Călugăreanu–White–Fuller theorem). While the value of  $L_k$  can be equated with single-twist ( $L_k = 1\pi$ ), double-twist ( $L_k = 2$ ), and higher-order ( $L_k > 2$ ) twisted (Möbius–Listing) annulenes, we suggest that the correct Huckel molecular-orbital treatment is to use  $T_w$  specifically in the  $2p_\pi-2p_\pi$  overlap correction first suggested by Heilbronner, rather than  $L_k$ . Quantitatively, because many of these systems project much of the finite value of  $T_w$  into  $W_r$ , a simple mechanism exists to increase the  $\pi$ -electron resonance stabilization beyond what simple Heilbronner theory predicts. Examples of a diverse set of such chiral annulenes are dissected into  $W_r$  and  $T_w$  contributions, which reveals that those with the minimum value of  $T_w$  are associated with the greater delocalized stability.

### 1. Introduction

In 1964, Heilbronner proposed<sup>1</sup> that cyclic  $4n$ -electron annulenes with 20 or more carbon atoms might be capable of existing in a Möbius conformation having a singlet closed-shell ground state. Interest in such systems has increasingly revived since 2003, with a reported synthesis of a [16] Möbius annulene<sup>2</sup> and two recent comprehensive reviews.<sup>3,4</sup> Heilbronner's argument for singlet stability of such systems was derived from two modifications to the basic Hückel secular equations. The first involved replacing the  $\beta_{C-C}$  term in the Hückel secular determinant by  $\cos(\pi/N)\beta_{C-C}$ , where  $\pi/N$  represents the local value of a single half-twist equally distributed around the  $N$   $2p$  atomic orbital (AO) adjacent pairs of the basis. The second was to replace one occurrence of  $\cos(\pi/N)\beta_{C-C}$  by  $-\cos(\pi/N)\beta_{C-C}$  to take into account the phase shift introduced in the AO basis by imparting a single half-twist (Figure 1). Heilbronner made the assumption that although the Möbius band is essentially a two-dimensional (2D) object, the resulting molecular orbital (MO) solutions would nevertheless be acceptable factors of a corresponding three-dimensional (3D) problem. Presciently, Heilbronner commented on the need to show whether such 3D potentials could exist for which his analysis was exactly or even approximately true.



**Figure 1.** (a) A higher-twist Möbius band (of height equal to half the width) containing 16 segments and bearing two half-twists, corresponding to  $L_k = 2\pi$  (even). Each segment represents one atomic orbital, each half-colored to produce red or yellow cubes, representing the two phases of a  $2p$  atomic orbital. A passage of exactly once around the ring joins each phase to one of the same color. There is no phase shift, but the two phases are linked in the manner of magician's rings. (b) The same band, but now bearing only one half-twist, corresponding to  $L_k = 1\pi$  (odd). One passage around the ring produces a phase shift at the (arbitrary) position shown by the arrow. The same result is obtained for any odd number of half-twists imparted to the band.

The need for such a 3D theory is highlighted by recent reports suggesting that imparting a higher-order double-twist to a carbon  $2p$  AO basis to give a basic figure-eight shape (a 3D form of the Bernoulli lemniscate) can result in surprising stability and also aromaticity for the specific case of a [14]annulene (**1**,  $x = 1$ )<sup>5</sup> and potentially accessible barriers for an aromatic pericyclic transition state bearing such a Möbius double-twist (**2**).<sup>6</sup>

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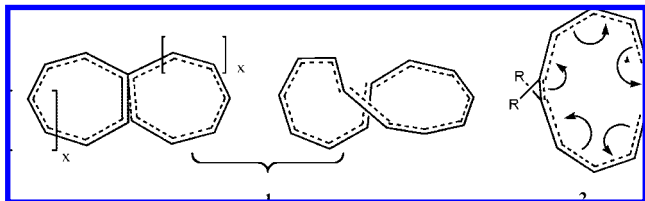
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An extension of Heilbronner's Hückel treatment to such multiply twisted systems<sup>7</sup> revealed the apparently obvious, that as the total twist distributed around the cycle increases, so the resulting Hückel resonance energy decreases, with the values for higher twisted systems always being smaller than for singly twisted cycles. To account for the relative calculated stability of **1**,  $x = 1$ , we speculated<sup>7</sup> that a 3D topological property known as writhe might be responsible. In the present article, we present a quantitative analysis of this hypothesis for a range of annulenes which addresses, at least in part, Heilbronner's concerns about the validity of his approach for three dimensions and which suggests that, while Heilbronner's approach is essentially correct, a subtle modification to the basic Hückel  $4n+2/4n$  aromaticity rules is indeed needed.

## 2. The Topology of Coiled Ribbons

Our starting point is the work of Călugăreanu, White and Fuller,<sup>8</sup> which has two relevant aspects:

1. White<sup>8a</sup> proved that a band to which two half-twists (or one full twist,  $2\pi$ ) had been imparted was topologically identical to a doubly encircled band to which no half-twists had been imparted (the analogy to winding a band of length  $2l$  around a sphere of circumference  $l$  twice before connecting the ends was noted by Tanada and co-workers<sup>9</sup>).
2. This was generalized<sup>8</sup> to the following relationship:  $L_k = W_r + T_w$ , where a linking number  $L_k$  (always a positive or negative integer quantity) comprises the sum of the geometrical twist  $T_w$  and the writhe  $W_r$ , neither of which individually needs to be an integer quantity. Any band that occupies 3D space and has initial twist imparted (as in the Heilbronner 2p AO basis above) can project some or all of that twist into writhe. Significantly, twist is a local property ( $T_w$  is obtained by integrating all the local rotation angles  $\gamma$  around the band), whereas writhe is not, and must be obtained by a double integration; it measures the extent to which coiling of the central curve can relieve the local twisting of the ribbon. This process is illustrated pictorially in Figure 2.

The significance to Heilbronner's approach is thus:

3. It is purely the value of the linking number  $L_k$  that determines whether a phase shift in the 2p AO basis must occur. If  $L_k$  is expressed in units of  $\pi$ , then we can now state that an **even** or zero value of  $L_k$  will result in **no** phase shift in a 2p AO basis (Figure 1a), whereas an **odd** value of  $L_k$  will result in at least one phase shift in the AO basis (Figure 1b). In terms of the Călugăreanu–White–Fuller theorem noted above, the linking number for either a doubly half-twisted or a doubly encircled

band is  $2\pi$  (even) in both cases. Any system with a non-zero value for  $L_k$  will also be chiral. In this sense, benzene, having  $L_k = 0$ , is actually a special case of a more general solution!

4. Heilbronner's derived selection rule can now be expressed thus: if the MOs derived from a cyclic conjugated AO basis set containing one phase shift are populated with  $4n$  electrons ( $n$  being a positive integer), the resulting system will exhibit closed-shell stability. A corollary can be added corresponding to the original Hückel rule: MOs derived from a cyclic 2p AO basis containing **no** phase shift will exhibit closed-shell stability (and potentially aromaticity) when populated with  $4n+2$  electrons.
5. Heilbronner's cosine term  $\cos(\pi/N)\beta_{C-C}$  must instead be computed purely from the **local** rotation angle between any two adjacent 2p AOs, which we term  $\gamma$ . A first-order approximation to  $\gamma$  is  $T_w/N$ , and  $\cos(T_w/N)\beta_{C-C}$  rather than  $\cos(\pi/N)\beta_{C-C}$  (for a singly half-twisted system) becomes a more appropriate description of the overlap of adjacent AOs in **3D space**.

The outcome of the above argument is that higher-order twisted annulenes need not necessarily lose resonance energy derived from the  $\cos(\pi/N)\beta_{C-C}$  term, since some proportion of the local property  $T_w$  can in fact be projected into the non-local property of writhe. Writhe in turn reflects the bending strain in the molecule rather than torsional twist. We also note at this stage that both  $W_r$  and  $T_w$  are independent **chiral** indices. Compounds identical in every regard except the signs of both  $T_w$  and  $W_r$  would be enantiomers (Figure 2).

## 3. Methodology

To evaluate this for some real molecular systems, we have analyzed a series of  $(CH)_n$  systems containing between two and seven half-twists imparted to the 2p AO basis. The models are all constructed as closed-shell systems using the B3LYP/6-31G(d) density functional approach,<sup>10</sup> with molecular symmetry imposed (normally  $D_n$ ,  $n = 2-7$ ). The electron count is adjusted to either  $4n$  or  $4n+2$  as appropriate by modeling as either a neutral system or a mono- or di-anion or -cation (the wrong electron count will often result in Jahn–Teller instabilities). The purpose was to provide an appropriate ribbon for analysis rather than to compare the energetic properties of such molecules. The procedure involved constructing a ribbon based on the coordinates of each carbon atom and those of an idealized 2p AO node placed at an arbitrary distance (usually between 0.25 and 1 Å; the precise value does not influence the results obtained) from the carbon. This was oriented perpendicular to the plane defined by  $C_2$ ,  $C_3$ , and  $H_4$  (Figure 3) and optimized to minimize the deviation from  $90^\circ$  of the angles defined by this point, the carbon, and the three atoms connected to that carbon (Figure 3). The optimized deviation from  $90^\circ$  varied from  $<1^\circ$  for the best cases to  $<5^\circ$  for the worst. Such a ribbon comprises the coordinates of each carbon in the ring, represented by  $\vec{r}_n$  as the center line, and the position of the idealized 2p <sub>$\pi$</sub>  orbital, represented by  $\vec{x}_n$  as the ribbon's edge.

We are interested in three properties of this ribbon, the linking number ( $L_k$ ), the writhe ( $W_r$ ), and the total twist ( $T_w$ ), which together obey the relation  $L_k = W_r + T_w$ .<sup>8</sup> We calculated all three separately and verified this relation for all the systems.

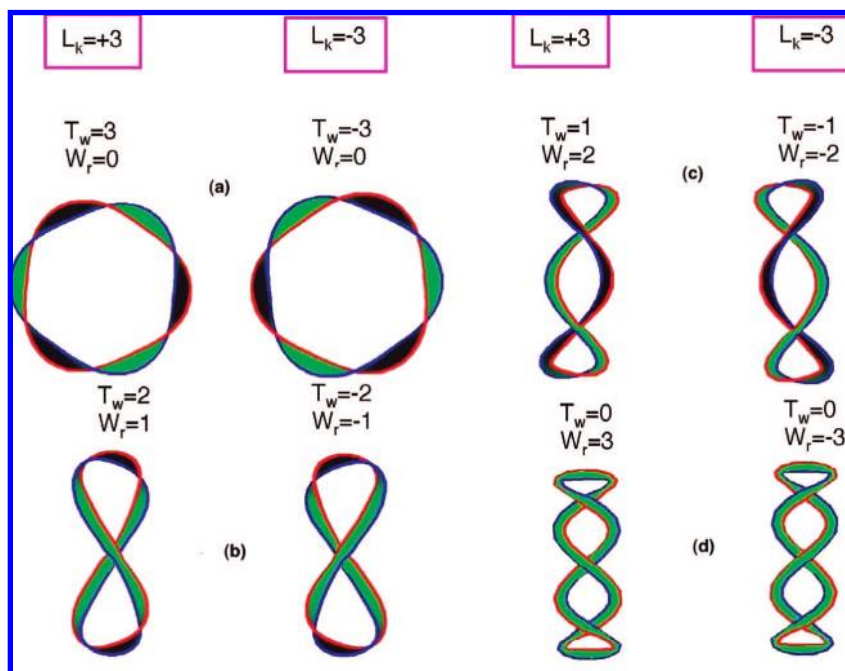
In principle, linking number is defined for an arbitrary number of links (i.e., closed curves) that do not intersect. However, the concept described in this paper is based on the topology of two links. Moreover, our interest is only in links that are strongly connected, one to another, in the following way. We denote the first link as  $\vec{r}_1(s)$ , where  $s$  is the arc length. The second link is defined as  $\vec{r}_2(s) = \vec{r}_1(s) + \varepsilon \hat{t}_1(s)$ , where  $\hat{t}_1(s)$  is a unit vector usually orthogonal to the tangent of the first link,  $\hat{t}(s) = d\vec{r}_1(s)/ds$ , and  $\varepsilon$  is

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(10) Frisch, M. J. *Gaussian 03*, Revision D.02; Gaussian, Inc.: Wallingford, CT, 2004.



**Figure 2.** Schematic illustrating the conversion of total twist  $T_w$  into writhe  $W_r$  for a system with a constant value of  $L_k = 3$  for a pair of dissymmetric enantiomers (a) showing only twist, through to (d) showing only writhe. Plot (b) shows the figure-eight lemniscular motif.

a small number corresponding to the distance between the two links. One can think of these two links as edges of a ribbon (i.e., stripe) or as the center line  $\vec{r}_1(s) = \vec{r}_c(s)$  and one of the edges  $\vec{r}_2(s)$ .  $L_k$  is invariant under elastic deformation, which means that any deformation of the two links without tearing either of them will preserve the  $L_k$ .  $L_k$  can be any integer, and for a ribbon topology, the meaning of this integer is the minimal number of cuts one has to make in order to make an unlinked ribbon,  $L_k = 0$ . In the work described in this article, we measured all properties in units of  $\pi$  instead of the usual mathematical units of  $2\pi$ . The linking number of any two links can be calculated by<sup>11</sup>

$$L_k = \frac{1}{2\pi} \oint ds \oint ds' \left( \frac{d\vec{r}_1(s)}{ds} \times \frac{d\vec{r}_2(s')}{ds'} \right) \cdot \frac{\vec{r}_1(s) - \vec{r}_2(s')}{|\vec{r}_1(s) - \vec{r}_2(s')|^3} \quad (1)$$

Using the previous definitions for the two links and in the limit of  $\varepsilon \rightarrow 0$  this integral can be split into two parts: the writhe,

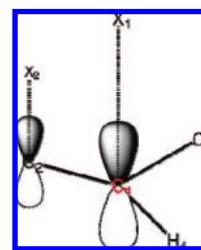
$$W_r = \frac{1}{2\pi} \oint ds \oint_{s \neq s'} ds' \left( \frac{d\vec{r}_1(s)}{ds} \times \frac{d\vec{r}_1(s')}{ds'} \right) \cdot \frac{\vec{r}_1(s) - \vec{r}_1(s')}{|\vec{r}_1(s) - \vec{r}_1(s')|^3} \quad (2)$$

and the twist,

$$T_w = \frac{1}{\pi} \oint ds [\hat{t}(s) \times \hat{t}_1(s)] \cdot \frac{d\hat{t}_1(s)}{ds} \quad (3)$$

these  $W_r$  and  $T_w$  obeying the White relation,  $L_k = W_r + T_w$ . While  $L_k$  and  $W_r$  are global properties corresponding to long-range interactions,  $T_w$  is an integration over the local angle  $\gamma$  corresponding to a local rotation of the edge around the center line. However, our interest is not with continuous ribbons. An annulene containing  $N$  carbon atoms is represented by a discrete curve built of  $N$  segments. The topology of a discrete curve can be calculated as follows. The tangent at the  $n$ th point is

$$\hat{t}_n = \frac{\vec{r}_{n+1} - \vec{r}_n}{|\vec{r}_{n+1} - \vec{r}_n|} = \frac{\vec{r}_{n+1} - \vec{r}_n}{s_n} \quad (4)$$



**Figure 3.** Method for constructing a ribbon. Angles  $C_2-C_1-X_1$ ,  $H_4-C_1-X_1$ , and  $C_3-C_1-X_1$  minimize the deviation from  $90^\circ$ , and the ribbon comprises pairs of coordinates for  $C_1, X_1$  up to  $C_N, X_N$ , where  $N$  is the size of the ring. The local rotation angle  $\gamma$  is illustrated by, e.g.,  $X_1-C_1-C_2-X_2$ .

where  $s_n$  is the length of the  $n$ th segment. Any point along the curve can be represented by the  $n$ th point and tangent:

$$\vec{S}_n(s) = \vec{r}_n + s\hat{t}_n \quad (5)$$

where  $0 \leq s \leq s_n$ . The curve that corresponds to the edge is represented in the same way:

$$\hat{t}_n^{(x)} = \frac{\vec{x}_{n+1} - \vec{x}_n}{|\vec{x}_{n+1} - \vec{x}_n|} = \frac{\vec{x}_{n+1} - \vec{x}_n}{s_n^{(x)}} \quad (6)$$

and:

$$\vec{S}_n^{(x)}(s) = \vec{x}_n + s\hat{t}_n^{(x)} \quad (7)$$

The double integral of eq 2 can be replaced by the sum

$$W_r = 2 \frac{1}{2\pi} \sum_{n=2}^N \sum_{m < n} W_{nm} \quad (8)$$

where

$$W_{nm} = \int_0^{s_n} \int_0^{s_m} ds ds' (\hat{t}_n \times \hat{t}_m) \cdot \frac{\vec{S}_n(s) - \vec{S}_m(s')}{|\vec{S}_n(s) - \vec{S}_m(s')|} \quad (9)$$

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The last integral can be calculated analytically in two ways, which are well described by Klenin et al.<sup>12</sup> The  $L_k$  number is calculated in a similar way:

$$L_k = \frac{1}{2\pi} \sum_{n=1}^N \sum_{m=1}^N L_{nm} \quad (10)$$

where

$$L_{nm} = \int_0^{s_m(x)} \int_0^{s_n} ds ds' (\hat{t}_n^{(x)} \times \hat{t}_m) \cdot \frac{\bar{S}_n^{(x)}(s) - \bar{S}_m(s')}{|\bar{S}_n^{(x)}(s) - \bar{S}_m(s')|} \quad (11)$$

The  $T_w$  of a discrete ribbon with  $N$  parts is calculated as the summation of  $N$  rotation angles, each corresponding to the angle between two planes defined by  $\hat{t}_n^{(1a)} = |\bar{\rho}_n \times \hat{t}_n|^{-1} (\bar{\rho}_n \times \hat{t}_n)$  and  $\hat{t}_n^{(1b)} = |\bar{\rho}_{n+1} \times \hat{t}_n|^{-1} (\bar{\rho}_{n+1} \times \hat{t}_n)$ , where  $\bar{\rho}_n = \bar{x}_n - \bar{r}_n$  is the orbital orientation of the  $n$ th carbon. The total twist is

$$T_w = \frac{1}{\pi} \sum \gamma_n \quad (12)$$

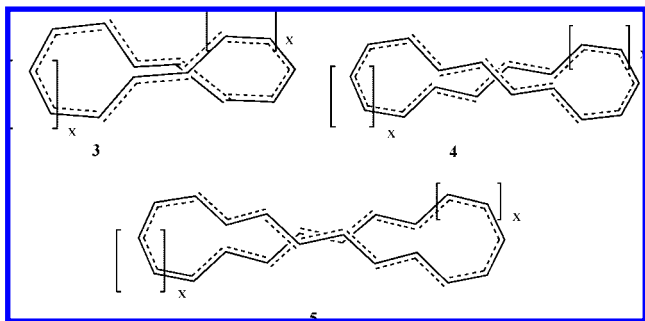
The local rotation angle is

$$\gamma_n = \arccos(\hat{t}_n^{(1a)} \cdot \hat{t}_n^{(1b)}) \text{sign}[(\hat{t}_n^{(1a)} \times \hat{t}_n^{(1b)}) \cdot \hat{t}_n] \quad (13)$$

In this work, the topology of half-twisted ribbons is also calculated ( $1\pi$ ,  $3\pi$ , etc). The center line in this case is defined by the positions of the  $N$  carbons, yet the edge in that case has  $2N$  points (two traversals around the cycle are required to return to the starting point). As the writhe is defined only by the center line, there is no difference in calculating it. However,  $L_k$  and  $T_w$  are defined also by the edge of the ribbon. In order to calculate these properties, we define  $\bar{r}_{n+N} = \bar{r}_n$  and use the same methods as for the regular molecules, but for  $2N$  points (notice that the summation in eq 10 is over  $N$  for the center line and  $2N$  for the edge). The total  $L_k$  and  $T_w$  are achieved by dividing the result by 2. Computer code for performing these calculations is available on request from the authors.

## 4. Results and Discussion

**4.1. Systems with Two Half-Twists.** Web-enhanced object 1 (WEO1) shows a series of  $[4n+2]$ annulenes with  $D_2$  symmetry in which a double-twist to the AO framework has been imparted by using *trans*-alkene motifs placed at the cross-over point of the lemniscate in four different series, **1**, **3**, **4**, and **5**, for different values of  $x$ . Each series differs only in the remaining number of carbons in each loop. Since the 3D character of these helical systems is difficult to envisage in two- dimensions, the reader is encouraged to view a rotatable 3D model via WEO1. In every case, the value computed for  $L_k$  is 2 (in units of  $\pi$ ). We note that, in different contexts,  $L_k$  is more conventionally expressed in units of  $2\pi$  and would hence have the value of 1 for these systems.



WEO1, available in the Web version of the article, shows the variation in  $T_w/W_r$  for  $L_k = 2$  as a function of  $D_2$ -symmetric  $[N]$ annulene ring size and *trans*-alkene geometry.

For each system,  $L_k$  has been decomposed into values for  $W_r + T_w$ , also in units of  $\pi$ . It is immediately apparent that  $T_w$  has a minimum (and  $W_r$  a maximum) value for each series. Thus, the previously reported [14]annulene<sup>5</sup> **1**,  $x = 1$ , represents a minimum in  $T_w$  as a function of ring size, and indeed only it is a proper geometric minimum in the potential surface. The adjacent [10]- and [18]annulenes have higher values of  $T_w$ , but these are not minima but transition states in the potential surface. The form of the transition state is also of itself interesting, corresponding to alternate bond shortening/lengthening to form a non-aromatic/bond-localized cyclo-polyene.<sup>13</sup> Such a form can sustain far greater local twist in the region of the long bond and has almost no local twist in the region of the short bond. Overall, the most favorable outcome for isomers with larger values of  $T_w$  is to indeed localize that twist. Unlike the [10]- and [18]annulenes, the [14]annulene **1**,  $x = 1$ , is fully delocalized not merely in its non-alternating bond lengths, but also in minimizing the variation in the local rotation angle  $\gamma$  around the ring (an aspect discussed in more detail below). Such variation (or lack of) in  $\gamma$  could be regarded as another expression/metric of aromaticity.<sup>3</sup>

Annulene **3** has an alternative *trans*-alkene motif at the cross-over point, and it is now the [18]annulene that has a stable minimum at the point where  $T_w$  is also a minimum. Annulene **4**, for which the cross-over point contains two adjacent *trans*-alkenes, shows only the [22]annulene to be a geometric minimum. The [26]annulene **5**, with three *trans* cross-over motifs, no longer has a minimum at any  $D_2$ -symmetric geometry (at the B3LYP/6-31G(d) level of theory); the form with the minimum  $T_w$  does, however, correspond to the smallest imaginary frequency for bond shortening/lengthening. It is quite probable that electron correlation effects for this size of ring are increasingly responsible for the lack of delocalization, and also that the balance between geometric minimum and transition state for any series is also sensitive to the theoretical procedure. Thus, the B3LYP density functional method is known to favor bond-delocalized forms.<sup>14</sup> We emphasize here not the significance of any particular minimum, but the trends observed as a function of the values of  $T_w$  and  $W_r$ . Investigation of the variation of these two parameters as a function of the theoretical procedures adopted, including the treatment of the electron correlation, is deferred to a future article.

**4.2. Systems with Two or More Half-Twists.** WEO2 shows the effect of imparting two or more half-twists to the 2p AO basis.<sup>5,15</sup> The 3D structures are illustrated more conventionally in Figure 4. The  $4n+2$  electron systems all have an even value for  $L_k$  ranging from  $2\pi$  to  $6\pi$ ; the  $4n$  systems all have an odd value for  $L_k$ , implying at least one phase shift in the AO basis. Here we also report the NICS(0) index values.<sup>16</sup> These are equal to or more negative than  $-10$  ppm (the value for benzene itself),

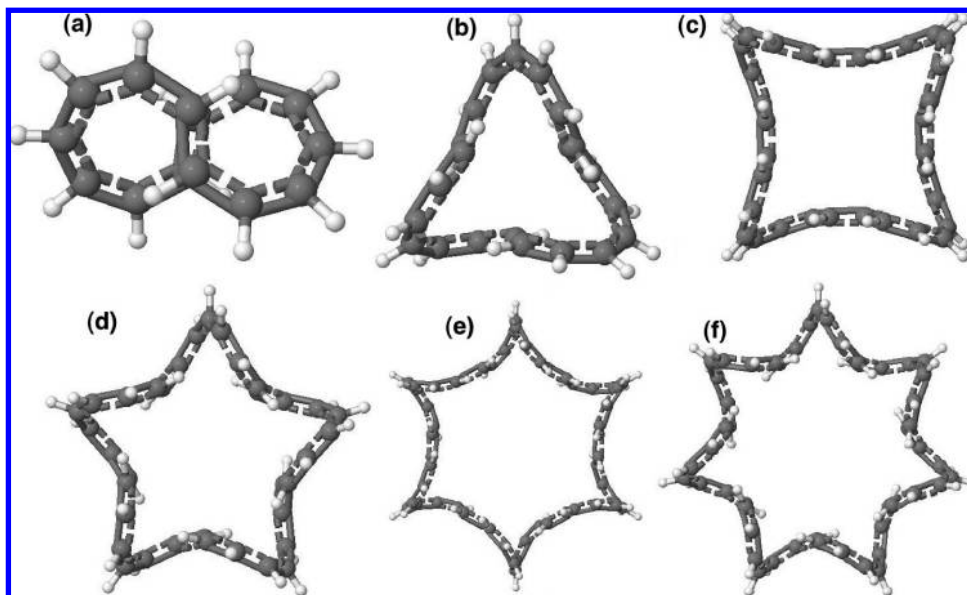
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(13) Such transition states were first proposed in a series of articles: (a) Castro, C.; Karney, W. L.; Valencia, M. A.; Vu, C. M. H.; Pemberton, R. P. *J. Am. Chem. Soc.* **2005**, *127*, 9704–9805. (b) Castro, C.; Karney, W. L.; McShane, C. M.; Pemberton, R. P. *J. Org. Chem.* **2006**, *71*, 3001–3006. (c) Pemberton, R. P.; McShane, C. M.; Castro, C.; Karney, W. L. *J. Am. Chem. Soc.* **2006**, *128*, 16692–16700. (d) Moll, J. F.; Pemberton, R. P.; Gutierrez, M. G.; Castro, C.; Karney, W. L. *J. Am. Chem. Soc.* **2007**, *129*, 274–275.

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(15) Three of the systems described in WEO2 originate from Wannere, C. S.; Rinderspacher, B. C.; Paul, A.; Rzepa, H. S.; Schaefer, F.; Schleyer, P. v. R., to be published.

(16) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.



**Figure 4.** 3D structures for higher-twist  $[N]$ annulenes for (a)  $N = 14$ ,  $D_2$  symmetry; (b)  $N = 21^+$ ,  $D_3$  symmetry; (c)  $N = 32^{2-}$ ,  $D_4$  symmetry; (d)  $N = 35^-$ ,  $D_5$  symmetry; (e)  $N = 54$ ,  $D_6$  symmetry; and (f)  $N = 49^+$ ,  $D_7$  symmetry.

Ⓜ WEO2, available in the Web version of the article, shows the variation in  $L_k$  for  $4n+2$ - and  $4n$ -electron  $[N]$ annulenes as a function of ring size.

indicating that each system sustains a strong diamagnetic ring current and hence is *aromatic* by this specific criterion, as implied by the selection rule set out in point 4 above. As the total linking number increases for a given *trans*-alkene motif, the value of  $T_w$  remains more or less constant, and it is  $W_r$  that absorbs the helical wind while relieving  $T_w$ . This implies that, from the point of view of loss of orbital overlap, a system with **six** half-twists is not necessarily worse off than one with merely one. Any instability from such systems would originate from other factors, such as ring strain or bond-localizing electron correlation effects, as well as large oscillations about the mean of the local rotation angle  $\gamma$ , which would also lead to loss of  $\pi$ -orbital overlap. Nevertheless, in retrospect, perhaps higher-order twisted systems as synthetic targets might not have been an entirely unreasonable objective.

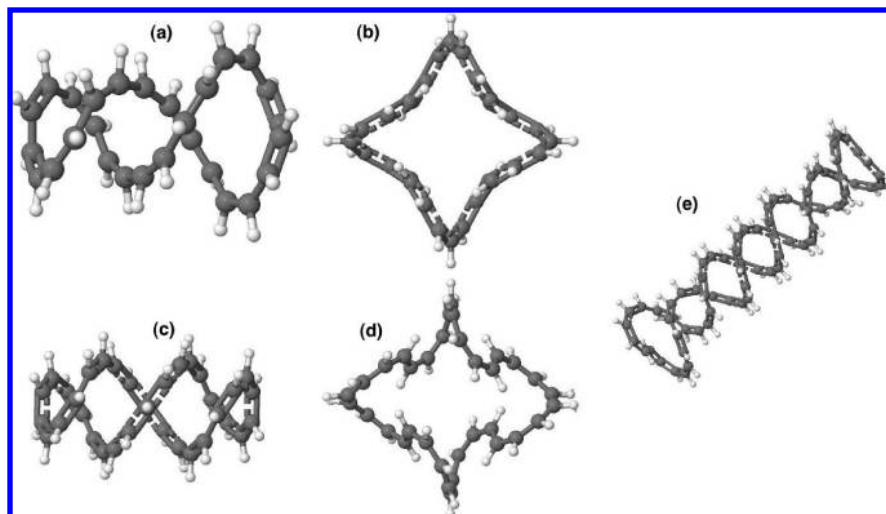
**4.3. Form of the Molecular Orbitals.** Intrinsic to the discussion above is that systems with, e.g., even values of  $L_k$  (corresponding to even values of  $n$  in the molecular symmetry  $D_n$ ) should exhibit no phase shift in the  $2p$  AO basis. This is reflected in the resulting MOs constructed from this basis; one such orbital (normally the most stable, but not necessarily so) will manifest continuous cyclic overlap of both orbital phases. WEO3 illustrates such orbitals for selected systems. An important caveat is that, for the hydrocarbon annulenes  $(CH)_N$ , the molecular symmetry no longer imposes any strict  $\sigma/\pi$  separation between the MOs resulting from the  $2p$  AO basis and the underlying  $\sigma$  framework, and significant contamination of the pure  $\pi$  system can occur by mixing with the C–H bonds. To minimize this, a series of fluorinated analogues were calculated,  $(CF)_N$ , where the lower energy of the C–F  $\sigma$  manifold reduces  $\sigma/\pi$  mixing and hence clarifies the intrinsic form of the  $\pi$ -MOs. The even-numbered  $D_n$  point groups have non-degenerate, irreducible representations for which the identity of these orbitals is unambiguous. Thus, the most stable  $\pi$ -like MO for [14]annulene has a characteristic “figure-eight” shape, in which both phases of the MO continuously circulate, and is classified in knot theory as a 2.2.1 torus link. This lemniscate motif is homologated for the [28]/[32] and [42] systems but

the continuity remains intact, and they are indeed examples of 4.2.1 and 6.2.1 torus links, respectively. The systems with odd  $L_k$  values, for  $L_k = 3$  or higher, all belong to point groups with degenerate E representations, and here all the canonical MOs exhibit at least one phase shift (cf. Figure 1) and hence are not continuous torus links.

Ⓜ WEO3, available in the Web version of the article, shows  $\pi$ -type MOs for  $[N]$ annulenes, illustrating the presence ( $L_k = 3$ ) or absence ( $L_k = 2, 4, 6$ ) of a phase shift.

**4.4.  $W_r$  and  $T_w$  Isomerism.** The topologic descriptors  $W_r$  and  $T_w$  are also independent. Illustrated in WEO4 and Figure 5 are two sets of isomers, each comprising the same molecular formula, but which differ in the values of  $W_r$  and  $T_w$ . Thus, one isomer of the [28]annulene has  $W_r$  and  $T_w$  of opposing signs, with a large numerical value of  $T_w$ , and it represents a transition state in the potential surface for bond shortening/lengthening. In the other isomer, the two values are of the same sign, resulting in a larger value for  $L_k$  but a smaller value for  $T_w$ , and this now represents a minimum in the B3LYP/6-31G(d) potential surface. Both are nevertheless “aromatic”, as indicated by the NICS(0) index. Another example is provided by the [34]annulene, although in this case, a large value of  $T_w$  does not necessarily result in the system being a transition state rather than a geometric minimum. The example of a [74]annulene is included as an illustration of an Archimedes screw-like molecule, where the substantial degree of writhe is nevertheless more than offset by the opposite sign of  $T_w$ , resulting in no particular stability. The absolute signs of  $T_w$  and  $W_r$  have no significance other than to indicate one enantiomer of a dissymmetric pair; as such, therefore, they are an interesting addition to the Cahn–Ingold–Prelog notations.

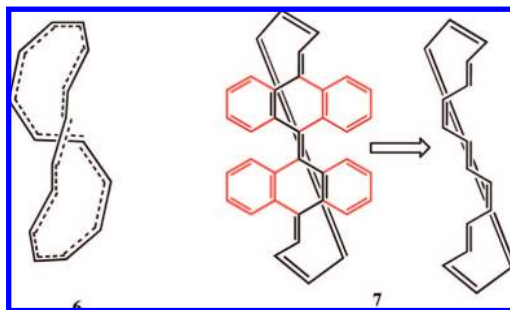
**4.5.  $W_r$  and  $T_w$  Analysis of Two Previously Reported Single-Twist Möbius Systems.** We have applied the  $W_r/T_w$  ribbon analysis to two previously reported single half-twist Möbius systems to see whether these too can be categorized by this method. A number of Möbius  $[4n]$ annulenes were reported by



**Figure 5.** 3D structures for  $D_{2/4}$ -symmetric  $[N]$ annulene examples illustrating  $T_w/W_r$  isomerism for (a)  $N = 28^{2-}$ ,  $D_2$  symmetry; (b)  $N = 28^{2-}$ ,  $D_4$  symmetry; (c)  $N = 34$ ,  $D_2$  symmetry; (d)  $N = 34$ ,  $D_4$  symmetry; and (e)  $N = 74^{2+}$ ,  $D_2$  symmetry.

WEO4, available in the Web version of the article, shows  $D_{2/4}$ -symmetric  $[N]$ annulene examples illustrating  $T_w/W_r$  isomerism.

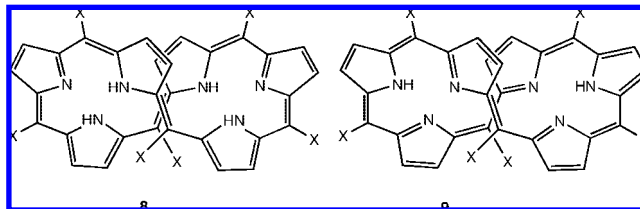
Castro and co-workers,<sup>17</sup> of which a [16]annulene **6** was particularly prominent in exhibiting almost no bond length alternation and significant aromaticity as measured using the NICS(0) index. This system is now revealed as having the appropriate value of  $L_k = 1$ , comprising  $T_w = 0.24$  and  $W_r = 0.76\pi$ . By projecting most of the  $T_w$  into writhe, this annulene becomes significantly more stable than one might have concluded from the original Heilbronner treatment. The other system included in this section is the backbone derived from the crystal structure of the Möbius [16]annulene **7** actually synthesized by Herges and co-workers.<sup>2</sup> In order to enable the synthesis, the system included benzo groups at strategic positions, and we have reduced this to a single ribbon by the editing process shown in **7**.



The values obtained for the backbone of **7** were  $T_w = 0.58$  and  $W_r = 0.42\pi$ , suggesting that the additional rigidity imposed by these benzo groups has limited the ability of the system to project twist into writhe, and hence to stabilize via extended conjugation.

**4.6.  $W_r$  and  $T_w$  Analysis of Porphyrins and Related Molecules.** In a recent review,<sup>4</sup> Herges noted a class of molecule known as the porphyrins and remarked that a number of larger porphyrins, and in particular the octaphyrins, adopt figure-eight, or lemniscular, conformations, which he suggested are well characterized examples of double-twist Möbius systems. In our analysis, these would correspond to  $L_k = 2\pi$ . Two related

systems for which crystal structures have been determined, **8** (a [28]hexaphyrin) and **9** (a [26]hexaphyrin), have now been analyzed<sup>18</sup> for their values of  $L_k$ ,  $W_r$ , and  $T_w$ . The former is in fact an example of a (crystalline!) double-twist  $4n$ -electron anti-aromatic Möbius molecule; the latter is its aromatic  $4n+2$ -electron oxidized form. The values of  $L_k$  for both systems were indeed confirmed as  $2\pi$ , and this was partitioned as  $T_w = 1.19$  and  $1.13\pi$  and  $W_r = 0.81$  and  $0.87\pi$  for **8** and **9**, respectively, based on the crystallographic coordinates. The writhe for these hexaphyrins is slightly smaller than those for the equivalent sized rings reported in WEO1, in part because the pyrrole units from which these rings originate are more rigid than simple C–C bonds, and hence less of the total twist can be converted to writhe.



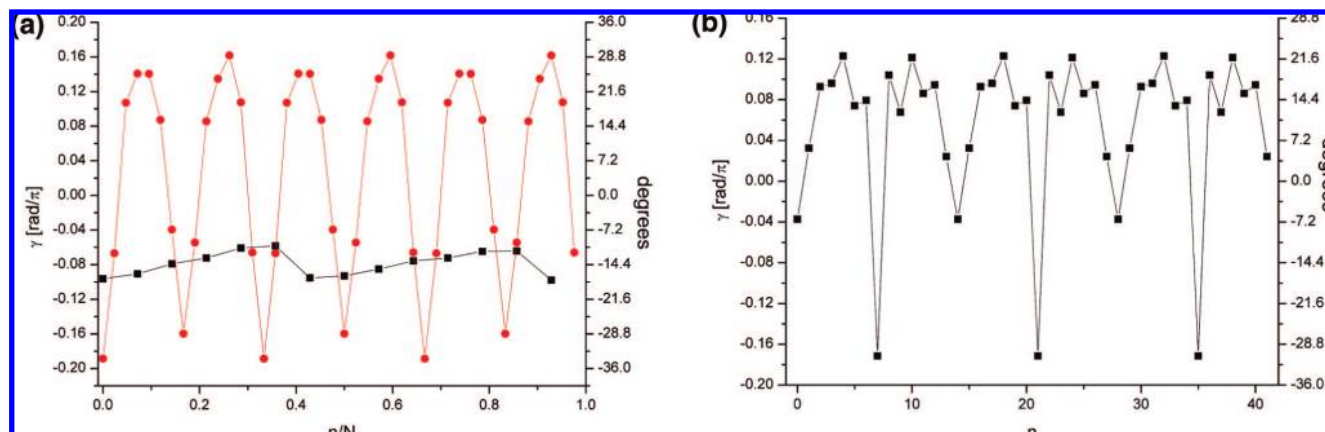
There are numerous other examples of such ring systems<sup>4</sup> which await such analysis.

**4.7. Analysis of Local Variation in  $T_w$ .** The key aspect of the analysis set out above is that, while  $W_r$  is defined as a non-local property,  $T_w$  is the sum of local twist components (rotation angles), and it is the latter, therefore, that relates directly to the  $\pi,\pi\pi$  conjugation in the cyclic annulenes we are using as models. These annulenes themselves can be placed in one of two categories: those for which the B3LYP/6-31G(d) method predicts the symmetric  $D_n$  ( $n = 2-7$ ) geometry to be a minimum in the potential surface, and those which are revealed as a transition state or a higher-order saddle point in this potential surface. Of the systems reported in WEO1, 3 belong to the former category, while the remaining 10 are in the latter. All these examples have a common value of  $L_k = 2$ , but they vary widely in the integrated twist  $T_w$ . The twist variability can be

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**Figure 6.** (a) Variation of  $\gamma$  (local rotation angle) for  $D_2$ -symmetric [14]annulene **1**,  $x = 1$  (squares), and  $D_6$ -symmetric [42]annulene (circles). (b) Variation of  $\gamma$  for  $D_3$ -symmetric [21]annulene, taking two cycles around the ring.

estimated from the standard deviation of the local rotation angles  $\gamma$ , given as  $\gamma_{SD}$  in WEO1. While the (three) energy minima all corresponded to the minimum value of  $T_w$  along each series, the correspondence is less good with the trend in the standard deviation  $\gamma_{SD}$ . Thus, although the [22]annulene is a proper minimum (at this level of theory),  $\gamma_{SD}$  has a relatively large variation of  $13.4^\circ$ . Conversely, the [26]annulene has smaller values for both  $T_w$  and  $\gamma_{SD}$  but is now a transition state for bond contraction/lengthening, leading to a bond-alternating geometry.

This variation is further illustrated via three examples (Figure 6) for which  $L_k$  varies. The local mean values of  $\gamma$  for the  $D_2$ -symmetric [14]annulene **1**, the  $D_3$ -symmetric [21]annulene, and the  $D_6$ -symmetric [42]annulene (WEO2) are respectively  $15.7 \pm 2.2$ ,  $10.1 \pm 13.7$ , and  $1.8 \pm 21.0^\circ$ . Along this series, despite the increasing value of  $L_k$ , the total twist  $T_w$  remains essentially constant by virtue of projection into  $W_r$ . As a result, although the mean value of  $\gamma$  decreases as the ring size increases, the local variation  $\gamma_{SD}$  rises due to increasing oscillation about the mean. This implies less efficient  $\pi$ -conjugation via local  $2p_\pi-2p_\pi$  overlaps around the cycle as the ring size increases. Whereas the local rotation angle  $\gamma$  (and its sum around the ring  $T_w$ ) is associated with local  $2p_\pi-2p_\pi$  twists,  $W_r$  can be interpreted as deriving from bending deformations within the  $\pi$  framework of the cycle. The increase in  $W_r$  with ring size may therefore reflect that angular distortions are the energetically most favorable response of the system to relieving ring strains, at the expense of less favorable  $2p_\pi-2p_\pi$  overlaps.

There is another distortion apparent from the computed force constants of these systems, which indicates that some of them are transition states (or in some cases higher-order stationary points; see WEO1 and WEO2). Those with one (or more) negative force constants may further relax by lengthening half the C–C bond pairs and concomitantly reducing the adjacent other half. This induced bond alternation has the effect of reducing the cyclic  $\pi$ -conjugation but allows greater local twisting to occur in the region of the lengthened (i.e., single) C–C bonds. It is also probable that  $\pi$ -electron correlation effects reduce the ability to delocalize larger values of  $T_w$  around the entire cycle; the largest ring for which we observed a true geometric minimum (at this level of theory) was the  $D_4$ -symmetric [36]annulene dianion. As noted above, the issue of whether these minima will persist at more accurate correlated levels of theory remains to be determined.

## 5. Conclusions

Since 1964, almost all of the research into Möbius conjugated molecules has focused on singly half-twisted systems. There was probably a tacit assumption that one half-twist was difficult enough to introduce, and hence that multiply twisted systems would be proportionately even more difficult to fashion. By considering the outcome of projecting such twisted ribbons into three dimensions and applying the concept of writhe, we have here shown that the outcomes of producing higher twisted systems may not necessarily be gloomy. By inspecting trends in  $T_w$  as functions of ring size and geometry, one can quantitatively estimate the most stable isomer, at least in terms of  $\pi$ -conjugation if not of angular ring strain. This conversion of ( $\pi$ -electronic) twist strain into  $\sigma$ -framework bending strain ( $W_r$ ) has a precise analogy in the elastic behavior of a plectonemically or supercoiled DNA molecule,<sup>19</sup> which is defined by elastic constants defining the bending and twist rigidities, and in stretched and twisted elastomeric filaments.<sup>20</sup>

Incorporating these concepts into the standard Hückel/Möbius aromaticity rules results in the following simple restatement: a cyclic conjugated annulene that exhibits an even linking number  $L_k$  will follow a  $4n+2$  electron rule for the closed-shell ground state, and maximum  $\pi$ -electronic stability will be achieved by maximizing the value of  $W_r$ . Systems with odd values for  $L_k$  will follow instead a  $4n$  electron rule. Both even and odd finite values of  $L_k$  imply (in the examples here, dissymmetric) chirality. Finally, we recapitulate that benzenoid aromatic systems, with a zero value for  $L_k$ , are in this sense typically achiral.

**Acknowledgment.** We are very grateful to Alexei Kornyshev and Dorothy Buck (Imperial College London) and Yitzhak Rabin (Bar-Ilan University, Israel) for valuable discussions.

**Supporting Information Available:** 3D rotatable models of the geometry of each system obtained via the digital repository entry shown for each WEO, numerical analysis for each ribbon (spreadsheet), and complete ref 10. This material is available free of charge via the Internet at <http://pubs.acs.org>

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