

Hückel and Möbius aromaticity and trimerous transition state behaviour in the pericyclic reactions of [10], [14], [16] and [18]annulenes[†]

Sonsoles Martín-Santamaría, Balasundaram Lavan and Henry S. Rzepa*

Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY

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The pericyclic reactions of a series of $[n]$ annulenes ($n = 10, 14, 16, 18$) reveal unusual differences in their behaviour related to their aromaticity. For $n = 10, 14$, synchronous pericyclic bond formation (trimerous behaviour) is possible, whereas the synchronicity is not apparent for $n = 18$. The formally anti-aromatic system $n = 16$ exhibits valence bond isomerism, asynchronous pericyclisation and a novel conformation which appears to be an example of a Heilbronner Möbius aromatic, as indicated by nucleus independent chemical shift calculations.

Our theoretical discovery of the novel trapezoidal pericyclisation reaction mode of substituted derivatives of [8]annulene¹ prompted us to wonder whether related reactions of the higher order members of the annulene series might reveal similarly unusual behaviour. Two aspects in particular caught our attention; whether any differences in behaviour between formally aromatic Hückel $4n + 2$ systems (species **1**, **3** and **10**, Scheme 1) and formally anti-aromatic $4n$ systems (species **5**, **6**, **7**) might be identified. We also speculated whether the degree and type of synchronicity in bond formation could be related to ring size and/or aromaticity.²

Focusing initially on the properties of [16]annulene, we note that experimental evidence implicates at least two conformations; that represented by **5** derives from the crystal structure,³ whereas **6** is implied by the reported⁴ formation of tricyclic **8a** by a presumed sequence of either consecutive or concurrent electrocyclic reactions. Since the $4n$ annulene series is also known to minimise anti-aromaticity *via* strong bond alternation, we thought that **7** might also be a distinct isomer, exhibiting its own characteristic reactivity. For example, the Woodward–Hoffmann rules require that cyclisation of **7** would require concurrent formation of two bonds *via* a $\pi 4_s + \pi 4_a$ cycloaddition reaction to give **9**, rather than the stereochemistry implied in **8a** or **8b**. In contrast, the potential delocalisation of the $4n + 2$ aromatic annulenes **1**, **3** and **10** *via* resonance forms implies there would be no distinction between the concurrent formation of two bonds in a $\pi 4_s + \pi 2_s$ cycloaddition, and two concurrent but separate electrocyclic reactions. The latter would proceed either with disrotation to form **4** or with conrotation to form **2** and **11**. Such reactions could be classified as trimerous transformations, the transition state having the characteristics of three individual pericyclic reactions.

To place these various hypotheses on a quantitative footing, a SCF-MO study was undertaken at semi-empirical and *ab initio* levels.[‡]

[†] Molecular coordinates in the form of MDL Molfiles for located stationary points are integrated into this article in an enhanced on-line form. For direct electronic access see <http://www.rsc.org/suppdata/p2/b0/b002082f/>

[‡] Geometries of all species were initially defined using the MacMolPlt⁹ and CaChe programs. All putative saddle points were characterised by calculation of the force constant matrix and normal coordinate analysis. Calculations at the RHF and B3LYP density functional level were performed using the Gaussian98 program system¹⁰ and at the semi-empirical SCF-MO MNDO-d level using the MOPAC2000 program.¹¹

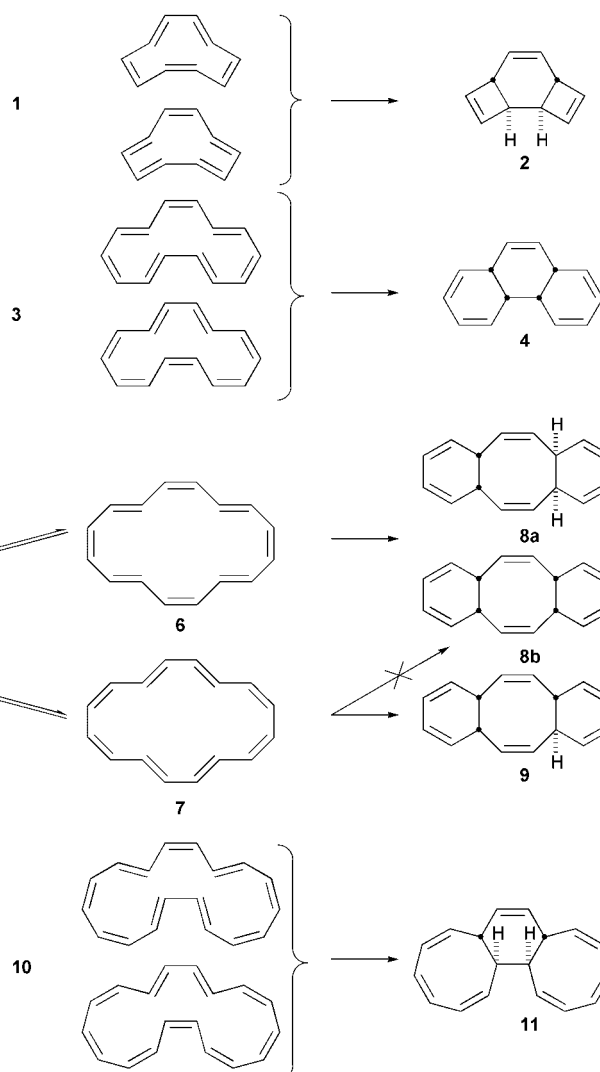
Results and discussion

The Hückel $4n$ annulenes

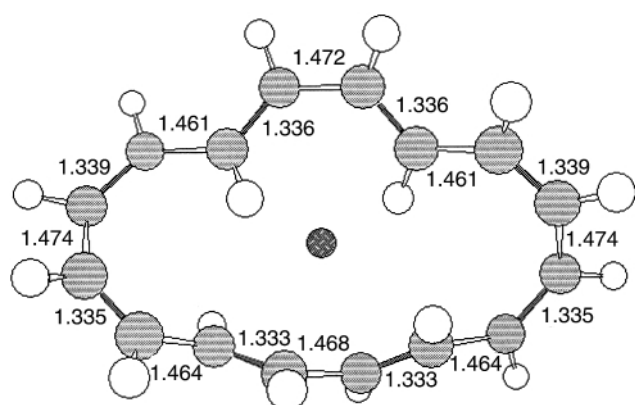
The lowest energy conformation of [16]annulene **5**, at both the AM1 and *ab initio* levels corresponds to that found in the crystal structure.[‡] It is characterised by having four hydrogen atoms in an equatorial orientation directed towards the centre of the ring, and a prominent saddle-shaped geometry. To set up electrocyclicisation, a different conformation **6** must be adopted, in which the inwardly pointing hydrogens adopt a more axial-like orientation, and the rings are set up for the suprafacial bond formation required of a $4n + 2$ pericyclic process. An electrocyclic transition state is readily located[§] but this clearly corresponds to formation only of the first C–C bond leading to formation of an intermediate bicyclic system. Attempts at the single determinantal level to locate any form of synchronous transition state or second order stationary point corresponding to a $\pi 4_s + \pi 4_s$ reaction giving **8** directly failed. This contrasts with the results we obtained for the homologous reaction of [8]annulene¹ where a $\pi 2_s + \pi 2_s$ stationary point was located, albeit with severe trapezoidal distortion. We note in passing that we find that the final product **8b** is in fact 3.0 kcal mol^{−1} more stable than **8a**.[§] The former was originally discounted in the original experimental report⁴ on circumstantial evidence, but on our evidence may in fact have been the actual product.

The valence bond isomer **7** of [16]annulene was also readily located, with an energy 4.2/7.7 kcal mol^{−1} (AM1/RHF-6-31G) above that of **5**. Its minimised conformation however, held a surprise. Unlike the saddle-like shape of **5**, isomer **7** appeared to have a Möbius-like twist distributed throughout the entire ring (Fig. 1). Heilbronner⁵ in 1964 had suggested that anti-aromatic species could reverse their aromaticity by a so-called Möbius twist of the ring. Hitherto, evidence of such an effect has largely been limited to application to pericyclic transition states rather than to stable species.⁶ Very recently, Jiao and von Schleyer have suggested that a Möbius twisted conformation of the $4n$ system C₉H₉⁺ is an example of a Heilbronner aromatic. The aromaticity of C₉H₉⁺ was evaluated using the NICS (nucleus independent chemical shift) computational procedure introduced by Jiao von Schleyer,⁶ which involves placing an NMR

[§] RHF/6-31G energy of **8a** and **8b** is −614.8470 and −614.8519 Hartree respectively. RHF/6-31G energy for the transition state for formation of one C–C bond from **6** is −614.7703 ($\nu_1 = 684$ i).



Scheme 1

Fig. 1 Geometry of **7** calculated at the RHF/6-31G level.

probe at the ring centroid. The NICS value at this probe (-13.7) was consistent with Möbius $C_9H_9^+$ having aromatic properties,⁷ given a value of ~ -10 for aromatic benzene and $\sim +18$ for anti-aromatic cyclobutadiene.

We followed the same procedure for conformation **5**, which exhibited a NICS value of $+1.9$ (RHF/6-31G) indicating weak anti-aromaticity at the ring centroid.[¶] This smaller value is

probably due in some part to the greater distance of the ring centroid of this large ring from the peripheral π -electrons. In contrast, **7** had a NICS value of -0.5 , providing evidence that the Möbius twist had indeed reversed the aromaticity of this species, although the effect is a small one. We also repeated these calculations for similar conformations of the fully fluorinated systems ($C_{16}F_{16}$), finding NICS values of -0.7 and -1.9 for the saddle and Möbius conformations respectively.

We have currently been unable to locate any $\pi_4s + \pi_4a$ or trapezoidally distorted transition states or stationary points for the reaction of **7**.⁸ Finally, we note that the potential surface of the $4n$ [12]annulene appears complex, and we will report on this in a subsequent article.

The Hückel $4n + 2$ annulenes

In contrast to **6**, a synchronous transition state for bicyclisation of the $4n + 2$ annulenes **1** and **3** can be found at both semi-empirical and *ab initio* RHF/6-31G(d) levels. These trimersous transition states therefore represent both a synchronous cycloaddition and two independent electrocyclic reactions, **1** proceeding with conrotation, **3** proceeding with disrotation. At all theoretical levels studied, these two stationary points have only a single computed negative force constant. Attempts to locate asynchronous transition states corresponding to the formation of only one C–C bond failed, even though this is allowed on a closed shell potential surface.

The behaviour of **10** is different. For this larger ring, a trimersous stationary point corresponding to synchronous

[¶] RHF/6-31G energy for **5** and **7** is -614.8539 and -614.8416 Hartree respectively and for the fully fluorinated analogues -2195.8522 and -2195.8412247 Hartree respectively.

Table 1 Energies (kcal mol⁻¹ for AM1 and PM3, otherwise Hartree), barriers (kcal mol⁻¹, in parentheses) and transition normal modes (cm⁻¹) for the stationary point structures of pericyclisation of **1**, **3** and **10**

	AM1	ν_1	PM3	ν_1	RHF/3-21G	ν_1	RHF/6-31G(d)	ν_1	B3LYP/6-31G(d)	ν_1
1	202.0 (73.5)	820 <i>i</i>	191.1 (58.9)	912 <i>i</i>	-382.0529 (62.5)	804 <i>i</i>	-384.2991 (68.4)	868 <i>i</i>	-386.8139 (87.9)	554 <i>i</i>
3	140.1 (27.3)	957 <i>i</i>	145.0 (26.5)	954 <i>i</i>	-535.1083 (27.7)	862 <i>i</i>	-538.0934 (37.6)	932 <i>i</i>	-541.7391 (21.4)	558 <i>i</i>
10a	179.0 (46.5)	817 <i>i</i> , 776 <i>i</i>	194.6 (55.2)	978 <i>i</i> , 939 <i>i</i>	-687.9852 (67.1)	589 <i>i</i> , 345 <i>i</i>	-691.8323 (74.7)	559 <i>i</i> , 337 <i>i</i>	-696.5341 (46.2)	479 <i>i</i> , 290 <i>i</i>
10b	166.6 (34.1)	792 <i>i</i>	179.6 (40.3)	954 <i>i</i>	-688.0241 (42.6)	674 <i>i</i>	-691.8740 (48.5)	734 <i>i</i>	-696.5638 (27.6)	364 <i>i</i>

electrocyclic and cycloaddition reactions can be located, but it is characterised at all theoretical levels as having two negative force constants in the Hessian matrix, and so is not a true transition state (**10a**, Table 1). The smaller of the two negative force constants distorts the trimorous geometry to a true electrocyclic reaction involving formation of only one concurrent bond (**10b**, Table 1) and being 18.6 kcal mol⁻¹ lower in energy (B3LYP/6-31G(d)). This asymmetry for the larger ring size may lend some support to McIver's postulate² that for reactions involving the formation of two bonds where synchronous behaviour is possible, the synchronicity would decrease as the ring size is increased.

Conclusions

The [10], [14], [16] and [18]annulenes exhibit some interesting differences in their behaviour towards pericyclisation. For the $4n + 2$ "aromatic" series, no distinction is possible between the two Kekulé resonance forms, and synchronous bond formation is allowed for the [10] and [14]annulenes *via* what we term a trimorous transition state. For the larger ring of [18]annulene, this is replaced by less synchronous behaviour. For the $4n$ [16]annulene, another mode is observed in which two individual valence bond isomers give rise to differing behaviours. One such isomer corresponds to a mildly anti-aromatic species which can undergo sequential electrocyclic reactions. The other valence bond isomer reveals a novel Möbius twist in the ring conformation which reverses the anti-aromaticity, consistent with it being a Heilbronner-type Möbius aromatic molecule.

References

- 1 C. Conesa and H. S. Rzepa, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2695.
- 2 J. McIver, *J. Am. Chem. Soc.*, 1975, **97**, 3632.
- 3 S. M. Johnson, I. C. Paul and G. S. B. King, *J. Chem. Soc. B*, 1970, 643.
- 4 G. Schroder, W. Martin and J. F. M. Oth, *Angew. Chem.*, 1967, **79**, 861.
- 5 E. Heilbronner, *Tetrahedron Lett.*, 1964, **29**, 1923.
- 6 H. Jiao and P. von R. Schleyer, *J. Phys. Org. Chem.*, 1998, **11**, 655.
- 7 M. Mauksch, V. Gogonea, H. Jiao and P. von R. Schleyer, *Angew. Chem., Int. Ed.*, 1998, **37**, 2395.
- 8 H. S. Rzepa and W. A. Wylie, *J. Chem. Soc., Perkin Trans. 2*, 1991, 939.
- 9 B. M. Bode and M. S. Gordon *J. Mol. Graphics Modell.*, 1998, 133.
- 10 GAUSSIAN98 (Revision A.1), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.
- 11 MOPAC2000, J. J. P. Stewart, Fujitsu Limited, Tokyo, Japan, 1999.