PERKIN 2

Twist localisation in single, double and triple twisted Möbius cyclacenes†

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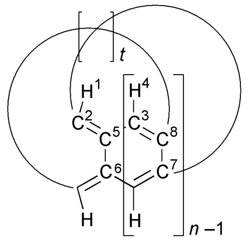
Received (in Cambridge, UK) 7th July 2000, Accepted 12th October 2000
First published as an Advance Article on the web 8th November 2000

The AM1 and *ab initio* calculated geometries of Möbius strips formed by imparting one, two or three twists to cyclacenes of various lengths reveal a localisation of the twist over 2–4 benzo rings. Various properties of these systems are reported, including the geometries, the form of the highest occupied molecular orbitals, the electrostatic potential, and the charge distributions in neutral, 6+ and 6− forms of these molecules. Factors influencing the localising tendency are discussed.

There has been a recent revival of interest in Möbius topologies in aromatic conjugated molecules. Several suggestions for Möbius-like systems in small and medium sized rings have been made,[1] and a Möbius-like conformation of [16]annulene has been proposed.[2] Türker[3] has considered (hypothetical) Möbius systems formed from a cyclic acene, or cyclacene (Scheme 1).



Scheme 1

Here the focus was on the aromaticity arising from the peripheral circuit, which in a Möbius system forms a single continuous edge. The schematic diagram shown of the geometry of this system[3] appeared to indicate a non uniform distribution of the twist present in the molecule. We now report an investigation of this aspect, together with results for doubly and triply twisted cyclacenes, which have not hitherto been reported.

Table 1 Calculated energies for cyclacenes

n	Charge	*t*	Energy/kcal mol^{-1}
8	0	1	528.0 (−1205.5326)[a]/[1213.6331][b]
15	0	1	551.0
15	+6	1	2168.4
15	−6	1	914.0
15	0	2	594.4
15	+6	2	2230.0
15	−6	2	975.2
15	0	3	701.2
15	0	3	728.1
15	+6	3	2293.7
15	−6	3	1040.9

[a] *Ab initio* RHF/STO-3G basis. [b] *Ab initio* RHF/STO-321 basis.

Computational procedure

Initial calculations were performed using the Chem3D (V 5.0) implementation of the AM1 semi-empirical SCF-MO method. Care was taken to optimise all geometries to a gradient norm value of less than 0.1 for cyclacenes containing either $n = 8$ or $n = 15$ benzenoid rings for ring twists corresponding to $t = 1$–3 (Scheme 1). Optimisation to a greater tolerance of 0.01 revealed no significant difference from the previously optimised values. *Ab initio* calculations at the STO-3G level used G98W.[4] The Chem3D interface was used to visualize the 3D form of the molecular orbitals and electrostatic potential. The 3D rendered orbitals were contoured at 0.005 au, saved in 3DMF file format, and compressed for display. To view these orbital models *via* the supplemental information version of this article (available *via* http://www.rsc.org/suppdata/p2/b0/b005560n) a 3DMF viewer such as the Quick3D browser plugin or 3DMF Optimizer is required, together with QuickDraw3D libraries.

Characteristics of single Möbius twist cyclacenes

The most conspicuous feature of the singly twisted systems ($n = 8$, 15, $t = 1$, Table 1) is indeed that the twist is not evenly distributed around the ring. The degree of regular bond alternation along the periphery (Fig. 1) increases noticeably in the more highly twisted region. The degree of twist can be quantified by measuring two types of dihedral angles, H1–C2–C3–H4 at the periphery and C5–C6–C7–C8 (Scheme 1) at the ring junctions. Fig. 2 shows the values for both a small highly strained cyclacene ($n = 8$) and for the larger system $n = 15$, which has 15 sets of C5–C6–C7–C8 (referred to as CCCC) and 30 sets of H1–C2–C3–H4 (referred to as HCCH) angles. For both sized rings, several effects merit discussion.

A clear maximum in the adjacent CCCC dihedrals is observed, indicating a significant degree of localisation of the twist. Two maxima are observed for the HCCH measurements, corresponding to two circuits of the ring back to the starting point, as is of course appropriate for a Möbius ring. We note particularly that the two maxima in this case are not equal in value. Inspection of the 3D geometry reveals that although there is only a single periphery, localisation of the twist means it has both an inside and an outside edge, each with different properties. This observation in turn reflects on another well known property of formal Möbius strips, their non orientable

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† Coordinates for all molecules, and 3DMF files for the molecular orbitals and electrostatic potential are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b005560n/

DOI: 10.1039/b005560n

properties, *i.e.* the distinction between left- and right-handedness cannot be preserved consistently over the whole surface. In a time-independent analysis, the localisation of the twist means the topology is indeed orientable. We also note that whilst the maximum value of the dihedral angle between two adjacent benzo rings is approximately 35°, the minimum value is actually of opposite sign. The difference between the maximum and minimum values increases as the ring size decreases. It remains to be established whether this localisation phenomenon will vanish for an infinitely large cyclacene.

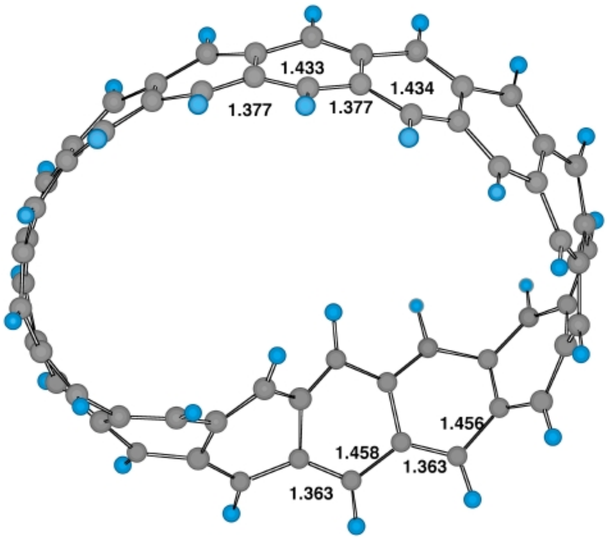

Fig. 1 Twist localisation and adjacent bond lengths (AM1) for cyclacene, $n = 15$, $t = 1$.

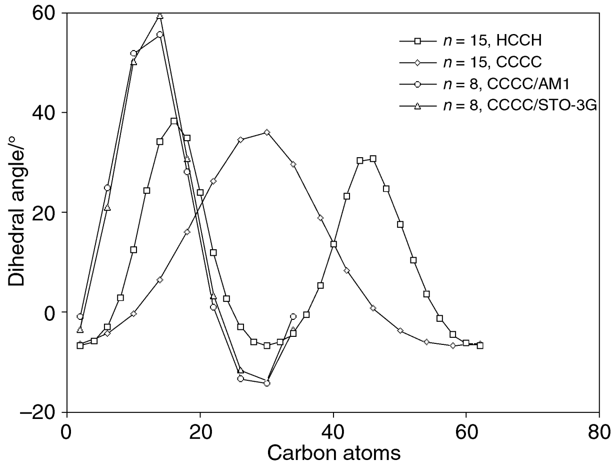

Fig. 2 HCCH and CCCC dihedral angles for cyclacenes, $n = 15$, $t = 1$ and $n = 8$, $t = 1$.

To evaluate whether the twist localisation was a feature of the Hamiltonian used, we also re-optimised for $n = 8$ at the *ab initio* level using an STO-3G or 3–21G basis, obtaining essentially identical results compared with AM1 (Fig. 2), implying the localisation may be insensitive to the precise nature of the potential energy function. Further analysis of the relationship between the potential function and propensity towards twist localisation will be reported in a subsequent article.

Localisation of the twist also impacts upon other computed properties of the cyclacene surface. The highest occupied molecular orbital (HOMO) and HOMO-1 (Fig. 3) differ in energy by 0.2 eV, and are both delocalised over approximately 12 of the 15 benzo rings, but the HOMO (and LUMO) has little density in the region of twist, whilst the lower energy HOMO-1 shows complementary behaviour, having larger coefficients in the region of the twist. The conventional expectation is that reducing orbital overlap by geometrical distortion will raise rather than lower the energy of a molecular orbital. This orbital behaviour is also seen for the *ab initio* 3G and 3–21G wavefunction. We note here a recent report[5] relating to the dynamics of creation and annihilation of soliton pairs upon photo excitation of polyene chains. The analogy with twist and charge localisation in the Möbius cyclacene system is currently being investigated. Finally in this section, we note that the computed molecular electrostatic isopotential (Fig. 4) indicates the negative region of the potential occurs on the inside concave surface of the aromatic π system.

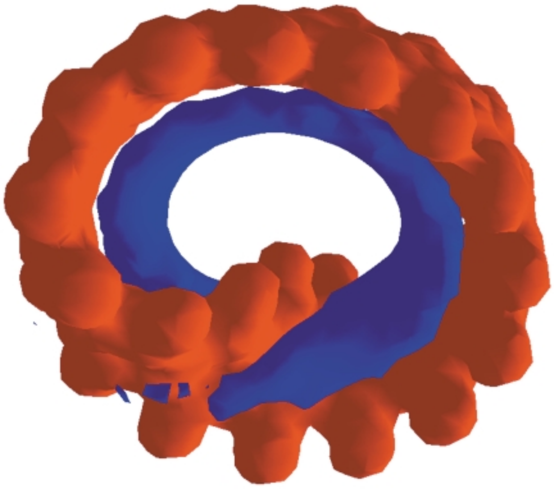

Fig. 4 AM1 computed molecular electrostatic potential for cyclacene, $n = 15$, $t = 1$.

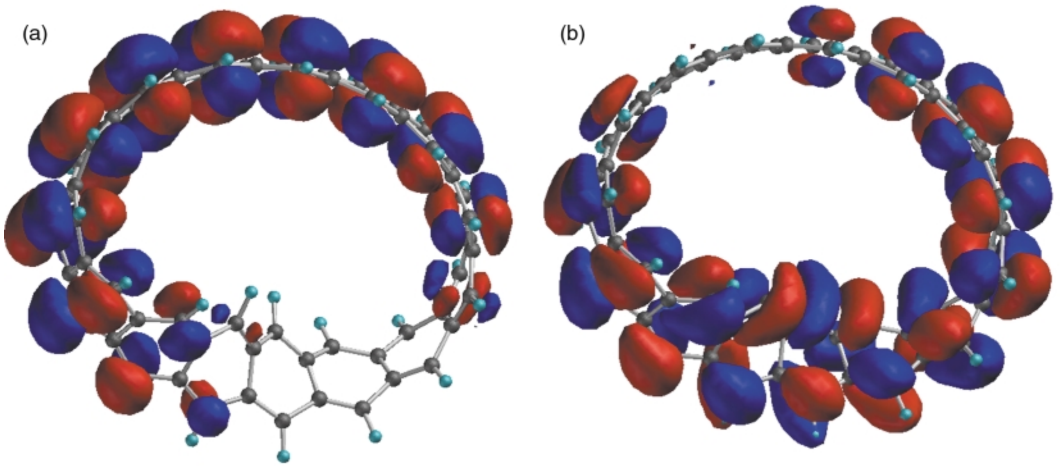

Fig. 3 (a) AM1 HOMO (−6.73 eV) and (b) HOMO-1 (−6.93 eV) for cyclacene, $n = 15$, $t = 1$.

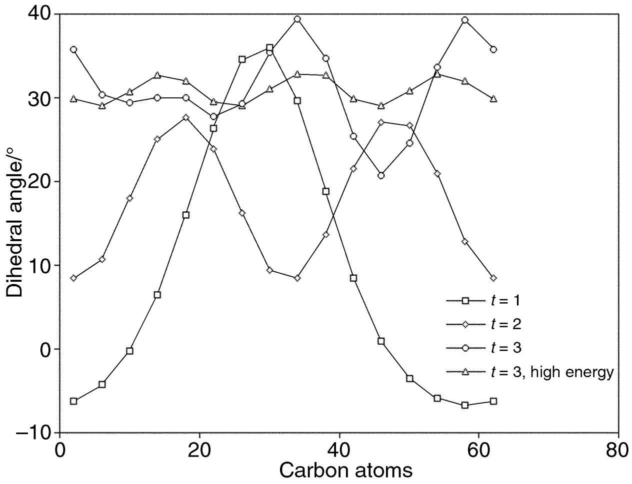

Fig. 5 CCCC dihedral angles for cyclacene, $n = 15$, $t = 1–3$.

Characteristics of neutral doubly and triply twisted cyclacenes

Fig. 5 illustrates the calculated CCCC dihedral angles for singly, doubly and triply twisted cyclacenes ($n = 15$, $t = 1–3$). As with the singly twisted system, the double twist shows two regions of localisation, although the difference between the maximum and minimum values (~18°) is less than half that of the singly twisted system. The triply twisted system unexpectedly resulted in location of two isomers differing in energy by 28 kcal mol^{-1} (Table 1). The more stable form appears to show two highly localised twist regions and a smaller less distinct one. The less stable isomer, which has C_3 symmetry, reveals three equally localised twist regions, but with a small difference (4°) between the maximum and minimum degree of twist. This form was verified as an energy minimum by calculating its force constant matrix. These two isomers also show different patterns of alternating bond lengths around the ring periphery (Fig. 6). Remarkably, the C_3 symmetric form shows regions along the periphery where almost no bond alternation occurs, and others where alternation of up to 0.1 Å is seen. We are unaware of any other conjugated system which shows such behaviour.

Characteristics of charged twisted cyclacenes

To probe the factors that might affect the characteristics of the twist in these systems, we also looked at the properties of the charged systems, arguing that adding or removing electrons would remove electrons from bonding π–π orbitals, or add them to antibonding orbitals, hence making the backbone more flexible and potentially influencing the ability of the ring to twist. The results indicate the single twist localisation is little changed by changing the electron occupancy by twelve electrons (Fig. 7). The charged double twist systems (Fig. 8) show that the effect of the charge is to increase the difference between the minimum and maximum twist values, indicating that making the benzo ring more flexible does have a small effect on the localisation. If greater flexibility increases the localising effect, then more rigidity would be required to remove it. It is difficult to see how this could be achieved chemically. Finally in this series we note the charged triple twist systems (Fig. 9) show the localisation phenomenon to be almost eliminated, this being more true of the negatively charged system.

Atomic charge distribution

Since charge distributions induced by twisting or photoexciting a polyene are of general interest in several areas of chemistry[5] we inspected the calculated AM1 Mulliken charges on the periphery. Those on the hydrogen atoms only (Fig. 10) reveal two small maxima associated with the maximum in the ring twist, that corresponding to the inside facing hydrogens being

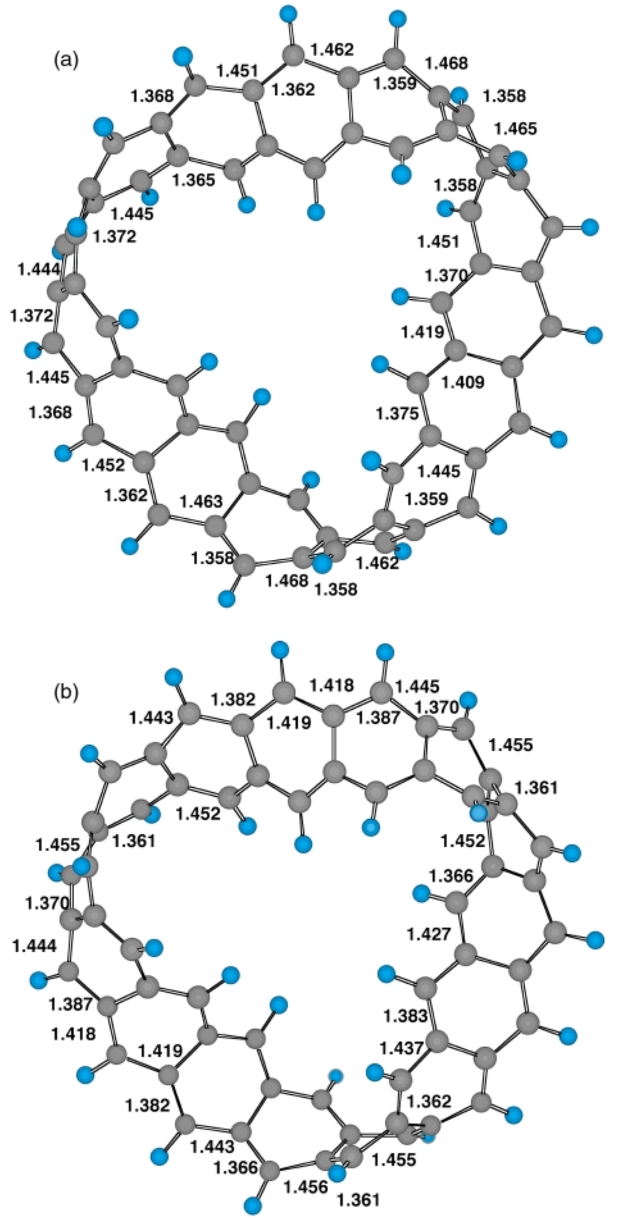

Fig. 6 Peripheral C–C bond lengths of cyclacene, $n = 15$, $t = 3$ for (a) low energy form; (b) high energy form.

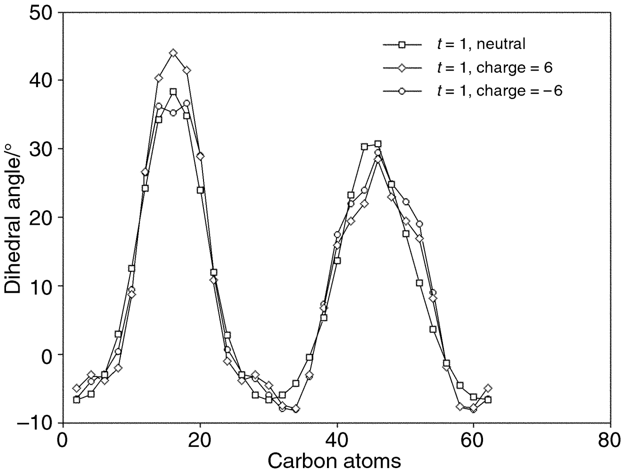

Fig. 7 HCCH dihedral angles for cyclacene, $n = 15$, $t = 1$, with charge 0, +6 and −6.

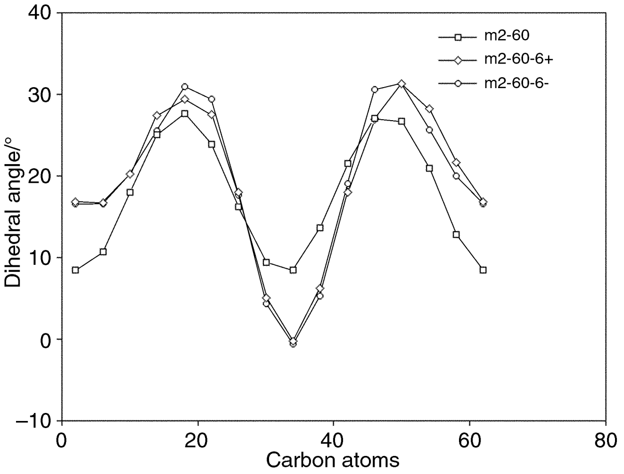

Fig. 8 CCCC dihedral angles for cyclacene, $n = 15$, $t = 2$, with charge 0, +6 and −6.

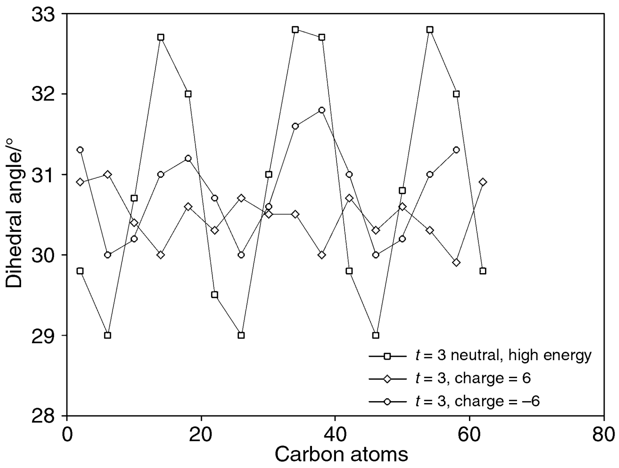

Fig. 9 CCCC dihedral angles for cyclacene, $n = 15$, $t = 3$, with charge 0, +6 and −6.

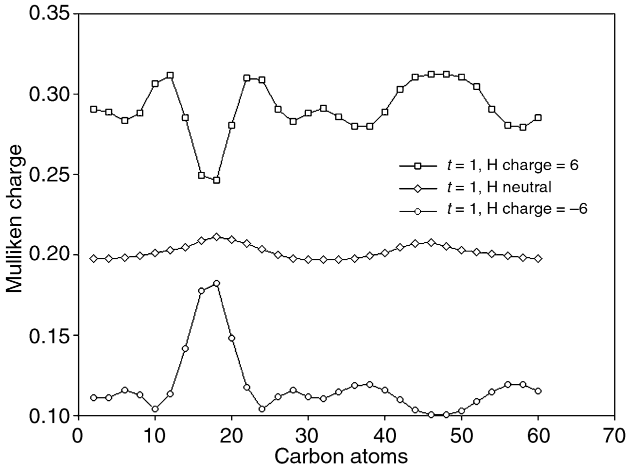

Fig. 10 Calculated Mulliken charge distributions on the H atoms for cyclacene, $n = 15$, $t = 1$, with charge 0, +6 and −6.

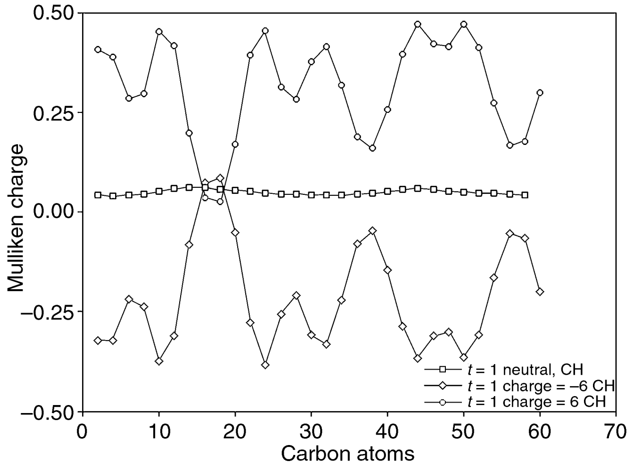

Fig. 11 Calculated Mulliken charge distributions on the combined HC atoms for cyclacene, $n = 15$, $t = 1$, with charge 0, +6 and −6.

the slightly more positive. The hexapositive system has more prominent features, with the least positive hydrogens now being clearly located in the region of inside facing twist, whilst the outside facing hydrogens are the most positive and are again associated with the region of maximum twist. The hexanegative system is essentially the mirror image of the positive system. Here the most positive hydrogens are inside the ring and localised at the twist. These effects are amplified if the charges on the hydrogen and the carbon it is connected to are summed (Fig. 11), as are additional maxima and minima in the charge distribution.

Conclusions

Whilst the mathematical features of Möbius strips have been studied since the last century, it is only recently that the construction of such topologies from flat molecular aromatic strips has attracted chemists' attention. The use of cyclacenes as a suitable model for quantitative modelling using molecular orbital Hamiltonians to describe their behaviour has revealed an interesting localisation phenomenon of the twist. Two features of these systems remain to be clarified. Firstly, is their localising behaviour essentially a chemical phenomenon, or does it have deeper topological meaning? Secondly, a molecular dynamics treatment will be required to understand their time-dependent properties, together with associated properties such as whether a rotating charge distribution in such a cyclacene can be induced, and *e.g.* its behaviour in a magnetic field.

Acknowledgements

We thank P. v. R. Schleyer (Erlangen) and I. Stewart (Warwick) for stimulating discussions.

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